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J. W. MELLOR

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PREFACE

A GLANCE down the "Table of Contents" will give some idea of the questions discussed in this volume. In explaining the theories of chemical change, I have been thankful that the nature of this book has allowed me to review the different guesses which have been made without calling upon the student to accept any one in particular. So far as the evidence goes to-day, I think that the "association, or intermediate compound theories" describe, in the most rational manner, the mechanism of the majority of reactions which have been investigated. No one can gainsay the facts, but every one has the right to interpret them his own way. At the same time we have to fight against the psychological "law" that facts which tell in favour of one's own 'doxy have more weight than those in a less fortunate position.

I do not think that it is possible for any one to read through this book and yet want a subject for a fruitful research—and that not always uhlan work. The student cannot help seeing how frequently we have to avoid making a direct statement, because of some little unsolved problem. I hope that the footnotes will put the student at once into direct or indirect contact with all that is known upon the question in hand.

It is no use trying to master the subject of Chemical

Kinetics without mathematics. I have therefore taken the liberty of referring to my *Higher Mathematics for Students of Chemistry and Physics* for details of the mathematical processes. In the second edition of that book I hope to give full particulars of the mathematical computations. I venture to hope, however, that the present "Introduction" will enable the neophyte, without mathematical knowledge, to see his way through the *ideas* involved; and he can take the mathematical *operations* on trust just as he would if I were to state that 81 is the cube root of 531441.

The reader has to thank my friends E. C. Edgar, Esq., M.Sc., for verifying the bulk of the three thousand odd references from the printed slips; and W. B. Jackson, Esq., B.Sc., for verifying those in the earlier part of the work.

J. W. MELLOR.

August 30, 1904.

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"THE beliefs which we have most warrant for have no safeguard to rest on, but a standing invitation to the whole world to prove them unfounded. If the challenge is not accepted, or is accepted and the attempt fails, we are far enough from certainty still; but we have done the best that the existing state of human reason admits of; we have neglected nothing that could give the truth a chance of reaching us; if the lists are open, we may hope that if there be a better truth, it will be found when the human mind is capable of receiving it; and in the mean time we may rely on having attained such approach to truth as is possible in our own day. This is the amount of certainty attainable by a fallible being, and this the sole way of attaining it."—JOHN STUART MILL.

CHEMICAL STATICS AND DYNAMICS

CHAPTER I

INTRODUCTION

§ 1. From the Beginning up to the Year 1777.

THE relative influence of one form of matter upon another has attracted the attention of observers from the earliest ages. Matter appears to be endowed with properties in virtue of which two or more dissimilar substances, when brought into close contact, give rise to other forms of matter possessing properties quite distinct from the original substance. The process of change is called a **chemical reaction.**

Chemical reactions may be studied from different points of view. For example, we may confine our attention to—

I. The result of the change, and ask, what kinds of matter have ceased to exist? What kinds of matter have come into existence? What relations exist between the weights and volumes of the substances which take part in the reaction? What changes of energy or of temperature occur during the reaction?

II. The course of the change.—Is it simple or does it consist of several changes? Are these dependent or independent, successive or simultaneous? At what rate does the change occur?

III. The circumstances modifying the change.—Under what conditions does the reaction occur? What is the influence of light, magnetism, electricity, and of heat on the course of the change? How is the chemical reaction influenced by the presence of a catalytic agent? Of the solvent?

And this is the purpose of chemical science, to describe in the simplest possible manner the phenomena associated with matter in the act of changing. The word "describe" has been selected with deliberation. The more important advances of modern science have been achieved by keeping the descriptive, not the causal, relations of phenomena constantly in view. Work only progresses along the natural path of experiment and observation. In consequence, "why" is rapidly disappearing from our vocabulary. We do not inquire *why* oxygen unites with hydrogen, but we do seek for all the conditions under which this transformation is possible. The search for the first cause has been relinquished. "How?" is the direct object of attack. Our laws relate "how," not "why," phenomena occur. A phenomenon is explained by showing how it resembles something already known. Newton's celebrated law epitomises in one simple statement how bodies have always been observed to fall in the past. Newton did not discover the cause of the falling of the apple, but he did show that it was due to the operation of the same forces which hold the earth, the planets and their satellites in their appropriate orbits. The scientific generalization explains the operations of Nature by showing the elements of sameness in what, at first sight, appears to be a confused jumble of phenomena. Generalization is the golden thread which binds many facts together in one simple description.

Let us contrast the old with the new. From the most remote periods of history efforts have been persistently directed to the discovery of the cause of chemical action. How sterile the results! What an array of arbitrary hypotheses and random guesses! The search for the "why" has ever proved an *ignis fatuus* luring men away beyond the bounds of truth. The story is an old one. Empedocles (*c.* 444 B.C.) explained chemical action by endowing the reacting elements with the human qualities of love and hate; chemical action appeared to him a marriage of the elements, decomposition a divorce.

Hippocrates (*c.* 468 B.C.) recast Empedocles' idea and imagined that simples united to form compounds because of the existence of a common principle or kinship to which J. C. Barchusen, in 1698, applied the word "affinitas." For these philosophers the word explained the fact. Elements united together because of their affinity. There the matter ended. In direct opposition to these notions, Heracleitos (*c.* 500 B.C.) maintained that chemical combination depended on contrast or an effort to fill up a want. He thus foreshadowed the polar doctrine developed later on by H. Davy, A. Avogadro, J. Berzelius, T. Graham, and B. C. Brodie.[1]

Then we have the purely mechanical views held by the old schools of Leucippus (*c.* 500 B.C.), Democritus (*c.* 400 B.C.), and Epicurus (*c.* 300 B.C.), in which the tendency of the atoms to combine was said to be due to the ultimate particles of matter bringing into use little hooks or points. The idea was revived, later on, by G. A. Borelli (*c.* 1656), and N. Lémery (1675), and we can still recognize the old fancies depicted in the diagrams of to-day's "Text-books of Organic Chemistry" to represent the linking of the carbon atoms. So we might bewilder ourselves with errors and prejudices as we wander on from one ill-founded supposition to another. Lavoisier's plaint might have been made to-day.[2] Some of us do trust to the imagination, and incline to make suppositions rather than draw conclusions.

The moral is obvious. No process of reasoning can establish a law of Nature. The elements of sameness—the law—must be actually discovered in the facts. The laws of chemical action are collocations of those circumstances which have been found by experiment and observation to accompany all chemical changes. The test of the generalization is that the statement holds good without exception. When the exact conditions are set up, the phenomenon as described by the "law" operates without variableness or shadow of turning.

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[1] E. J. Mills, *Phil. Mag.* [4], **33.** 1, 1867; *Laboratory*, **1.** 4, 53, 1867.

[2] A. L. Lavoisier's *Traité élémentaire de Chimie*, Paris, **1.** x., 1789; R. Kerr's trans., **1.** xvi., 1790.

The law is then regarded as an objective power. This power is called a force, and further, the force is said to be the cause of the phenomenon. Thus, gravitation is regarded as an attractive force causing one particle to attract every other particle in the universe; chemical affinity is regarded, in this sense, as a selective force, which causes certain substances, when placed in contact, to undergo chemical change.

R. Boyle (1684) subjected the theories of his contemporaries, Borelli and Lémery, to severe criticism. He attributed the cause of chemical action to the reciprocal action of small particles of matter acting upon one another with different degrees of attraction. Newton (1701) introduced the idea of "action at a distance," and referred chemical action back to the presence of attractive forces "indwelling in matter" which acted as functions of the distance between the atoms. The result of a chemical action was thought to lie wholly in favour of that substance having the stronger attraction. Bergmann is usually regarded as the leading exponent of this school. When two substances, AB and C, are brought into contact, it was said that "if the attraction of C for A is greater than that of B for A, then B will be displaced from its combination with A, and the final result will be a mixture of AC and B."[1]

J. R. Glauber (1648) and R. Boyle (1664) both proposed to arrange chemically related substances in series according to their power of displacing one another from combination, and at the beginning of the eighteenth century St. F. Geoffroy (1718) and G. E. Stahl (1720) drew up their "Verwandtschaftsreihe," or "Affinity Tables," designed to show at a glance the order in which different substances would displace one another from a given compound. "If A displaces B, and B displaces C from a compound, then the order of affinity of these substances is A, B, C."

These tables were continually improved and extended,

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[1] T. Bergmann's *De Attractionibus Electivis*, Upsala, 1775; anonymous translation, *A Dissertation on Elective Attractions*, London, 6, 65, 1785; *Opuscula physica et chimica*, Upsala and Leipzig, 3, 291, 328, 1783.

notably by T. Bergmann (1775), G. de Morveau (1781), and by T. Kirwan (1790). It soon became obvious that some perturbing influence was at work. Facts which could not be explained on the simple assumption that chemical action depended solely upon the *nature* of the reacting substances, began to accumulate in an ominous manner. C. F. Wenzel (1777) first recognized the disturbing element in the influence of *quantity* of reacting substance upon chemical transformation.

As a matter of fact, T. Bergmann (1775) had some perception of the influence of mass, for he noticed that when two substances, AB and C, are mixed together, in spite of the fact that the affinity of C for A is greater than that of B for A, "in order to displace B from its combination with A, it is frequently necessary to employ two, three, or may be six times the amount of C actually required to saturate A." But Bergmann does not appear to have attached much importance to this observation.

Wenzel's views on the nature of affinity were very much the same as those of his contemporaries, but he introduced a new method of attacking the problem. Just as in mechanics the magnitude of a force is measured by its influence upon the motion of a particle, so did Wenzel seek to determine the magnitude of the force—chemical affinity—between acids and the metals by measuring the *rate* of dissolution of different metals by different acids. This appeal to Nature furnished the missing clue. Wenzel found that the rate of dissolution of a metal by an acid depended not only upon the nature, but also upon the quantity or concentration of the acid. Hence followed the important generalization: "chemical action is proportional to the amount of substance taking part in the reaction."

It is so necessary to have a clear idea of what is implied by the term "the velocity of a chemical reaction" that a lengthy digression may be useful.

§ 2. **Average and Instantaneous Velocities.**

The time occupied by a train in passing from one point to another obviously depends upon its speed, velocity, or rate[1] of progression. It is usual to define velocity—rate of motion—as the distance traversed in unit time, say, one second. If a body travels with a velocity of two centimetres per second, it will take two seconds to travel four centimetres, three seconds for six centimetres, and generally it will require t seconds to travel s cms. If the body travels with a uniform velocity of v cms. per second, we may write—

$$\text{Distance traversed} = \text{velocity} \times \text{time};$$

or, in symbols—

$$s = vt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Hence, by a simple transposition—

$$\text{Velocity} = \frac{\text{distance traversed}}{\text{time required}} = \frac{s}{t}. \quad . \quad . \quad . \quad (2)$$

Now, suppose that a particle passed over 0·05 cm. in $\frac{1}{100}$ of a second, the rate of motion of the particle *during* that portion of a second will be—

$$\text{Velocity} = \frac{0\cdot05}{\frac{1}{100}} = 5 \text{ cms. per second.}$$

It is quite immaterial how the particle travelled during the remainder of the second. Our data only show that the particle progressed at the rate of 5 cms. per second during the interval stated.

The converse statement does not hold good. If a particle travelled at the rate of 5 cms. per second for one second, it would not do to say that the particle travelled 0·05 cm. during the $\frac{1}{100}$ part of a second unless we knew that the particle was moving with a uniform velocity during the whole second. The velocity of the particle might have been slowing down in such a way that it progressed much faster during the first hundredth part of the second. In that case 5 cms. per second would represent the mean or average velocity[2] throughout the

---

[1] "Velocity" is directed speed, but I here use the three terms "rate," "speed," and "velocity" synonymously.

[2] See A. Fuhrmann, *Zeit. phys. Chem.*, **4**. 520, 1889, for the distinction between "mean velocity" with regard to equal portions of time, and with regard to equal amounts of substance transformed.

whole second. We understand the **mean or average velocity** of a moving body in any given interval of time to be that distance which would be traversed in unit time if the body were to move uniformly throughout the interval in question.

$$\text{Average velocity} = \frac{\text{distance traversed}}{\text{time occupied}}.$$

Again, if we found that the body travelled 0·05 cm. during the $\frac{1}{100}$ part of a second, we could not infer that it would travel 0·005 cm. in the $\frac{1}{1000}$ part of a second; still less could we say that it would travel 0·000005 cm. during the millionth part of a second.

How then can we get the actual measure of the velocity at any instant? In order to obtain the velocity of a particle at, say, the instant it passes a certain point, it would be necessary to measure the distance traversed "during" that particular instant. But any measurement we can possibly make must occupy *some* time, and consequently the velocity of the particle has time to alter while the measurement is in progress. It is thus impossible to measure directly a velocity *at* any instant of time.

In spite of this fact, it is frequently necessary to reason about this ideal condition. An instantaneous velocity is represented symbolically in the following manner. Let ds represent the distance traversed by a particle during an instant of time dt; let ds and dt be taken so small that all errors due to any variation of speed during the time dt vanish away, then, from the above definition of velocity (2)—

$$\text{Velocity at any instant} = \frac{ds}{dt} = v. \quad . \quad . \quad (3)$$

The symbol for an instantaneous velocity, ds/dt, is sometimes called a *differential coefficient*. In place of (3) we may write—

$$ds = v \, . \, dt, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where ds and dt are called differentials.

By a "velocity at any instant," therefore, we understand the average velocity of the particle during an interval of time so small that the rate of motion has not had time to suffer any appreciable change.

The letters "d" are not to be taken algebraically. They cannot be dissociated from the appended s and t. These letters mean nothing more than that the space s and the time t have been taken small enough to satisfy the above definition.

Just as a certain time is required for a particle to travel from one point to another, so every chemical change takes a certain time to complete itself. The change may be slow or rapid. A mixture of hydrogen and oxygen will combine in the fraction of a second, while the transformation of white into grey tin may occupy centuries. The conception of a velocity at any instant, therefore, may be extended to chemical changes, so that in place of rate of motion we must understand rate of material transformation. Hence, for chemical changes—

$$\text{Velocity} = \frac{\text{amount of substance transformed}}{\text{time occupied}} = \frac{x}{t}, \quad . \quad (5)$$

where x denotes the amount of substance[1] transformed in a given time t. Similarly, the expression—

$$\frac{dx}{dt},$$

may be employed to represent the velocity of a chemical reaction at any instant of time. This concept, it may be noted, includes "rate of dissociation," "speed of catalysis," and related notions.

If we conventionally agree to represent a movement towards the east with a positive sign, motion westwards would be symbolized by prefixing a negative sign. So in chemistry we usually represent the rate of formation of a compound by the symbol dx/dt, but rates of decomposition, or of dissociation,[2] are symbolized by $-dx/dt$.

The symbol dx/dt represents the rate of formation of a

---

[1] By "amount of substance" we understand "number of gram-molecules" per litre of solution. "One gram-molecule" is the molecular weight of the substance expressed in grams. *E.g.*, 18 grms. of water is 1 gram-molecule; 27 grms. is 1·5 gram-molecules; 36 grms. is 2 gram-molecules, etc. We use the terms "amount," "quantity," "concentration," and "active mass" synonymously.

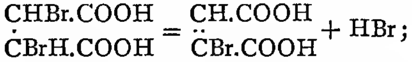
[2] Note that the rate of formation of the products of any reaction is a rate of decomposition with respect to the original substance.

compound during an interval of time so small that all errors due to variation of speed have been eliminated; similarly, $-dx/dt$ denotes the rate of decomposition of a compound under the same conditions.

§ 3. The Measurement of Instantaneous Velocities.

Let us now return to the question: How can the velocity of a chemical reaction during an immeasurably short interval of time be found? The answer is simple enough. The instantaneous velocity of a chemical reaction is found by a process of guessing and verification, as will be shown below.

For the sake of clearness, let us take a concrete example. When dibromosuccinic acid ($C_4H_4O_4Br_2$) is boiled with water it is transformed into bromomaleïc acid with the separation of hydrogen bromide, as shown in the following equation:—



$$\begin{array}{l}\text{CHBr.COOH}\\ \dot{\text{C}}\text{BrH.COOH}\end{array} = \begin{array}{l}\text{CH.COOH}\\ \ddot{\text{C}}\text{Br.COOH}\end{array} + \text{HBr};$$

Dibromosuccinic acid = Bromomaleïc acid, etc.

The problem to be solved is to find the velocity of this reaction at any instant, t minutes after the reaction has started. Let x denote the amount of dibromosuccinic acid present in the system at any moment. The instantaneous velocity cannot be measured. Does the velocity depend on x in any way? Numberless guesses might be proposed. Suppose we try one—the rate at which dibromosuccinic acid is disappearing at any moment is proportional to the amount of this acid actually present in the system at that instant of time. This can scarcely be called a "random" guess, because it appears more or less probable from the fact that the reaction generally goes faster the more concentrated the solution.

This provisional hypothesis may be expressed symbolically. $-dx/dt$ represents the rate at which dibromosuccinic acid is disappearing at any instant of time—the need for the negative sign will be apparent. We have guessed that—

$$-\frac{dx}{dt} \text{ is proportional to } x.$$

A well-known rule in algebra states that when one magnitude is proportional to another, the one magnitude is equal to the product of the other with some arbitrary constant called the constant of proportionality.[1] Hence we may express the above hypothesis by means of the equation—

$$-\frac{dx}{dt} = kx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the constant of proportion.

To find the physical meaning of k, let us suppose that $x = 1$, that is to say, suppose that unit mass of dibromosuccinic acid is present. Hence—

$$-\frac{dx}{dt} = k,$$

or, k denotes the rate of transformation of unit mass of substance; that is, the rate at which the reaction would proceed were the reacting substance originally present and continually maintained at unit concentration.[2] k is usually called the **velocity constant**, or, since the "constant" is not always constant under the conditions of any given experiment, the words **velocity coefficient** are sometimes preferred. Arrhenius[3] calls k the **specific speed of reaction**, meaning the rate of change divided by the concentration of the reacting substance (or substances).

The guess we have just made respecting the velocity of transformation of dibromosuccinic acid into bromomaleïc acid must be compared in some way with facts. If it were possible

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[1] Thus if x varies as y, or if x is proportional to y, $x = y \times$ constant. See Mellor's *Higher Mathematics*, § 190. A "constant" is a magnitude which remains invariable during a given operation (*ib.*, § 9).

[2] The experimental conditions were realized by R. Bunsen and H. E. Roscoe (*Phil. Trans.*, **147**. 355, 1857; *Pogg. Ann.*, **96**. 373, 1855). A mixture of hydrogen and chlorine gases, standing over water saturated with the two gases, was exposed to a constant source of light. The hydrogen chloride was absorbed by the solution as fast as it was formed. Hence the mixture of hydrogen and chlorine retained the same concentration throughout the reaction, and the rate of formation of hydrogen chloride remained constant.

[3] S. Arrhenius, *Zeit. phys. Chem.*, **1**. 110, 1887.

to measure the velocity of chemical change corresponding to different values of x, and we found that—

Velocity = constant × quantity of dibromosuccinic acid present,

we should think the guess worthy of closer examination; if otherwise, the guess might be put on one side valueless. It is, however, impossible to test our provisional hypothesis in this way, dx and dt are far too small to be measured.

If our assumption is true, the velocity of the reaction is obviously fastest when x—the amount of dibromosuccinic acid—is greatest. That can only be at the beginning of the reaction, when $t = 0$. After that the speed gradually slows down until x is zero. The reaction is then completed.

The numerical value of the constant k depends on the particular reaction under consideration and the unit of time adopted. In this case it happens that $k = 0{\cdot}0309$; for the transformation of monochloroacetic acid into glycollic acid, $k = 0{\cdot}00037$; for the decomposition of hydrogen peroxide by hydriodic acid, $k = 0{\cdot}0106$; for the hydrolysis of cane sugar, $k = 0{\cdot}322$. I shall show later on how the numerical value of k may be determined.

Let $k = 0{\cdot}031$. The velocity of the reaction under investigation may now be written—

$$-\frac{dx}{dt} = 0{\cdot}031x, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where dx denotes the amount of dibromosuccinic acid transformed in the time dt. Since dt is too small to be measured, let us try to approximate to it as closely as we can. First, suppose that dt represents 10 minutes. This means that if we start with 5·11 units of substance—

$$-dx = 0{\cdot}031 \times x \times dt = 0{\cdot}031 \times 5{\cdot}11 \times 10 = 1{\cdot}58 \text{ units}$$

of dibromosuccinic acid will have disappeared, and 3·53 units will remain behind. In other words, at the end of the first ten minutes, $x = 3{\cdot}53$, $t = 10$.

During the second interval—

$$dx = 0{\cdot}031 \times x \times .dt = 0{\cdot}031 \times 3{\cdot}53 \times 10 = 1{\cdot}09 \text{ units}$$

more of dibromosuccinic acid will have been converted into bromomaleïc acid, and 2·44 units will remain. Hence at the end of the second ten minutes, $x = 2·44$, $t = 20$.

Similarly, at the end of the third ten minutes, $x = 1·68$, $t = 30$; and so on.

Let us now place these results in juxtaposition with some measurements made by Van't Hoff.[1] 5·11 units of dibromosuccinic acid were treated with hot water, and the amounts of this acid present in the system after the elapse of 0, 10, 20, 30 . . . minutes are shown in the third horizontal line below—

When t =	0,	10,	20,	30,	40,	50,	60,	. . . min.;
x (calc.) =	5·11,	3·53,	2·44,	1·68,	1·16,	0·80,	0·55,	. . . units;
x (obs.) =	5·11,	3·77,	2·74,	2·02,	1·48,	1·08,	0·80,	. . . units.

The calculated reaction shows that 4·56 units of dibromosuccinic acid have disappeared; in reality, only 4·31 were found to have gone. Why the discrepancy? Either our prevised assumption or our method of calculation is wrong. Let us look more carefully into the latter. We have supposed (i.) that the speed of the reaction is the same at the end of the ten minutes as it was at the beginning; and (ii.) that the speed of the reaction at the end of the ten minutes suddenly slackens down to a rate corresponding with the amount of dibromosuccinic acid then present in the system. This is shown graphically in the following diagram (Fig. 1), where the ordinates represent the values of x, abscissæ the times of observation.

The series of steps in Fig. 1 show graphically what we have supposed to be the state of the velocity. The velocity is assumed to have gone on steadily for the first ten minutes at the rate of 0·158 units per minute, then the speed is supposed to have suddenly slowed down to 1·09 units per minute. This rate is then supposed to have gone uniformly on for another ten minutes and then suddenly fallen to 0·076 units per

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[1] J. H. van't Hoff's *Études de dynamique chimique.* Amsterdam, 14, 1884; E. Cohen's edition, *Studien zur chemischen Dynamik,* 1896; T. Ewan's trans., 1896.

minute, and so on. Nature, however, does not make jumps in this manner. Natural changes do not take place abruptly. Even when a bullet comes suddenly to rest it passes insensibly through all intermediate stages between its maximum velocity and perfect rest. So with chemical changes, as soon as ever so small a quantity of dibromosuccinic acid has been transformed, x is no longer 5·11 units, and the instant 5·11 is diminished the new value also diminishes, and so on, instant by instant. But since x determines the velocity of the reaction, the rate of transformation of dibromosuccinic acid obviously diminishes insensibly from moment to moment by a series of exceedingly small gradations represented by the "curve of diminishing velocity" (Fig. 1).

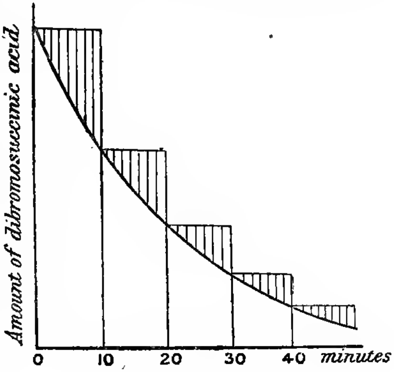

FIG. 1.

This is a possible explanation of the discrepancy. The reaction, after the first instant, is not going so fast as we have supposed. Let us shorten the interval dt to, say, five minutes, and then try if the calculated numbers come nearer to the observed results. During the first five minutes the amount of dibromosuccinic acid decomposed will be—

$$-dx = 0{\cdot}031 \times 5{\cdot}11 \times 5 = 0{\cdot}79 \text{ units};$$

hence 4·32 units remain. The following scheme shows the results obtained for the succeeding intervals:—

When t =	0,	5,	10,	15,	20,	25,	30,	... min.;
x (calc.) =	5·1,	4·3,	3·7,	3·1,	2·6,	2·2,	1·9,	... units;
x (obs.) =	5·11,	—	3·77,	—	2·74,	—	2·02,	... units.

0·80 units of dibromosuccinic acid were actually found in the system at the end of 60 minutes, the amount calculated on the assumption that the velocity changes every ten minutes is 0·55 units, against 0·7 units calculated on the assumption that the velocity changes every five minutes. By lessening the time during which the velocity is supposed to remain uniform we have diminished the error. These results are plotted in Fig. 2 on the same scale as in Fig. 1. By comparing the areas of the darkened portions in the two diagrams, we see at once that the error has been considerably diminished. By continually shortening the interval in this way, the calculated result approximates more and more closely to the observed result. This is shown graphically in Fig. 3, where the greater slope of the two lower curves shows that the velocities of the reaction calculated for $dt = 10$ and for $dt = 5$ exceed the experimental curve for $dt = 0$, and the deviation is greater the greater the interval dt.

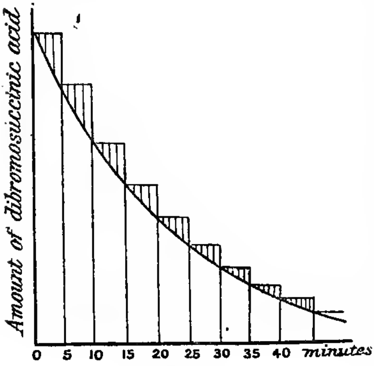

FIG. 2.

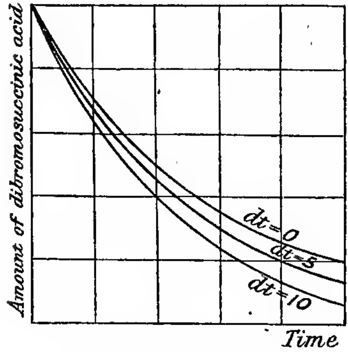

FIG. 3.—Velocity curves.

Some students find a difficulty in the interpretation of these curves. A **velocity curve** is obtained by plotting the *amount of substance* present in the system with the *time*. The *slope* of the curve at any point represents the *velocity* of the reaction, $dx\ dt$, at that moment. The greater the slope of the curve the greater the velocity. An **acceleration curve** is obtained by plotting the *velocity of a reaction* with the corresponding intervals of *time* (Fig. 11). The *slope* of the curve denotes the "rate of change of velocity," *i.e.* the *acceleration*. A curve sloping upwards from left to right means that the velocity is increasing, while if the curve slopes downwards from left to right, the velocity is diminishing.

When dt is made very small, the labour of calculation becomes greater, owing to the large number of intervals to be treated. When dt is made so small that the calculated and observed results coincide, an infinite number of values of dx have to be added together, thus—

$$-\Sigma dx = 0{\cdot}031x.dt + 0{\cdot}031x.dt + 0{\cdot}031x.dt + \ldots + \text{to infinity.}$$

Here the symbol "Σdx" is used in place of "the sum of all the dx's."

It is, of course, an arithmetical impossibility to add up an infinite number of intervals. Nevertheless, the operation can be performed by means of the so-called methods of integration. Integration is a method of adding up an exceedingly large number of exceedingly small quantities. The operation is represented by the symbol "$\int$," just as the operation of addition is represented by the symbol "+," or of division by "÷." Hence in place of (3) we write—

$$-\int dx = \int 0{\cdot}031x.dt.$$

To show that the time is taken from 0 to 6 minutes, we write the upper limit "6" as a superscript and the lower limit as a subscript to the symbol of integration "$\int$."[1] Similarly the limits x_0 and x show that the integration or summation is taken between the limits $x = x_0$ and x. Hence—

$$-\int_{x_0}^{x} \frac{dx}{x} = \int_0^6 0{\cdot}031dt,$$

since it is usual to collect all terms containing x on one side of the equation, and all terms containing t on the other, before performing the integration.

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[1] The symbol of integration is a distorted *s*, the first letter of the word "summation."

It would here be a hopeless task to attempt to explain the mechanical processes of integration. For these the reader must consult a suitable text-book.[1] It will be found sufficient for the student who is unable to verify the mechanical details of integration to take my results on trust in the same way that he has probably taken for granted that my additions and multiplications have been correctly performed. I said "sufficient" because "to one incapable of following out the details of a mathematical demonstration, the conviction afforded by verified prediction must stand in place of that purer and more satisfactory reliance which a verification of each step in the process of reasoning can afford" (J. F. W. Herschel). But the student of physical chemistry cannot hope to master "modern theory" without mathematics. "Ere long," said P. Schützenberger, in the introduction to his *Traité de Chimie Générale* (1880), "mathematics will prove to be as useful to the chemist as the balance." In the mean time it must be remembered that the symbol dx/dt always means the rate of change of x measured during an interval of time so small that all errors due to variation of speed during that interval have been eliminated; while the symbols—

$$\int dx = \int \ldots dt$$

always mean that dt has been taken so small that when all the corresponding values of dx are added together, the result is not affected by any error due to variations in the velocity of the reaction under investigation.

If—

$$-\frac{dx}{dt} = kx,$$

we obtain, by integration—

$$\frac{1}{t}\log\frac{x_0}{x} = k, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or the equivalent form—

$$x = x_0 e^{-kt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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[1] Chaps. IV. and VII. of J. W. Mellor's *Higher Mathematics.*

Now x can be measured and t can be measured; x_0 is the original amount of dibromosuccinic acid taken when $t = 0$; e is a number numerically equal to 2·718.[1] The expressions (4) and (5) are said to be the integrals of (1).

If our initial assumption as to the rate of decomposition of dibromosuccinic acid be correct, by substituting the values of t, x_0, and x given by experiment in equation (4), we ought to get k very nearly constant. This has been done in the following table:—

Time (min.)	x	$\frac{x_0}{x}$	$\log \frac{x_0}{x}$	$k = \frac{1}{t} \log \frac{x_0}{x}$
0	5·11	—	—	—
10	3·77	1·35	0·3001	0·0300
20	2·74	1·86	0·6206	0·0310
30	2·02	2·52	0·9243	0·0308
40	1·48	3·45	1·2384	0·0309
50	1·08	4·73	1·5539	0·0311
60	0·80	6·39	1·8547	0·0309
90	0·29	17·62	2·8679	0·0318
		Mean		0·0309

I have promised to show how to evaluate the constant k in equation (1), and here, in the last column, the operation has been performed. Had it been taken for granted that the reader understood how to integrate, this long preamble would not have been required. It would only have been necessary to put the guess proposed for the instantaneous velocity of the given chemical reaction in symbols; to integrate the resulting expression; and then to compare the different values of k computed from the corresponding values of t, x, and x_0 determined by experiment. When the values of k so calculated are nearly all the same,[2] we have *primâ facie* evidence that the guess is a good one. If the initial assumption had not led

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[1] See J. W. Mellor's *Higher Mathematics*, §§ 16, 188.

[2] That is, within the limits of experimental error.

to a constant value for k, we should test some other guess in the same manner, in the hope that, among many wrong guesses, we should meet with the right one. We are told that "Newton discovered the law of gravitation." But how? By first admitting the hypothesis, and then testing his guess by comparison with facts.

H. von Helmholtz likens the search for the right guess to a groping in darkness for the material to build up an integral, whose accuracy must in all cases be tested by an appeal to observation and measurement. It does not necessarily follow that an hypothesis must be abandoned because it does not give results in harmony with the observed facts. Some other event may be interfering with the regular course of the change, as will be shown in the chapter on consecutive reactions.

4. The Use of Mathematics in Chemistry.

About three hundred years ago Francis Bacon pointed out that "many parts of Nature . . . cannot be demonstrated with sufficient perspicuity . . . without the aid and intervention of mathematics." I have just outlined one method of using mathematics in scientific investigation. We began an investigation on the rate of conversion of dibromosuccinic acid into bromomaleïc acid by guessing that the "velocity of a chemical reaction was proportional to the mass of the substance taking part in the reaction." This working hypothesis was expressed in mathematical symbols—

$$-\frac{dx}{dt} = kx.$$

But dx/dt cannot be measured, and the conjecture can only be compared with laboratory measurements after the mathematical operation of integration has been performed; the hypothesis then assumes the form—

$$\frac{1}{t}\log\frac{x_0}{x} = k.$$

Here x_0, x, and t are accessible to measurement. Thus integration bridges the gap between theory and fact by reproducing the hypothesis in a form suitable for experimental verification. C. F. Wenzel (1777), or rather C. L. Berthollet (1799), first clearly enunciated our provisional hypothesis, but it remained for L. Wilhelmy (1850) to carry the hypothesis through the four stages just indicated—

Hypothesis → Differential Equation[1] → Integration
→ Observation.

Chemists call Berthollet's guess the law of mass action. We shall have more to say about this later on.

It must be pointed out that an hypothesis, *after* passing through the mathematical mill, is neither more nor less entitled to confidence than *before.* The appearance of accuracy conveyed by the mathematical symbols is illusory. "Mathematics may be compared to a mill of exquisite workmanship which grinds you stuff of any degree of fineness; but nevertheless what you get out depends on what you put in."[2] The verbal description of the hypothesis, the differential equation, and the integral, are three different ways of stating one concept. *A clear physical view must precede the application of mathematics.*

The truth or falsity of an hypothesis can only be established by comparison with facts. There is no other way. Mathematics can never prove that Nature must act exactly as she does.[3]

There is a prevailing notion that the agreement between the "calculated" and "observed" results is an infallible crucial test of any hypothesis. The agreement only shows that the hypothesis *may* be true. G. W. von Leibnitz long ago remarked that success in explaining facts is no *proof* of the validity of an hypothesis. Scores of formulæ have been proposed to express the relation between the temperature and the vapour-pressure of water. All give good results, and possibly all are

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[1] That is, an equation containing differentials (§ 2).

[2] T. H. Huxley's *Collected Essays*, London, 8. 333, 1896.

[3] See E. Mach's *Die Mechanik in ihrer Entwickelung historisch-kritisch dargestellt*, Leipzig, 72, 1883; T. J. McCormack's trans., 77, 1902; M. Faraday's *Researches in Chemistry and Physics*, London, 458, 1859.

wrong. It is even possible to draw right conclusions from false premises, as must occur when conflicting hypotheses adequately explain what we know about certain phenomena.

§ 5. What is Energy?

Heracleitos has said that "everything is in motion," and daily experience teaches us that changes are continually taking place in the properties of bodies around us. Change of position, change of motion, of temperature, volume, and chemical composition, are but a few of the myriad changes associated with bodies in general. As a first approximation, every change may be supposed to be due to the action of some external agent which is called **energy**; in other words, energy is that which has the power of changing the properties of bodies. Whenever a body changes its condition, there energy is in action. Energy is the cause, change of condition the effect.

The action of energy may be resisted. Change can only take place when the restraint is withdrawn. The action by which energy produces a *tendency* to change is called a **force.** Energy and force are related as cause and effect. Force is destructible, energy is indestructible. Force is but a manifestation of energy. Whenever resistance is overcome, energy must be expended. Hence energy is sometimes defined as "the power to overcome resistance." **Work** is said to be performed whenever change takes place in opposition to a force opposing that change. The amount of work done is equal to the quantity of energy transferred. Work is done at the expense of the energy.

$$\text{Work performed} = \text{energy expended.}$$

Consequently energy is sometimes defined as "the capacity for doing work." Two factors are involved in the expenditure of energy—(1) the magnitude of the resistance; and (2) the extent to which the resistance is overcome. When a particle moves a distance s by the application of a force F, the amount of energy transferred from the source of energy is—

$$E = Fs. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

§ 6. Different Forms of Energy.

In order to keep a grindstone in motion it is evident a certain amount of, say, muscular energy must be expended in order to overcome the resistance opposed by the air, axle bearings, etc. If a piece of steel be pressed against the stone, the steel soon becomes warm. Exact measurements have shown that the amount of heat produced is proportional to the energy expended in maintaining the motion of the grindstone. Again, in the "hot-air engine" heat is employed to set bodies in motion. Heat and mechanical motion, therefore, are two forms of energy. If a vulcanite tire be placed on the grindstone and the rim pressed with a piece of flannel, electricity[1] will be developed. But electricity can also be readily reconverted back into mechanical motion. Electricity, therefore, is also a form of energy. The "motive power" used in the industrial arts is mainly derived from the chemical action between carbon and oxygen in the furnace of the steam engine. Heat and electricity are also well-known concomitants of chemical action. Hence we infer that heat, electricity, mechanical motion, and chemical action are all different forms of one distinct entity —energy.

Observations show—

1. That one form of energy can be transferred directly, or by intermediate steps, into any other form. **(Law of transformation of energy.)**

2. When any quantity of one form of energy is made to disappear, an equivalent quantity of another form, or forms, of energy reappears. **(Law of conservation of energy.)**

"The transactions of the material universe," says J. C. Maxwell, in that inimitable work, *Matter and Motion*, "appear to be conducted, as it were, on a system of credit. Each transaction consists of a transfer of so much credit or energy from one body to another. The act of transfer or payment we call work."

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[1] Some will object to the wording of this sentence. I speak of electrification. Discussions on the nature of electricity are just now "in the air." There is no telling what will crystallize from all this talk.

§ 7. Total, Available, and Potential Energy.

We have no means of measuring the absolute or total amount of energy which a body possesses. Air confined in a closed vessel at atmospheric pressure might appear to possess no energy, because it can do no work. But reduce the pressure of the surrounding air, and the air confined in the vessel is then capable of performing work. The total amount of energy associated with any body is possibly independent of the external conditions. In the study of natural phenomena, we are only concerned with that portion of the total energy which can be utilized for doing work. This is called the **free or available energy.**

There is an important difference between a stone lying on the ground and a similar stone lying on the table. Both are alike motionless, yet the latter possesses more available energy than the former. For example, the stone, in descending to the ground, could be made to transfer its energy to the mechanism of a clock. The available energy would then be transformed into mechanical motion. For the same reason a wound watch-spring possesses more energy than a similar spring not wound up.[1] Thus, available energy may be active (*i.e.* kinetic) or passive (*i.e.* latent or potential).

When a marble is rolling along the ground it has the power, in virtue of that motion, to change the state of motion of any other marble with which it might collide. A body,

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[1] If two similar springs, one wound and the other unwound, were both dissolved in acid, it is supposed that the dissolution of the wound spring would be attended with the production of a greater amount of heat. The energy stored up in the wound spring would then be converted into thermal, not kinetic, energy. This supposition has never been verified experimentally. But let two pieces of soft steel wire be cut from the same piece, and let one piece be hardened by hammering or burnishing. Dip the two pieces in dilute acid and connect up with a suitable galvanometer. The swing of the needle corresponds with the extra store of energy in the hardened wire. The extra energy stored in the hardened wire will be transformed into electrical energy. For a discussion on the old crux "the energy of a coiled spring," see *English Mechanic*, **78.** 467 *seq.*, 1904.

therefore, might possess energy in virtue of its motion. This energy is said to be in a **kinetic** or active condition. It is found that the available kinetic energy K of a body of mass m, moving with a velocity v, is—

$$K = \frac{1}{2}mv^2.$$

Potential energy, on the other hand, is said to be "potential to" or "possible to" the body in virtue of its position. When a stone is lifted above the ground, the energy expended and the work done depend on the weight w of the stone and on its height h above the ground. Consequently, the available potential energy E of the raised stone will be—

$$E = wh.$$

The meaning is that a measurable quantity of energy is "stored up" or "rendered passive" in some way, and that this same energy can be recovered in a measurable form. For example, when the stone returns to the ground it will, in falling, acquire an equivalent amount of kinetic energy. Again, water in an elevated position can do work in virtue of the law that "all liquids will flow to the lowest level that circumstances will permit." Consequently water at the top of the hill possesses potential energy. A bent spring, a raised hammer, compressed air, and a piece of iron in the vicinity of a magnet, all possess potential energy. Substances which, in virtue of their relative position or the motions of their molecules, are capable of entering into chemical actions, are also said to possess potential energy. Such is gunpowder, a mixture of zinc and sulphuric acid, etc. The light, heat, sound, and mechanical motion which attend the explosion of gun-cotton are equivalent to the chemical energy stored in the explosive.

Water may be transported from the top of a mountain to the valley beneath in a variety of ways; it may come down in underground channels, rivers, rain, or in the form of snow, glaciers, or an avalanche. So may energy pass from a state of high to a state of lower potential in many and various ways giving rise to mechanical, thermal, actinic, chemical, electrical, or magnetic phenomena. In reality the so-called "different forms of energy" correspond with the tendencies which any given system may have to change in particular directions. If there is a tendency for the different parts of a system to come into closer contact, we have *gravitation* and *cohesion*; if there is a tendency to an equalization of temperature, *thermal energy;* and when there is a tendency to undergo transformation into another substance, *chemical energy*.

Hence the definition: **a chemical reaction is one mode by which energy can be transferred from one state to another.**

§ 8. What determines the Transfer of Energy?

It is interesting to examine the subject a little more closely. Water will only flow from one vessel to another when there is a difference in the level of the liquid in the two vessels. The actual volume of the water in either vessel does not matter. Heat will only pass from one body to another when the temperature of the one is higher than the temperature of the other. The flow of heat is not determined by the quantity of heat in either the hot or the cold body. If two reservoirs of gas be connected by a cylinder fitted with a sliding piston, the motion of the piston will not be determined by the volume of the reservoir, nor by the quantity of energy contained in the gas, but it will be determined by the pressure of the gas in the two cylinders. In this sense we can imagine the different forms of energy to be compounded of two factors—mass of water and difference of level; thermal capacity[1] and temperature; volume and pressure of gas. The one factor is called the quantity or **capacity factor**, and the other the **intensity factor** or strength.

Available energy = capacity (quantity) factor × intensity (strength) factor.

When the capacity factor is constant, or nearly so, more work can be got from a definite amount of energy with a high than with a low intensity factor, and a moment's reflection will show that in every transformation the intensity factor will be diminished. Energy becomes less available for doing work. Every change which takes place in Nature does so at the cost

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[1] See F. G. Donnan's *Thermodynamics* for more precise information.

of a certain amount of available energy. **(Law of degradation of energy.)** When we inquire whether or not any given transformation can take place, the question to be considered is whether or not the occurrence will involve the degradation of the available energy. If not, the transformation will not take place under the given conditions (Lord Rayleigh).

What are the factors of chemical energy? If chemical energy can be resolved into two factors, the one factor must be analogous to the capacity, and the other to the intensity factor of thermal energy. J. W. Gibbs calls the intensity factor of chemical energy the **chemical potential,** and G. Helm calls it the **chemical intensity.** These terms are employed with the idea of avoiding the vagueness of the old term, **chemical affinity,**[1] which is undoubtedly the correct designation for "chemical intensity." Now, the quantity of any substance which takes part in any chemical change is proportional to the "equivalent weight" of the substance; and assuming that the chemical equivalent is the capacity factor of chemical energy, we may write—

Chemical energy = equivalent weight × chemical affinity;

or—

Chemical energy = equivalent weight × chemical intensity.

§ 9. What determines Chemical Action?

If two bodies at the same temperature be placed in contact, there will be no conduction of heat from the one to the other; but when the temperature of the one body is higher than that of the other, heat will pass from the hot to the cold body, so that the cold body is warmed and the hot body is cooled. So with chemical energy. We assume that the molecules of every substance possess a specific amount of chemical energy, which has a definite intensity under certain specified conditions. One substance can only react with another when the intensity of the energy associated with the original mixture

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[1] Or "chemism." Do not confuse "potential" with "potential energy."

is greater than that of the final system. If the intensity of the energy associated with the original mixture be the same as that associated with the products of the reaction, no reaction will take place; if the intensity factors are not equal, the energy will not be at rest. Water placed in a series of vessels in communication with one another will only come to rest when the surface of the water is at the same level in each vessel. "Difference of level" here means that the gravitational energy has a different intensity factor in each vessel. An electric current will flow whenever there is an inequality of the intensity factor—*i.e.* a difference of potential—at different parts of the circuit.

If the intensity factors of any particular form of energy in a system are not equal, the system will be in a state of unstable equilibrium. Such a condition will not be permanent, and energy will flow, so to speak, from one part to another until the different intensity factors become equal.

Ostwald has drawn attention to the fact that if the chemical process is performed in a voltaic cell, the work derived from that process will be transformed into an equivalent amount of electrical energy. And since, by Faraday's law, the capacity factor—quantity of electricity—is proportional to the quantity of matter decomposed, the capacity factor of the electrical energy will be proportional to the capacity factor of the chemical energy. Hence the respective intensity factors of chemical and electrical energies will also be proportional. But electromotive force is proportional to the intensity factor of electrical energy, and therefore *electromotive force is proportional to chemical affinity.*[1] We see, then, with Faraday,[2] that "the forces called electricity and chemical affinity are one and the same." Our problem is solved for conductors of electricity—electrolytes. Chemical action takes place when the potential of the reacting substances is greater than that of the reacting

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[1] See R. A. Lehfeldt's *Electrochemistry* for a full discussion on the measurement of chemical affinity in terms of electromotive force.

[2] M. Faraday, *Phil. Trans.*, **125**. 425, 1834; *Experimental Researches in Electricity*, London, **1**. 273, 1849; G. Salet, *Laboratory*, **1**. 248, 1867.

products. We can express the "affinity" between two reacting substances in terms of difference of potential. How this may be done for non-conductors of electricity, and for other forms of energy, has not yet been determined.

If we had an instrument capable of measuring the chemical intensity of different substances in the same way that the thermometer measures intensities of thermal energy, or the electrometer measures intensities of electrical energy, we should be able to determine whether or not any given substance will react with another, just as surely as the thermometer indicates whether heat will be communicated from one body to another. Such an hypothetical instrument is called, by Ostwald, a *chemometer*.[1]

It is now easy to say why chemical action takes place. We describe the cause of chemical action, as a particular case of Lord Kelvin's principle of *degradation of energy*. **The cause of chemical action is the universal tendency[2] of chemical energy at different intensities to attain the same degree of intensity.**

We naturally ask why is it possible to keep coal an indefinite length of time in the presence of oxygen gas when the chemical intensity of coal and oxygen is so much greater than the chemical intensity of the products of combustion? Why can we keep gunpowder, nitroglycerine, and nitrogen chloride known to possess higher chemical intensities than the products of their decomposition? These questions will be discussed in a subsequent chapter.

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[1] W. Ostwald, *Zeit. phys. Chem.*, **16**. 399, 1895.

[2] Some object to the use of the words "tendency" and "inclination" in scientific terminology on account of their vague meaning. We see that a "difference of intensity" is the cause of anything that happens, and every difference of this kind represents a tendency or inclination of the system to equalize itself. The equalization of intensities may be prevented. "Tendency" then means that the action will take place the moment the restraining influence is withdrawn. Thus, difference of chemical energy may be compensated by an opposing difference of electrical intensity (potential); the latter may be made to vanish by the use of a conductor. Chemical action then sets in.

§ 10. The Measurement of Force.

We regard chemical affinity as a force which tends to make certain substances react with one another, just as gravitation is regarded as the force which tends to cause bodies to approach or recede from one another. The problem, therefore, presents itself, how can we measure the "strength" of the chemical affinity between different substances? There are two general methods.

I. Statical methods.—The magnitude of a force is frequently measured by placing the unknown force in opposition to a known force just sufficient to balance it. Thus a force which is capable of supporting a weight of 20 lbs. is just twice as great as a force capable of supporting a weight of 10 lbs. In the same way, if two acids are competing for some base which is not present in sufficient quantity to neutralize both acids, we assume that, after equilibrium has been established, the stronger acid will have neutralized more of the base than the weaker acid.

Some physical method must be employed to measure the relative distribution of the base between the two acids, in order that the state of equilibrium may not be disturbed in the act of measurement. Thomsen determined the "state of equilibrium" by measuring the change of temperature which occurs during the reaction; Ostwald measured the change of volume or density; Jellet, the change of optical properties; Berthelot and Ogier, the specific heat; Gladstone, the change of colour; and Wiedemann, the change in the magnetic properties of the solution.

II. Dynamical methods.—If a ball be sent rolling with a velocity of 20 cms. per second, the force applied to the ball would have to be twice as great as the force required to make the same ball travel with a velocity of 10 cms. per second during the same time. The intensities of two forces are therefore proportional to the velocities which they impart to equal masses during the same time. In the above examples, therefore, the intensities of the two forces are related as 2 : 1. In the same manner, if, say, two acids under exactly the same physical conditions set up two reactions with different velocities, the acid which generates the greater velocity will be exerting the greater chemical force.

It is necessary to emphasize the fact that we must not say "the velocity of a chemical reaction is a measure of chemical affinity," because the velocity is modified by a great many accidental circumstances. Thus, Wenzel's, and Guldberg and Waage's experiments on the rate of dissolution of cylinders of different metals in different acids do not furnish a measure of the intensity of the chemical force subsisting between metal and acid, because the rate of dissolution of the metal depends upon the velocity of diffusion, the specific gravity of the products of the reaction, etc. The same objection applies to the experiments of Boguski and Kajander on the rate of dissolution of marble in different acids.

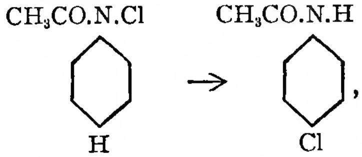
W. Ostwald first showed the possibility of finding comparable numerical values of the relative strengths of the acids from their influence on the rate of hydrolysis of acetamide. The results, however, were only approximate because the progress of the reaction is not quite free from secondary reactions due to the formation of ammonium salts. Better results were obtained during the hydrolysis of ethyl or methyl acetates, and the inversion of cane sugar in the presence of different acids. The relative strengths of the different bases has also been determined from their effect on the rate of saponification of the esters. Of this anon.

CHAPTER II

HOMOGENEOUS CHEMICAL REACTIONS

§ 11. Unimolecular Chemical Reactions.

THE most simple type of chemical change occurs when only one substance is undergoing transformation. For example, when acetochloranilide is converted into *p*-chloracetanilide—



only one molecule is involved in the process of transformation. The velocity of the change can be readily determined by removing a portion of the solution at different intervals of time, adding a solution of potassium iodide, and titrating the liberated iodine by means of a standard solution of sodium thiosulphate. *p*-chloracetanilide does not react with potassium iodide, acetochloranilide does.

If the experiment is started with a gram-molecules of acetochloranilide per litre of solution, and if, at the end of a certain time t, x gram-molecules of acetochloranilide have been transformed, $a-x$ gram-molecules of unchanged acetochloranilide will remain in solution. Then, according to the law of mass action, the velocity of transformation, at any moment, will be proportional to the amount of acetochloranilide then present in the solution; hence—

$$\frac{dx}{dt} = k(a - x); \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and by integration we get—

$$\frac{1}{t}\log\frac{a}{a-x} = k;\ \text{or,}\ \frac{1}{t_2-t_1}\log\frac{a-x_1}{a-x_2} = k, \quad (2)$$

where x_1 and x_2 respectively denote the amounts of substance transformed at the end of the intervals of time t_1 and t_2. The meaning of k is found by putting $x = 0$, and $a = 1$. It denotes the rate of transformation of unit mass of substance. The value of k, be it noted, is independent of a, the original concentration of the substance undergoing transformation.

J. J. Blanksma[1] has measured the velocity of the above reaction, and obtained results which agree closely with equations (1) and (2). Thus, from the first of equations (2)—

t hours.	cc. thiosulphate, *i.e.*, $a - x$.	k
0	49·3	—
1	35·6	0·139
2	25·75	0·140
3	18·5	0·140
4	13·8	0·138
6	7·3	0·138
8	4·8	0·139

If we employ the second of equations (2) we get the same constant, and, moreover, we can start the measurement or calculation of the constants at any time we please. For example, let $t_1 = 1$, $t_2 = 4$; in that case—

$$\frac{1}{4-1}\log\frac{35{\cdot}6}{13{\cdot}8} = 0{\cdot}138.$$

The moment at which the reaction begins is not well defined, because (1) the uniform mixing of the substances taking part in the reaction occupies a certain amount of time; and (2) the heat of the reaction also causes a rise of temperature, which usually accelerates the velocity of the reaction. This acceleration continues until the further heating of the

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[1] J. J. Blanksma, *Rec. trav. Pays-Bas.*, **21**. 366, 1902; **22**. 290, 1903.

solution is prevented by the conduction or radiation of heat away from the reacting system.

These initial disturbances become more marked the greater the velocity of the reaction. In order to eliminate their effects, it is usual to neglect the irregular velocity coefficients determined for the initial stages of the reaction.

It will here be noticed that the concentration of only one molecule of the substance is undergoing change. Such reactions are termed *unimolecular* (or monomolecular) reactions, or reactions of the first order.

Among other reactions of the first order which might be mentioned, we have the conversion of dibromosuccinic acid into bromomaleïc acid;[1] the decomposition of aqueous solutions of ammonium nitrite;[2] the conversion of synaldoximes into the anti-form;[3] the decomposition of nickel carbonyl;[4] the decomposition of the diazo salts of the benzene series,[5] and of the naphthalene series;[6] of hyoscyamine into atropine;[7] the "Beckmann" rearrangement,[8] *e.g.* the conversion of acetophenoxime into acetanilide; the decomposition of sodium isonitrosoacetophenone;[9] the conversion of persulphuric acid into "Caro's" acid;[10] the formation of pyruvic acid phenylhydrazone from oxalacetic acid phenylhydrazone;[11] and the decomposition of hydrogen iodide in light.[12]

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[1] J. H. van't Hoff, *Études*, 14, 1884.

[2] V. H. Veley, *Journ. Chem. Soc.*, **83**. 736, 1903.

[3] H. Ley, *Zeit. phys. Chem.*, **18**. 376, 1895; A. Hantzsch, *ib.*, **13**. 509, 1894.

[4] A. Mittasch, *Zeit. phys. Chem.*, **40**. 1, 1902.

[5] J. Hausser and P. T. Muller, *Bull. Soc. Chim.* [3], **7**. 721, 1892; **9**. 353, 1893; *Compt. Rend.*, **114**. 549, 669, 760, 1438, 1892; J. C. Cain and F. Nicoll, *Journ. Chem. Soc.*, **81**. 1412, 1902.

[6] J. C. Cain and F. Nicoll, *Journ. Chem. Soc.*, **83**. 206, 1903.

[7] G. Bredig and W. Will, *Ber.*, **21**. 2777, 1888; A. Mazzucchelli, *Gazz. Chim. Ital.*, **30**. ii., 476, 1900.

[8] C. A. Lobry de Bruyn and C. H. Sluiter, *Koninklijke Akad. van Wetenschappen*, 773, 1904.

[9] C. H. Sluiter, *Koninklijke Akad. van Wetenschappen*, 453, 1904.

[10] M. Mugdan, *Zeit. Elektrochem.*, **9**. 719, 1903.

[11] H. O. Jones and O. W. Richardson, *Journ. Chem. Soc.*, **81**. 1140, 1902.

[12] M. Bodenstein, *Zeit. phys. Chem.*, **13**. 116, 1894; for a short

§ 12. When does a Chemical Reaction end?

It is interesting to notice that the integral of (1), page 10, may be written in the form—

$$x = a(1 - e^{-kt}),$$

from which it is easy to see that when t is infinite—

$$e^{-kt} = 0; \therefore x = a.$$

This means that if the reaction obeys the "law" symbolized by the differential equation (1), the reaction can only come to an end after the expiration of an infinitely long period of time. Or, as Mills[1] puts it, "the process of exhaustion of the chemical energy of a substance requires an infinitely great period of time for its accomplishment. Hence," he continues, "we can understand how a chemical reaction is possible. It can begin because it has never ended . . . every substance retains a minute but real reserve of unexhausted energy."

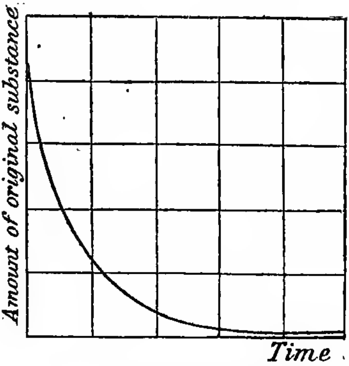

FIG. 4.—Velocity curve.

This conclusion also follows directly by plotting either of equations (2), as in Fig. 4. The curve continually approaches the t-axis as time goes on and the value of x approaches a, but it can only touch this axis when t is infinite and $x = a$.

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bibliography see R. B. Warder, *Proc. Amer. Assoc. Science*, **32.** 155, 1883; and W. Herz's *Chemische Verwandtschaftlehre* (of *Ahrens' Sammlung*, **8.** 1903); for an application of velocity determinations to organic chemistry, H. Goldschmidt, *Zeit. angew. Chem.*, **13.** 1208, 1899; for a set of "lecture" experiments illustrating the laws of chemical reactions—velocity, equilibrium, ionization—see A. A. Noyes and A. A. Blanchard, *Journ. Amer. Chem. Soc.*, **22.** 726, 1900; *Zeit. phys. Chem.*, **36.** 1, 1901.

[1] E. J. Mills, *Phil. Mag.* [5], **1.** 1, 1876.

In practice the end state is so nearly attained in a relatively short time, that it is often convenient to find the value of a in terms of x, by allowing the reaction to run a sufficient length of time and then to put $x = a$.

Why do not all the molecules undergo change at one time? What regulates the speed of the reaction in such a way that only a certain fraction of the total number of molecules changes in unit time? If all the molecules were in the same condition, then either no chemical change would take place at all, or else all the molecules would undergo transformation at the same instant.

No definite answer is forthcoming. Quite a number of explanations have been suggested. For example, we have—

(i.) The "intermediate compound theory," in which the intramolecular change is supposed to take place only when the substance is associated, in some way, with another substance. This theory is discussed in a later chapter.

(ii.) The atoms of the molecule have also been supposed to undergo a series of vibratory, or cyclic motions resembling the movements of the planets of the solar system.[1] It is further supposed that one particular configuration of the atoms is unstable, so that instead of the atoms of the molecule returning to their former orientation, they take up a more stable configuration. In other words, the molecule undergoes chemical transformation.

(iii.) According to the kinetic theory a certain number of molecules, at any given instant, possess a much greater, and others a much smaller, velocity of translation than the average.[2] It is assumed that the kinetic energy of the translatory motions of the molecules may be converted into energy of atomic vibrations,[3] and when the latter exceeds a certain limiting

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[1] D. Mendeléeff's *The Principles of Chemistry*, **2**. 417, 1891 (Royal Inst. Lecture, 1889); S. Haughton, *Proc. Roy. Irish Acad.* [3], **1**. 631, 1891.

[2] J. C. Maxwell, *Phil. Mag.* [4], **19**. 22, 1860; *Phil. Trans.*, **157**. 49, 1867.

[3] E. Wiedemann, *Wied. Ann.*, **37**. 177, 1889; *Phil. Mag.* [5], **28**. 149, 248, 376, 493, 1889. But see the "intermediate compound theory," pp. 316, and 298.

value, the atoms of the molecule take up a more stable configuration. The rate of chemical transformation is the rate at which the velocities of the molecules are accelerated beyond the limiting value. This is a favourite mode of explanation, but the influence of temperature upon the velocity of translation of the molecules does not agree with its influence upon the velocity of chemical action.

The rate of decay of the radioactivity of the emanation from radium salts, and the rates of transformation of thorium into thorium X, and of uranium into uranium X, follow the unimolecular law.[1]

Since radioactive changes are not perceptibly influenced by external agents—temperature, combination with an inactive element, etc.—it has been suggested that the atom of radium consists of a number of small particles in a state of rapid, irregular motion, and that an "explosive" rearrangement of the particles with the ejection of parts of the system occurs when the system assumes certain configurations.

§ 13. Bimolecular Reactions.

The preceding equations do not hold good when more than one substance changes concentration, and chemical reactions in which two substances are simultaneously undergoing transformation are much more frequently met with in chemistry. The law of mass action must therefore be extended. We assume that when two or more bodies are simultaneously undergoing chemical change, the rate of change, at any moment, of any one member of the system is proportional to its active mass, and the total change, at any moment, is proportional to the product of the active masses of all the substances undergoing change.

The hydrolysis of ethyl acetate by sodium hydroxide is a bimolecular reaction, or reaction of the second order, because

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[1] E. Rutherford and F. Soddy, *Journ. Chem. Soc.*, **81**. 321, 837, 1902; *Phil. Mag.* [6], **5**. 445, 1903; P. Curie, *Compt. Rend.*, **135**. 187, 1902.

two of the reacting substances disappear during the progress of the reaction—

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

If we start with a gram-molecules of each substance, then at the end of a certain time t, the same number of molecules of sodium hydroxide and of ethyl acetate will have disappeared, and $a - x$ gram-molecules of each substance will remain in the solution. The fundamental assumption still holds good: the velocity of the reaction is still proportional to the amount of each substance taking part in the reaction. In other words, the rate of formation of sodium acetate and of ethyl alcohol is proportional to the amounts of ethyl acetate and sodium hydroxide present in the solution; or—

$$\frac{dx}{dt} = k(a - x)^2, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which on integration assumes the form—

$$\frac{1}{t} \cdot \frac{x}{a - x} = ak; \text{ or, } \frac{1}{t_2 - t_1}\left(\frac{1}{a - x_2} - \frac{1}{a - x_1}\right) = k, \quad (4)$$

where x_1 and x_2 respectively denote the amounts of each substance which have disappeared in the times t_1 and t_2. Note that since a is a constant, the product ka is also a constant. It will also be noticed that k is inversely proportional to the initial concentration a of the reacting substances.

Berthelot[1] first suggested an equation of this type, in 1862, to represent the rate of formation of ethyl ester by the action of acetic acid upon ethyl alcohol. But he does not appear to have made any special use of it. Harcourt and Esson,[2] in 1865, first employed the equation to test the hypothesis which we now call Wilhelmy's law. Guldberg and Waage[3] independently adopted the same formula in their celebrated memoir "On Chemical Affinity." R. B. Warder's experiments[4] on the

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[1] M. Berthelot, *Ann. Chim. Phys.* [3], **66.** 110, 1862.

[2] A. V. Harcourt and W. Esson, *Phil. Trans.*, **156.** 193, 1866.

[3] C. M. Guldberg and P. Waage's *Études sur les affinités chimiques.* Christiania, 1867.

[4] R. B. Warder, *Ber.*, **14.** 1311, 1881; *Amer. Chem. Journ.*, **3.** 340, 1882.

rate of hydrolysis of ethyl acetate by sodium hydroxide may be cited to illustrate the application of the above formula—

t	x	ak
5	5·76	0·113
15	9·87	0·107
25	11·68	0·108
35	12·59	0·106
55	13·69	0·108
120	14·90	0·113

The result is in agreement with the law of mass action.

It is not necessary to start with equivalent amounts of ethyl acetate and sodium hydroxide. Suppose, for example, that we start with a gram-molecules of sodium hydroxide and b gram-molecules of ethyl acetate. In that case, the bimolecular reaction must be represented by the equation—

$$\frac{dx}{dt} = k(a - x)(b - x), \quad . \quad . \quad . \quad . \quad (5)$$

which becomes, on integration—

$$\frac{1}{t} \log \frac{b(a - x)}{a(b - x)} = (a - b)k;$$

$$\text{or, } \frac{1}{t_2 - t_1} \log \frac{a - x_2}{b - x_2} - \log \frac{a - x_1}{b - x_1} = (a - b)k, \quad (6)$$

where the product $(a - b)k$ is constant.

Equations (3) and (5) follow as a direct consequence of the kinetic theory of gases with the assumption that chemical action takes place whenever two molecules come sufficiently near to each other.[1]

A moment's examination of equation (5) will show that the velocity of a bimolecular reaction, for which $a + b$ is constant, will be greatest when a and b are equal, that is, when—

$$a - x = b - x,$$

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[1] R. Clausius, *Pogg. Ann.*, **105**. 250, 1858; *Phil. Mag.* [4], **17**. 81, 1859; L. Joulin, *Ann. Chim. Phys.* [4], **30**. 284, 1873; L. Boltzmann's *Vorlesungen uber Gastheorie*, Leipzig, **2**. 177, 1898.

just as a square has the greatest area of all parallelograms which have the sum of two adjoining sides of a certain fixed length. This agrees with Bunsen and Roscoe's measurements of the rate of combination of hydrogen and chlorine in light. The velocity of the reaction was fastest with equal volumes of hydrogen and chlorine.[1]

L. T. Reicher's experiments[2] on the rate of hydrolysis of ethyl acetate by sodium hydroxide furnish us with data to test expressions (5) and (6).

Alkali in excess.				Ester in excess.			
t	$a - x$	$b - x$	$(a - b)k$	t	$a - x$	$b - x$	$(a - b)k$
0	0·5638	0·3114	—	0	0·3910	0·6593	—
393	0·4866	0·2342	0·0335	342	0·2885	0·5568	0·0346
669	0·4467	0·1943	0·0342	670	0·2239	0·4222	0·0347
1010	0·4113	0·1589	0·0339	888	0·1925	0·4605	0·0345
1265	0·3879	0·1354	0·0346	1103	0·1677	0·4350	0·0344

Similar results have been obtained for the action of acids upon acetamide;[3] the esterification of the chloroacetic acids;[4] the formation of anilides;[5] and of alkaline xanthates;[6] the action of alkyl sulphides upon alkyl iodides,[7] and of ethyl iodide upon silver nitrate;[8] the transformation of sodium monochloracetate into sodium glycollate by the action of sodium hydroxide;[9]

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[1] R. Bunsen and H. E. Roscoe, *Phil. Trans.*, **147**. 381, 1857; A. Gautier and H. Hélier's experiments (*Compt. Rend.*, **124**. 1129, 1267, 1897) with the same gases do not appear to be so exact.

[2] L. T. Reicher, *Liebig's Ann.*, **228**. 257, 1885; **232**. 103, 1886.

[3] W. Ostwald, *Journ. prakt. Chem.* [1], **27**. 1, 1883.

[4] D. M. Lichty, *Amer. Chem. Journ.*, **17**. 27, 1895; **18**. 590, 1896; R. B. Warder, *Journ. Phys. Chem.*, **1**. 149, 1896.

[5] H. Goldschmidt and C. Wachs, *Zeit. phys. Chem.*, **24**. 353, 1897.

[6] N. V. Moro, *Gazz. Chim. Ital.*, **26**. i., 494, 1896.

[7] G. Carrara, *Gazz. Chim. Ital.*, **26**. i., 483, 1896.

[8] V. Chiminello, *Gazz. Chim. Ital.*, **25**. ii., 410, 1895.

[9] L. C. Schwab, *Rec. Travs. Pays-Bas*, **2**. 46, 1883; J. H. van't Hoff, *Études*, 20, 1884.

the hydrolysis of the nitrobenzamides;[1] the oxidation of formaldehyde by hydrogen peroxide;[2] the diazotization of aromatic amines;[3] the decomposition of diphenyliodonium iodide and chloride in aqueous solution;[4] the replacement of halogens by oxy-alkyl groups in aromatic nitrohaloid compounds;[5] the reduction of Fehling's solution;[6] the action of bromine on the fatty acids,[7] and the action of chlorine upon carbon monoxide.[8]

The student is particularly recommended to study the papers by Conrad and his co-workers in the *Zeitschrift für physikalische Chemie*, vols. 3 to 7,[9] on the rate of formation of ethers.

The rate of ionization, and the rate of recombination of the ions of a gas, also follow the bimolecular law.[10]

The constant k of a unimolecular reaction is not affected by the units chosen for expressing the concentration—a and x—of the reacting substance, for if we use a system of units, say, n times less than that adopted in this work, a and x of equation (2), § 11, must be replaced by na and nx respectively. But n now cancels out. This means that k is independent of

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[1] I. Remsen and E. E. Reid, *Amer. Chem. Journ.*, **21**. 281, 1899.

[2] J. H. Kastle and A. S. Loevenhart, *Journ. Amer. Chem. Soc.*, **21**. 262, 1899.

[3] M. Schümann and A. Hantzsch, *Ber.*, **32**. 1691, 1899; M. Schümann, *ib.*, **33**. 527, 1900.

[4] E. H. Büchner, *Koninklijke Akad. van Wetenschappen*, 646, 1903.

[5] P. K. Lulofs, *Rec. Travs. Pays-Bas*, **20**. 292, 1901; A. Steger, *ib.*, **18**. 9, 1899; *Dissertation*, Amsterdam, 1899; C. A. Lobry de Bruyn, *Koninklijke Akad. van Wetenschappen*, 144, 1898.

[6] F. Urech, *Ber.*, **15**. 2687, 1882; **16**. 2825, 1883; **17**. 495, 1539, 1884.

[7] F. Urech, *Ber.*, **13**. 483, 1687, 1880; **14**. 340, 1881; **19**. 1700, 1886; **20**. 234, 1634, 1887; *Itinerarium durch die theoretische Entwickelungsgeschichte der Lehre von der chemischen Reaktionsgeschwindigkeit*, Berlin, 1885; with C. Hell, *Ber.*, **13**. 531, 1880.

[8] M. Wildermann, *Phil. Trans.*, **199**. 337, 1902.

[9] M. Conrad with W. Hecht, *Zeit. phys. Chem.*, **3**. 450, 1889; with W. Hecht and C. Brückner, *ib.*, **4**. 273, 1889; with C. Brückner, *ib.*, **4**. 631, 1889; with W. Hecht and C. Brückner, *ib.*, **5**. 289, 1890; with C. Brückner, *ib.*, **7**. 274, 283, 1891.

[10] E. Rutherford, *Phil. Mag.* [5], **44**. 422, 1897 [5], **47**. 109, 1899; R. K. McClung, *ib.* [6], **3**. 283, 1902; J. A. McClelland, *ib.* [5], **46**. 29, 1898.

n. Not so for a bimolecular reaction. It can be shown, by treating (3) or (6) in the same way, that the constant k is augmented n times when the unit of concentration is diminished n times.

§ 14. Bimolecular Reactions apparently of the First Order.

There are several bimolecular reactions which behave as if they were unimolecular. For example, the inversion of cane sugar, first studied by Wilhelmy in 1850,[1] takes place according to the equation—

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

Although two molecules—cane sugar and water—really take part in the reaction, yet the measurements of the velocity of inversion furnish a "constant" when substituted in the unimolecular equation—

$$\frac{dx}{dt} = k_1(a - x) ; \ \frac{1}{t} \log \frac{1}{a - x} = k_1. \quad . \quad . \quad (7)$$

This is clearly shown by the following measurements of the rate of inversion of cane sugar ($a = 10{\cdot}023$) :—

t	x	k_1
0	0	—
30	1·001	0·00152
60	1·946	0·00156
90	2·770	0·00156
130	3·726	0·00155
180	4·676	0·00151

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[1] L. Wilhelmy, *Pogg. Ann.*, **81**. 413, 499, 1850; W. Ostwald's *Klassiker*, No. 29; G. Fleury, *Ann. Chim. Phys.* [5], **7**. 381, 1876; W. Ostwald, *Journ. prakt. Chem.* [2], **29**. 385, 1884; see also A. von Sigmond, *Zeit. phys. Chem.*, **27**. 385, 1898 (hydrolysis maltose); F. Urech, *Ber.*, **13**. 1696, 1880; **15**. 2130, 2457, 1882; **17**. 47, 2165, 1884; **18**. 3047, 1885.

In order that the anomaly may be clearly understood, let us now calculate the result of including the change of concentration of the water in our calculation, so that—

$$\frac{dx}{dt} = k_2(a - x)(b - x)\,;\ \frac{1}{t}\log\frac{b(b - x)}{a(a - x)} = k_2. \qquad (8)$$

In the above series of measurements $a = 10{\cdot}023$, $b = 89{\cdot}977$.

t	$a - x$	$b - x$	Constants.	
			k_1	k_2
0	10·023	89·977	—	—
30	9·022	89·924	0·00152	0·00150
60	8·077	89·875	0·00156	0·00155
90	7·253	89·832	0·00156	0·00154
130	6·297	89·788	0·00155	0·00154
180	5·347	89·731	0·00151	0·00151
		Mean . . .	0·00154	0·00153

We see at once that if x is small in comparison with b, b and $b - x$ are practically equal to one another. Cancelling out these factors, we get the unimolecular equation (7).

Since the values of k_1 and k_2 in the last two columns of the preceding table agree within the range of experimental error, it will be evident that when the amount of water present greatly exceeds the amount of cane sugar, the relatively slight change in the concentration of the water which takes place during the hydrolysis is not sufficient to affect the value of the constant. At all events, the method of measurement is not sufficiently sensitive to distinguish between the uni- and bi- molecular reaction.

The same result is shown graphically in Fig. 5, where curve I. is the graph of equation (7) for $a = 1$; curve II. the graph of equation (8) for $a = 1$, $b = 2$; curve III. for $a = 1$, $b = 4$; and curve IV. is for $a = 1$, $b = 10$. In all the constants k_1 and k_2 have been put equal to unity. The gradual approach of the velocity curves for the bimolecular reaction to the curves for a unimolecular reaction as the amount of one of the reacting components of the bimolecular reaction is increased, shows very clearly how the course of a bimolecular reaction might appear unimolecular when one of the reacting components is in excess. This fact is sometimes overlooked.

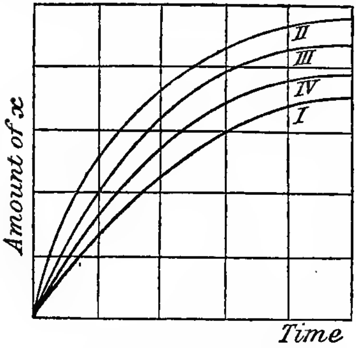

FIG. 5.—Velocity curves.

Other reactions of this type have been observed during the reduction of potassium permanganate by a great excess of oxalic acid;[1] the action of chlorine upon water in the light,[2] of hydrogen peroxide upon hydrogen iodide;[3] the hydrolysis of methyl acetate;[4] the transformation of monochloracetic acid into glycollic acid by the action of water;[5] the action of water of carbonyl sulphide;[6] the transformation of diamido- into amidoazo- compounds;[7] the formation of olefines

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[1] A. V. Harcourt and W. Esson, *Phil. Trans.*, **156**. 193, 1866; *Proc. Roy. Soc.*, **14**. 470, 1865.

[2] C. Wittwer, *Pogg. Ann.*, **94**. 598, 1855; W. Ostwald's *Lehrbuch der allgemeinen Chemie*, Leipzig, **2**. i., 1034, 1903.

[3] A. V. Harcourt and W. Esson, *Phil. Trans.*, **157**. 117, 1867; *Journ. Chem. Soc.*, **20**. 476, 1867; *Proc. Roy. Soc.*, **15**. 262, 1867; see also Bredig's work on the decomposition of hydrogen peroxide by catalytic agents; G. Bredig and R. Müller von Berneck, *Zeit. phys. Chem.*, **31**. 296, 1901; G. Bredig and K. Ikeda, *ib.*, **37**. 63, 1901; G. Bredig and W. Reinders, *ib.*, **37**. 336, 1901; G. Bredig and J. H. Walton, jun., *Zeit. Elektrochem.*, **9**. 114, 1903; J. M. Bell, *Journ. Phys. Chem.*, **7**. 61, 1903; J. H. Walton, jun., *Zeit. phys. Chem.*, **47**. 185, 1904; T. S. Price and A. D. Deeming, *ib.*, **46**. 89, 1903; G. Bredig, *ib.*, **48**. 368, 1904.

[4] W. Ostwald, *Journ. prakt. Chem.* [2], **28**. 449, 1883; A. von Hemptinne, *Zeit. phys. Chem.*, **31**. 35, 1899.

[5] J. H. van't Hoff, *Études*, 14, 1884.

[6] G. Buchböck, *Zeit. phys. Chem.*, **23**. 123, 1897.

[7] H. Goldschmidt and R. V. Reinders, *Ber.*, **29**. 1369, 1899, 1896.

from aliphatic iodides;[1] the formation of sulphonic ethers;[2] the hydrolysis of phosphoric ethers;[3] the hydration of meta- and pyro- phosphoric acids;[4] and the action of chlorine upon benzene in light.[5]

§ 15. Substitutes for Integration.

It may not always be convenient, or even possible, to integrate the differential equation; in that case a less exact method of verifying the theory embodied in the equation must be adopted. For the sake of illustration, take an equation of the first order—

$$\frac{dx}{dt} = k(a - x); \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a denotes the initial concentration. Let dt denote unit interval of time, and let Δx denote the difference between the initial and final quantity of substance transformed in unit interval of time, then $\frac{1}{2}\Delta x$ denotes the average amount of substance transformed during the same interval of time. Hence we write—

$$\Delta x = k_1(a - \tfrac{1}{2}\Delta x),$$

which, by algebraic transformation, becomes—

$$\Delta x = \frac{k_1 a}{1 + \frac{1}{2}k_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For the next interval—

$$\Delta x = k_1(a - x - \tfrac{1}{2}\Delta x), \text{ etc.}$$

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[1] S. Brussoff, *Zeit. phys. Chem.*, **34**. 129, 1900.

[2] W. Sagrebin, *Zeit. phys. Chem.*, **34**. 149, 1900.

[3] J. Cavalier, *Compt. Rend.*, **127**. 114, 1898; G. Belugon, *Bull. Soc. Chem.* [3], **21**. 166, 1899.

[4] C. Montemartini and V. Egidi, *Gazz. Chim. Ital.*, **31**. i., 394, 1901; **32**. i., 381, 1902; P. Sabatier, *Compt. Rend.*, **106**. 63, 1888; **108**. 738, 804, 1889; J. C. and F. C. Blake, *Amer. Chem. Journ.*, **27**. 68, 1902; H. Giran, *Ann. Chim. Phys.* [7], **30**. 203, 1903.

[5] A. Slator, *Journ. Chem. Soc.*, **83**. 729, 1903.

These expressions may be used in place of the integral of (1)—

$$k = \frac{1}{t} \log \frac{a}{a - x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for the verification of (1).

With equations of the second order—

$$\frac{dx}{dt} = k_2(a - x)^2, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

we get in the same way—

$$\Delta x = \frac{k_2 a^2}{1 + k_2 a}; \quad \Delta x = \frac{k_2(a - x)^2}{1 + k_2(a - x)}, \text{ etc.} \quad . \quad (5)$$

by putting, as before, Δx in place of dx, $dt = 1$, $x = \frac{1}{2}\Delta x$, and remembering that the second power of Δx is negligibly small. The regular integral of (4) is—

$$k_2 = \frac{1}{at} \cdot \frac{x}{a - x}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By way of numerical illustration, let us suppose that k_1 and k_2 are both equal to 0·1, and that $a = 100$. From (2)—

$$\Delta x = \frac{0{\cdot}1 \times 100}{1{\cdot}05} = 9{\cdot}52; \ \therefore a - x = 100 - 9{\cdot}52 = 90{\cdot}48;$$

$$\Delta x = \frac{0{\cdot}1 \times 90{\cdot}48}{1{\cdot}05} = 8{\cdot}62; \ \therefore a - x = 90{\cdot}48 - 8{\cdot}62 = 81{\cdot}87.$$

Again from (5), for reactions of the second order—

$$\Delta x = \frac{0{\cdot}1 \times 10{,}000}{1 + 0{\cdot}1 \times 100} = 90{\cdot}99; \ \therefore a - x = 100 - 90{\cdot}09 = 9{\cdot}09;$$

$$\Delta x = \frac{(9{\cdot}09)^2 \times 0{\cdot}1}{1 + 0{\cdot}1 \times 9{\cdot}09} = 4{\cdot}33; \ \therefore a - x = 9{\cdot}09 - 4{\cdot}33 = 4{\cdot}76.$$

The following table shows that the results obtained by this method of approximation compare very favourably with those obtained from the regular integrals (3) and (6). There is, of course, a slight error, but that is within the limits of experimental error.

First order.			Second order.		
t	$a - x$		t	$a - x$	
	by (2)	by (3)		by (5)	by (6)
0	100	100	0	100	100
1	90·48	90·48	1	9·09	9·09
2	81·86	81·86	2	4·76	4·76
3	74·08	74·06	3	3·23	3·23
4	67·03	67·01	4	2·44	2·44
5	60·65	60·63	5	1·96	1·96
6	54·88	54·86	6	1·64	1·64
7	49·66	49·64	7	1·41	1·41
8	44·93	44·91	8	1·23	1·24

§ 16. Termolecular Reactions.

If three substances take part in the reaction, we have termolecular (or trimolecular) reactions represented by the equation—

$$\frac{dx}{dt} = k(a - x)(b - x)(c - x), \quad . \quad . \quad . \quad (1)$$

which, on integration, assumes the form—

$$-\frac{1}{t} \cdot \frac{\log \left(\frac{a}{a - x}\right)^{b - c}\left(\frac{b}{b - x}\right)^{c - a}\left(\frac{c}{c - x}\right)^{a - b}}{(a - b)(b - c)(c - a)} = k, \quad (2)$$

where a, b, and c respectively denote the initial concentrations of the reacting substances.

I. In exemplification of the preceding formula, we may take the reaction—

$$6FeSO_4 + KClO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + KCl + 3H_2O,$$

which was thought by Hood[1] to be bimolecular. According to Noyes and Wason,[2] the analogous reaction—

$$6FeCl_2 + KClO_3 + 6HCl = 6FeCl_3 + KCl + 3H_2O,$$

is termolecular. For example, it was found that when the concentration of $FeCl_2 = a = 0{\cdot}1$; $KClO_3 = b = 0{\cdot}05$; $HCl = c = 0{\cdot}2$,

t	x	Constant × 10^7
5	2·30	157
12	4·80	160
40	11·74	164
70	15·53	161
110	18·49	154
170	21·04	149

II. If the concentration of two of the reacting substances is the same, so that, say, $a = b$, the differential equation assumes the form—

$$\frac{dx}{dt} = k(a - x)^2(c - x), \quad . \quad . \quad . \quad . \quad (3)$$

and the integral—

$$\frac{1}{t} \cdot \frac{1}{(c - a)^2}\left\{\frac{(c - a)x}{a(a - x)} + \log\frac{c(a - x)}{a(c - x)}\right\} = k. \quad . \quad (4)$$

In one of Noyes and Wason's experiments, $a = 0{\cdot}05$, $b = 0{\cdot}05$, $c = 0{\cdot}2$.

t	x	Constant × 10^7
5	1·10	153
15	2·18	164
50	8·02	165
100	11·86	162
160	14·65	165
250	16·90	160

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[1] J. J. Hood, *Phil. Mag.* [5], **6**. 371, 1878; **8**. 121, 1879; **20**. 323, 1885.

[2] A. A. Noyes and R. S. Wason, *Zeit. phys. Chem.*, **22**. 210, 1897.

If the factor $c - a$ be small, the calculated values of k will not be very accurate. The difficulty can be got over by using another process of integration,[1] which furnishes the expression—

$$\frac{1}{t}\left[\frac{1}{2}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\} - \frac{c-a}{3}\left\{\frac{1}{(a-x)^3} - \frac{1}{a^3}\right\} + \ldots\right] = k, \quad (5)$$

which must then be used in place of (4). The first term is free from the factor $c - a$, and it will be found accurate enough as it stands without taking succeeding "correction terms" into consideration.

III. Finally, if the concentration of all three reacting substances is the same, $a = b = c$, the differential equation must be written—

$$\frac{dx}{dt} = k(a-x)^3, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which becomes, on integration—

$$\frac{1}{t}\cdot\frac{1}{2}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\} = k. \quad . \quad . \quad . \quad . \quad (7)$$

Selecting one of Noyes and Wason's experiments in which $a = 0{\cdot}1$, $b = 0{\cdot}1$, $c = 0{\cdot}1$, we have—

t	x	Constant × 10^7
5	1·19	171
15	3·02	162
35	5·88	168
60	8·12	166
110	11·17	173
170	12·98	165

All these observations furnish very satisfactory values for the constants, and show that Wilhelmy's method may be employed to deal with more complex systems than the simple case of the inversion of cane sugar.

In further exemplification of termolecular reactions we

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[1] "Integration in Series," *vide* Mellor's *Higher Mathematics.*

have the action of benzaldehyde upon sodium hydroxide;[1] of stannous chloride upon ferric chloride;[2] of silver nitrate upon sodium formate;[3] the polymerization of cyanic acid;[4] the decomposition of potassium hypoiodite;[5] the union of hydrogen and oxygen;[6] the oxidation of sulphur dioxide;[7] and possibly the reaction between phosphorous acid and mercuric chloride.[8]

It will be noticed that k is inversely proportional to the square of the initial concentration of the reacting substances. By comparing this result with the values of k for reactions of the first, second, and higher orders, it will be seen that *for reactions of the nth order, the coefficient k is inversely proportional to the* $(n-1)$*th power of the initial concentration of the reacting substances.*

§ 17. Number and Kind of Reacting Molecules.

The reduction of silver acetate by sodium formate is a termolecular process, although only two substances take part in the reaction.

$$2CH_3COOAg + HCOONa = 2Ag + CO_2 + CH_3COOH + CH_3COONa.$$

A constant value for k is obtained when the experimental data

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[1] C. Pomeranz, *Sitz. d. Wein. Akad.*, **109**. ii., 282, 1900. If aldehyde is in excess, the reaction is of the second order.

[2] A. A. Noyes, *Zeit. phys. Chem.*, **16**. 546, 1895; **21**. 16, 1896; *Technology Quarterly*, **8**. 90, 1895; L. Kahlenberg, *Amer. Chem. Journ.*, **16**. 314, 1894, thinks the reaction is bimolecular; F. L. Kortright, *ib.*, **17**. 116, 1895, thinks ferric chloride is hydrolysed in solution, and only the non-hydrolysed part takes part in the reaction.

[3] A. A. Noyes and G. J. Cottle, *Zeit. phys. Chem.*, **27**. 579, 1898.

[4] J. H. van't Hoff, *Études*, 90, 1884.

[5] A. Schwicker, *Zeit. phys. Chem.*, **16**. 303, 1895; but this is doubtful (see E. L. C. Forster, *Journ. Phys. Chem.*, **7**. 640, 1903).

[6] M. Bodenstein, *Zeit. phys. Chem.*, **29**. 665, 1899; or *Gas Reaktionen in der chemischen Kinetik*, Leipzig, 93, 1899.

[7] G. Bodländer and K. Köppen, *Zeit. Elektrochem.*, **9**. 559, 1903.

[8] C. Montemartini and V. Egidi, *Gazz. Chim. Ital.*, **32**. ii., 182, 1902 (doubtful).

is substituted in the usual equation (4) or (7). Similar results were obtained by Noyes for the reaction—

$$2FeCl_3 + SnCl_2 = FeCl_2 + SnCl_4,$$

provided equivalent quantities of the two chlorides are employed; when equivalent amounts of ferric and stannous chlorides are not employed, the constancy of *k* is by no means satisfactory. For example—

$SnCl_2 = FeCl_3 = 0·0625$			$SnCl_2 = 0·05$; $FeCl_3 = 0·025$		
t	*x*	$k \times 10^7$	*t*	*x*	$k \times 10^7$
1	0·01434	88	1	0·00434	176
3	0·03664	81	5	0·00978	116
7	0·03612	84	10	0·01264	98
11	0·04102	87	26	0·01786	104
40	0·05058	85	43	0·02054	127

The numbers in the last column might leave some doubt as to whether the reaction is really of the third order, but the result is still less satisfactory when the experimental data are substituted in the equation for a bimolecular reaction. It is also found that an excess of ferric chloride accelerates the reaction much more than an equivalent excess of stannous chloride. If the reaction were of the third order, this is just what we should expect; for, with a reaction of the second order, a definite excess of either constituent would produce, other things being equal, the same effect. The bimolecular equation is symmetrical with respect to *a* and *b*.[1] If the above reaction were of the second order, two equivalents of iron chloride and one equivalent of tin chloride would produce the same effect as two equivalents of tin chloride and one equivalent of iron chloride.[2]

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[1] Confirmed by the work of T. L. Reicher, *l.c.*; J. J. Hood, *l.c.*; F. Lengfeld, *Amer. Chem. Journ.*, **11.** 40, 1889; F. Urech, *Ber.*, **18.** 95, 346, 1885.

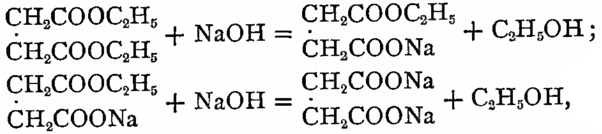
[2] Of course, assuming no side or catalytic actions occur.

The discordant results no doubt indicate that the reaction really takes place in a series of stages. This question will be discussed in a subsequent chapter.

We see, therefore, that the course of a reaction is not always that indicated by the differential equation corresponding with the chemical equation. Again, the action of sodium hydroxide upon ethyl succinate—

$$C_2H_4(COOC_2H_5)_2 + 2NaOH = C_2H_4(COONa)_2 + 2C_2H_5OH,$$

is probably made up of the two bimolecular reactions[1]—



$$\begin{matrix} CH_2COOC_2H_5 \\ \dot{C}H_2COOC_2H_5 \end{matrix} + NaOH = \begin{matrix} CH_2COOC_2H_5 \\ \dot{C}H_2COONa \end{matrix} + C_2H_5OH;$$

$$\begin{matrix} CH_2COOC_2H_5 \\ \dot{C}H_2COONa \end{matrix} + NaOH = \begin{matrix} CH_2COONa \\ \dot{C}H_2COONa \end{matrix} + C_2H_5OH,$$

because the whole reaction is in agreement with the bimolecular constant. So, too, Reicher[2] found that the hydrolysis of ethyl acetate by calcium hydroxide is of the same order as when potassium or sodium hydroxides are employed, while the corresponding chemical equations are respectively ter- and bi- molecular—

$$2CH_3COOC_2H_5 + Ca(OH)_2 = (CH_3COO)_2Ca + 2C_2H_5OH;$$
$$CH_3COOC_2H_5 + KOH = CH_3COOK + C_2H_5OH.$$

Still further, the reaction between potassium chlorate, ferrous chloride, and hydrochloric acid, appears to involve the interaction of thirteen molecules; as a matter of fact, the reaction is of the third order.

These examples show that it is necessary for us to distinguish between the *kind* and *number* of molecules taking part in a reaction. If C_1, C_2, C_3, . . . denote the concentrations of the reacting substances A_1, A_2, A_3, . . ., and n_1, n_2, n_3, . . . the number of molecules of A_1, A_2, A_3, . . . taking part in

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[1] O. Knoblauch, *Zeit. phys. Chem.*, **26**. 96, 1898; T. L. Reicher, *Maandblad voor natuurwetenschappen*, **12**. 105, 1885; *Rec. trav. Pays-Bas*, **4**. 350, 1885.

[2] T. L. Reicher, *Liebig's Ann.*, **228**. 257, 1885.

the chemical change, then the velocity of the reaction will be represented by the equation—

$$-\frac{dC}{dt} = kC_1^{n_1}C_1^{n_2}\ \ldots,$$

where $n_1 + n_2 + n_3 + \ldots$ denotes the *total number of molecules* taking part in the reaction. If one molecule of each kind of substance takes part in the reaction, and $n_1 = n_2 = \ldots = 1$, and if $C_1 = C_2 = \ldots = C_n = C$,

$$-\frac{dC}{dt} = kC^n,$$

where n denotes the number of molecules, as well as how many *different kinds of substances* take part in the reaction.

It is often convenient to use the symbols C_1, C_2, . . . in place of the usual $a - x$, $b - x$, to denote the concentration of the reacting substances. The subscripts 1, 2, . . . may also be replaced by the chemical symbol of the molecule, whose concentration is represented by C. Thus the reaction—

$$2CH_3COOAg + HCOONa = 2Ag + CO_2 + CH_3COOH + CH_3COONa,$$

might be represented by the equation—

$$-\frac{dC}{dt} = kC^2_{CH_3COOAg}C_{HCOONa}.$$

Note the use of the minus sign to indicate that the concentration of the original substance is diminishing. The chemical symbol, too, is often itself used to express the concentration of a substance in gram-molecules per litre.

It might also be pointed out the terms uni-, bi-, ter-, . . . and multi-molecular, or, what is equivalent, mono-, di-, tri-, . . . and poly-molecular reactions, were introduced by van't Hoff to indicate the number of molecules which take part in the reaction. While there can be no doubt that measurements of the velocity of a chemical reaction do sometimes tell us the number of molecules concerned in the process, and so furnish us with a direct insight into the mechanism of the change, yet we must also remember that there is frequently no apparent relation between the number of molecules taking part in any specific reaction and the number of molecules depicted symbolically in the regular chemical equation. Bone and Wheeler,[1] for example, found that measurements of the rate of combination of hydrogen and oxygen would lead us to assume that the reaction is unimolecular, whereas, in reality, the reaction must be at least bi-, and probably is termolecular. Here, then, we might adopt Ostwald and Fuhrmann's expressions,[2] and say that a reaction is of the first, second, third, or *n*th order, according to the degree of the term on the right side of the differential equation concerned, without reference to the number of molecules taking part in the reaction.

§ 18. Quadrimolecular Reactions.

Very few reactions of the fourth order are known, and these have not been investigated very closely. If four molecules take part in the reaction—

$$\frac{dx}{dt} = k(a - x)(b - x)(c - x)(d - x). \quad . \quad (1)$$

For the special case where the initial concentrations $a = b = c = d$,

$$\frac{dx}{dt} = k(a - x)^4; \text{ or, } \frac{1}{t} \cdot \frac{1}{3}\left\{\frac{1}{(a - x)^3} - \frac{1}{a^3}\right\} = k. \quad (2)$$

Scobai's[3] measurements of the decomposition of potassium chlorate at 395° furnish data which can be employed to test the preceding result. Here $a = 5$.

t	x	k
9	0·0250	0·0000392
24	0·0373	0·0000380
48	0·0720	0·0000352
72	0·0954	0·0000376
96	0·1130	0·0000362
120	0·1211	0·0000339
144	0·1274	0·0000377

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[1] W. A. Bone and R. V. Wheeler. Private communication.

[2] A. Fuhrmann, *Zeit. phys. Chem.*, **4**. 89, 1889.

[3] J. Scobai, *Zeit. phys. Chem.*, **44**. 319, 1903.

Hence it is supposed that the first action of heat on potassium chlorate must be represented by the equation—

$$4KClO_3 = KCl + 3KClO_4.$$

The presence of potassium perchlorate and of a small quantity of potassium chloride exercise no perceptible influence on the velocity of the reaction;[1] and, further, the potassium perchlorate suffers no perceptible decomposition at the temperature of the experiment.

Other quadrimolecular reactions occur between hydrogen bromide and bromic acid;[2] between chromic and phosphoric acids;[3] and in the action of bromine upon benzene.[4]

§ 19. Quinquemolecular Reactions.

The reaction between potassium ferricyanide and potassium iodide in neutral solutions appears to be of the fifth order, so that—

$$\frac{dx}{dt} = k(a - x)^2(b - x)^3,$$

where $a - x$ and $b - x$ respectively denote the concentrations of the potassium ferricyanide and of potassium iodide at any moment.[5] Values of k have not yet been published.

Reactions of higher order than the second are not very common. This is easily understood if we assume that bimolecular reactions are caused by the collision of two molecules, termolecular reactions by the collision of three molecules, etc. The probability of a simultaneous collision between three molecules is very much less than between two molecules, and the greater the number of molecules taking part in a given transformation, the more likely is the reaction to proceed by

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[1] C. Marignac, *Bibliothèque universelle de Genève*, **45**. 346, 1843; J. Berzelius, *Jahresber.*, **24**. 192, 1844.

[2] W. Judson and J. W. Walker, *Journ. Chem. Soc.*, **73**. 410, 1898.

[3] G. Viard, *Compt. Rend.*, **124**. 148, 1897.

[4] L. Bruner, *Zeit. phys. Chem.*, **41**. 513, 1902.

[5] F. G. Donnan and R. Le Rossignol, *Journ. Chem. Soc.*, **83**. 703, 1903.

some other path than by the simultaneous collision of the reacting molecules. One example has already been cited—the hydrolysis of ethyl succinate by sodium hydroxide; among other examples we have the action of potassium persulphate upon potassium iodide,[1] which is bi-, not ter- molecular; and the hydrolysis of the fats by sodium hydroxide,[2] which is a bi-, not a quadri- molecular reaction.

§ 20. Reactions between Ions.

According to the ionic theory, the sodium hydroxide which effects the transformation of ethyl acetate in the reaction—

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH,$$

is dissociated into positive sodium ions and negative hydroxyl ions, while the sodium acetate formed during the transformation is dissociated into positive sodium ions and negative CH_3COO ions. Consequently the reaction may be represented by the equation—

$$CH_3COOC_2H_5 + Na^{\cdot} + OH' = CH_3COO' + Na^{\cdot} + C_2H_5OH;$$

where the sign "$\cdot$" is conventionally used in place of "+", and "$'$" in place of "−".

The sodium remains in the ionic condition before and after the reaction, so that the equation really reduces to a reaction between ethyl acetate and hydroxyl ions, namely—

$$CH_3COOC_2H_5 + OH' = CH_3COO' + C_2H_5OH,$$

a reaction of the second order.

Reicher's previously quoted experiments on the hydrolysis of ethyl acetate, which appears to be a bimolecular reaction, no matter whether sodium or calcium hydroxide be employed, receives a simple explanation by the ionic theory, for the hydrolysis is supposed to be effected by the hydroxyl ions,

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[1] T. S. Price, *Zeit. phys. Chem.*, **27**. 474, 1898.

[2] A. C. Geitel, *Journ. prakt. Chem.* [2], **55**. 429, 1897; **57**. 113, 1898; J. Lewkowitsch, *Journ. Soc. Chem. Ind.*, **17**. 474, 1898.

and it makes no difference to the order of the reaction whether these ions are derived from NaOH or from $Ca(OH)_2$.

In a similar manner we see that the reduction of silver acetate by sodium formate may be resolved into the ionic reaction—

$$2Ag^{\cdot} + HCOO' = 2Ag + CO_2 + H^{\cdot}.$$

The quinquemolecular reaction between potassium ferricyanide and potassium iodide, formerly symbolized by the equation—

$$2K_3FeCy_6 + 2KI = 2K_4FeCy_6 + I_2,$$

is represented by Donnan and Le Rossignol[1] as a reaction between $FeCy_6'''$ ions and I′ ions, which results in the formation $FeCy_6''''$ and I_3' ions; thus—

$$2FeCy_6''' + 3I' = 2FeCy_6'''' + I_3';$$

or else—

$$2Fe''' + 3I' = 2Fe'' + I_3',$$

which may mean that the reaction takes place between the *molecules* indicated in the equation—

$$2K_3FeCy_6 + 3KI = 2K_4FeCy_6 + KI_3.$$

The mathematical representation of a reaction is generally the same, whether we employ molecular or ionic equations.

§ 21. To find the Number of Molecules taking part in a Reaction.

J. H. van't Hoff, in his epoch-making book, *Études de dynamique chimique*, first showed us how a study of the velocity coefficients of chemical reactions could furnish us with valuable information about the mechanism of a reaction which could never have been obtained by purely chemical methods. The older chemistry was mainly concerned with a study of the *result* of a chemical reaction; at this day, however, a great deal of attention is directed to a study of the *course* of chemical

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[1] F. G. Donnan and R. Le Rossignol, *Journ. Chem. Soc.*, **83**. 703, 1903.

reactions. And one of the most important questions we can ask is: How many molecules take part in a reaction?

Let phosphine gas be introduced into the bulb *A* (Fig. 6), which is kept at the temperature of boiling sulphur. The phosphine decomposes into phosphorus and hydrogen gas. The decomposing phosphine is kept at a constant volume by raising or lowering the tube *B* so as to keep the mercury constantly at the level *C*. The pressure of the gas in *A* is given by the difference in the levels of *C* and *B*.

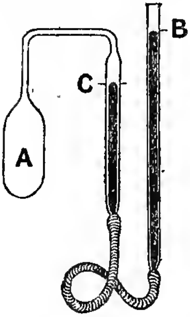

FIG. 6.

Let p_0 denote the original pressure of the gas when *a* gram-molecules of PH_3 per unit volume are present; p_1 the pressure of the gaseous mixture at the time *t* when a fraction *x* of *a* has decomposed. Since for every two volumes of phosphine which disappears three volumes of hydrogen must remain, when *ax* gram-molecules of phosphine have disappeared the pressure will be $1\frac{1}{2}$ times *ax*. Hence $a - ax$ gram-molecules of phosphine and $\frac{3}{2}ax$ gram-molecules of hydrogen remain at the time *t*. The pressure p_1 is due to the undecomposed phosphine and hydrogen present.

$$\therefore p_1 = (1 - x)a + \tfrac{3}{2}ax; \text{ and } p_0 = a.$$

$$\frac{p_1}{p_0} = 1 + \frac{x}{2}; \therefore x = \frac{2p_1}{p_0} - 2; \ (1 - x)a = \left(3 - \frac{2p_1}{p_0}\right)a.$$

If, therefore—

$$PH_3 = P + 3H,$$

$$\frac{dx}{dt} = k_1(a - ax); \ k_1 = \frac{1}{t}\log\frac{a}{a - ax} = \frac{1}{t}\log\frac{p_0}{3p_0 - 2p_1};$$

and if—

$$4PH_3 = P_4 + 6H_2,$$

$$\frac{dx}{dt} = k'_4(a - ax)^4; \ k_4 = \frac{1}{t}\left\{\frac{1}{(a - ax)^3} - \frac{1}{a^3}\right\} = \frac{1}{t}\left\{\left(\frac{p_0}{3p_0 - 2p_1}\right)^3 - 1\right\}.$$

Here k_4 is written in place of $k'_4 p_0^3$ in the last member only.

Kooij[1] has measured the pressure p_1 at different intervals of time, and his numbers are shown in the first three columns of the following table :—

t hours.	p_1 mm.	Per cent. decomposed.	k_1	k_4
0	715·21 ($=p_0$)	0	—	—
7·83	730·13	4·17	0·00236	0·0173
24·17	759·45	12·37	0·00237	0·0201
41·25	786·61	19·97	0·00235	0·0229
63·17	819·96	29·29	0·00238	0·0288
89·67	855·50	39·23	0·00241	0·0385

The constancy of k_1 and the variation in the value of k_4 is supposed to show that the reaction is not quadri- but uni-molecular. And since the phosphorus and hydrogen formed during the decomposition have the composition P_4 and H_2, it is still further assumed that the first action of heat is—

$$PH_3 = P + 3H,$$

and that the subsequent formation of the molecules of phosphorus and hydrogen is extremely rapid.

But another interpretation of Kooij's experiments must here be suggested. The number of molecules taking part in a gaseous reaction cannot always be determined from the observed order of the reaction. If chemical action only takes place on the surface of the glass, the fact that the decomposition of phosphine or of arsine is a reaction of the first order only means that *the velocity of the reaction is proportional to the pressure of the gas.* Bodländer,[2] and Bone and Wheeler,[3] have shown that reactions like—

$$2SO_2 + O_2 = 2SO_3; \ 2H_2 + O_2 = 2H_2O; \ 2CO + O_2 = 2CO_2,$$

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[1] D. M. Kooij, *Zeit. phys. Chem.*, **12**. 155, 1892 (phosphine, arsine); A. Stock and O. Guttmann, *Ber.*, **37**. 901, 1904; M. Bodenstein, *ib.*, **37**. 1361, 1904 (stibine).

[2] G. Bodländer, *Zeit. Elektrochem.*, **9**. 559, 787, 1903.

[3] W. A. Bone and R. V. Wheeler. Private communication: M. Bodenstein, *Zeit. phys. Chem.*, **46**. 725, 1903; **49**. 41, 1904.

which must be polymolecular, behave like unimolecular reactions. The probable interpretation is that chemical action only takes place on the surface of the glass, or on the surface of any catalytic agent which may be present, and that the velocity of the reaction is proportional to the rate of absorption of the gas by the surface of the solid; this latter, in turn, is proportional to the pressure of the gas, just as Ernst[1] found that the rate of combination of hydrogen and oxygen dissolved in water in contact with electrolytic gas is proportional to the rate of solution of the mixed gases, which is, in turn, proportional to the pressure of the gases lying above the surface of the water.

The different methods which have been proposed for finding the order of a reaction are as follows:—

I. The method of integration.—The order of a reaction can be determined by the method of trial and failure just outlined. Historically, this was the first method employed for evaluating n, the order of a reaction. The change in the concentration of the reacting substances is determined at wide intervals of time, and the results are substituted in equations of the first, second, or nth order. The one that gives the most satisfactory constant is supposed to represent the course of the reaction. If the equation is of the first order, the reaction is unimolecular, etc.

This method is extensively used. In addition to the many examples which precede, it has been employed for the hydrolysis of salicine;[2] the transformation of diazoamidobenzene;[3] the birotation of the sugars, etc.[4]

W. Meyerhoffer[5] tried to find the order of the reaction between hydriodic and bromic acids by taking equivalent

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[1] C. Ernst, *Zeit. phys. Chem.*, **37**. 448, 1901.

[2] A. A. Noyes and W. J. Hall, *Zeit. phys. Chem.*, **18**. 240, 1895.

[3] H. Goldschmidt and R. V. Reinders, *Ber.*, **29**. 1369, 1896.

[4] H. Trey, *Zeit. phys. Chem.*, **18**. 193, 1895; **22**. 424, 1897; A. Levy, *ib.*, **17**. 301, 1895; Y. Osaka, *ib.*, **35**. 661, 1900; P. T. Muller, *Compt. Rend.*, **118**. 425, 1894.

[5] W. Meyerhoffer, *Zeit. phys. Chem.*, **2**. 585, 1888.

amounts of the two acids and substituting the results in the integral of—

$$\frac{dC}{dt} = kC; \text{ or, } \frac{1}{t_1 - t_0} \cdot \frac{1}{n-1}\left(\frac{1}{C_1^{n-1}} - \frac{1}{C_0^{n-1}}\right) = k. \qquad (1)$$

n was put successively equal to 1, 2, 3, 4, 5, 6, 7 without success, the method breaks down because none of these equations furnish satisfactory constants. The disturbing influences of side and successive reactions may induce very great modifications in the value of the velocity coefficient k.

II. The differential method of van't Hoff is based upon the fact that the velocity of a reaction is proportional to the nth power of the concentration of the substances undergoing transformation.[1]

$$-\frac{dC}{dt} = kC^n,$$

where C denotes the concentration of the reacting substance.

If we make two experiments with different initial concentrations, C_1 and C_2, of the reacting substances, we get—

$$-\frac{dC_1}{dt} = kC_1^n; \quad -\frac{dC_2}{dt} = kC_2^n.$$

Take logarithms of each expression and divide the first by the second. Then solve for n—the order of the reaction—

$$n = \frac{\log \frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log C_1 - \log C_2}. \quad . \quad . \quad . \quad . \quad (2)$$

This method has been applied by van't Hoff[2] to Reicher's experiments on the action of bromine on fumaric acid; by O. Burchard[3] to the oxidation of hydrogen iodide by oxy-acids; to the reaction between potassium persulphate and potassium iodide;[4] to the reaction between ferric or chromic chloride upon the alkaline iodides;[5] to the decomposition of

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[1] J. H. van't Hoff, *Études*, 87, 1884.

[2] J. H. van't Hoff, *Études*, 89, 1884.

[3] O. Burchard, *Zeit. phys. Chem.*, **2**. 796, 1888.

[4] T. S. Price, *Zeit. phys. Chem.*, **27**. 474, 1898.

[5] A. Schükarew, *Zeit. phys. Chem.*, **38**. 353, 1901.

carbon dioxide;[1] to the oxidation of quinine by chromic acid;[2] and to the action of bromine upon ethyl alcohol,[3] etc.

In illustration, it was found for the last-named reaction—

t	C_1	$-\frac{dC_1}{dt}$	t	C_2	$-\frac{dC_2}{dt}$	n
0	0·00814	0·00051	0	0·000424	0·00028	0·91
4	0·00610		4	0·000314		

To calculate n, assume that the change of concentration dC_1 is given by the difference 0·00814 − 0·00610, and that dt is approximately represented by the difference 4 − 0, etc. Let C_1 and C_2 be represented by the mean values 0·00712 and 0·00369 respectively, then—

$$n = \frac{\log 0\cdot00051 - \log 0\cdot00028}{\log 0\cdot00712 - \log 0\cdot00369} = \frac{\bar{4}\cdot7076 - \bar{4}\cdot4472}{\bar{3}\cdot8525 - \bar{3}\cdot5670} = 0\cdot91,$$

which is very close to the value required for a reaction of the first order.

In cases where the products of the reaction and not the original substance set up disturbances, this method may be usefully employed because, at the beginning of the reaction, the products of the reaction, not being present to any great extent, have least influence on the velocity of the change. Unfortunately, when the small changes of concentration which take place at the beginning of a reaction are substituted in place of dC_1 and dC_2, there is a large experimental error, due, firstly, to the difficulty of measuring small changes of concentration, and, secondly, to certain perturbing influences which frequently modify the preliminary stages of chemical reactions.

It might be possible to work on so large a scale that the amount of change in a suitable interval of time is sufficient for

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[1] A. Smits and L. K. Wolff, *Zeit. phys. Chem.*, **45**. 199, 1903.

[2] E. Goldberg, *Zeit. phys. Chem.*, **41**. 1, 1902.

[3] S. Bugarszky, *Zeit. phys. Chem.*, **38**. 561, 1901.

accurate analysis, and the concentration of the products of the reaction is small in comparison with the concentration of the reacting substances. In this way the influence of the products of the reaction would be negligibly small.

On the other hand, if large changes of concentration are employed, the tacit assumption is made that the speed of the reaction is not affected by changes in the concentration of the reacting substances. The magnitude of this error is not generally known. Of course, the error affecting dC_1 is partly neutralized by the error affecting dC_2, since the same assumption affects both magnitudes. This difficulty does not affect the next method.

III. Integration of the same fractional parts of the reacting substance.—While investigating the influence of different acids upon the progress of the reaction—

$$HBrO_3 + 6HI = HBr + 3H_2O + 3I_2,$$

Ostwald[1] showed that the normal course of the change was disturbed by the iodine produced during the reaction. Assuming that the effect of the iodine is in all cases the same, it follows that with two analogous reactions the intervals of time required to transform a certain amount of the reacting substance will be inversely proportional to the velocity constants of the two reactions. This will be evident from the following considerations:—

The general equation for the velocity of a reaction is—

$$-\frac{dC}{dt} = kC^n; \text{ or, } \frac{1}{n-1}\left(\frac{1}{C_1^{n-1}} - \frac{1}{C_0^{n-1}}\right) = kt,$$

where C_0 denotes the initial concentration of the reacting substance, and C_1 the amount present at the time t.

Now let a series of independent measurements be made under the same conditions, but in which different amounts of the reacting substances are taken at the start. Let the several reactions be allowed to proceed until the same fraction of

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[1] W. Ostwald, *Zeit. phys. Chem.*, **2.** 127, 1888.

the original substance is transformed in each case; that is, so that—

$$\frac{C_{10} - C_1}{C_{10}} = \frac{C_{20} - C_2}{C_{20}} = \frac{C_{30} - C_3}{C_{30}} = \ldots, \quad . \quad . \qquad (3)$$

where C_{10}, C_{20}, C_{30}, . . . respectively denote the initial concentrations of the reacting substances in experiments 1, 2, 3, . . . Hence, by an algebraic transformation—

$$\left(\frac{C_{20}}{C_{10}}\right)^{n-1} = \left(\frac{C_2}{C_1}\right)^{n-1}; \text{ etc.} \quad . \quad . \quad . \quad . \qquad (4)$$

Again, for each reaction—

$$\frac{1}{n-1}\left(\frac{1}{C_1^{n-1}} - \frac{1}{C_{10}^{n-1}}\right) = k_1t_1;$$

$$\frac{1}{n-1}\left(\frac{1}{C_2^{n-1}} - \frac{1}{C_{20}^{n-1}}\right) = k_2t_2; \; . \; . \; .$$

By division—

$$\frac{(C_{10}^{n-1} - C_1^{n-1})C_2^{n-1}C_{20}^{n-1}}{(C_{20}^{n-1} - C_2^{n-1})C_1^{n-1}C_{10}^{n-1}} = \frac{k_1t_1}{k_2t_2}; \text{ etc.} \quad . \quad . \qquad (5)$$

Multiplying out and substituting from (3) and (4)—

$$\left(\frac{C_{20}}{C_{10}}\right)^{n-1} = \frac{k_1t_1}{k_2t_2}; \text{ etc.} \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

If the reaction is of the first order, $n = 1$, and the left member reduces to unity, thus showing that the time required for the transformation of equal fractions of the original substance is independent of the initial concentration. In other words, the velocity constants and the intervals of time required for the transformation of the same fractional part of the original substance retain the same constant ratio, and therefore—

$$k_1 : k_2 : k_3 : \ldots = \frac{1}{t_1} : \frac{1}{t_2} : \frac{1}{t_3} : \ldots \quad . \quad . \qquad (7)$$

Thus, Bugarszky[1] found the numbers indicated in the

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[1] S. Bugarszky, *Zeit. phys. Chem.*, **38.** 561, 1901; see also H. Goldschmidt and A. Merz, *Ber.*, **30.** 670, 1897; H. Goldschmidt and F. Buss, *Ber.*, **30.** 2075, 1897.

following table for the action of bromine upon ethyl alcohol, when half of the original amount of ethyl alcohol had been transformed.[1]

C_{10}	C_{20}	t_1	t_2	$t_1 : t_2$
0·00814	0·00424	14·14	12·35	1·14
0·00104	0·00207	14·14	10·50	1·34
0·00424	0·00207	12·35	10·50	1·18

If the reaction be of the second order, $n = 2$, the velocity constants k_1 and k_2 will be proportional to the concentration of the reacting substance, and the intervals of time required for the transformation of the same fractional part of the original substance will be inversely proportional to the initial concentration. By doubling the concentration we halve the time required for the transformation of the same quantity of the reacting substance.[2] More generally, *the intervals of time required for the transformation of the same fractional part of the original substance are inversely proportional to the* $(n-1)$*th power of the initial concentrations.*

Noyes[3] has shown that by rearranging the terms of equation (6), and assuming that k is independent of the concentration of the reacting substance during a given reaction, $k_1 = k_2$, we get—

$$n = 1 + \frac{\log t_1 - \log t_2}{\log C_{20} - \log C_{10}} . \quad . \quad . \quad . \quad (8)$$

It is also assumed that the course of the reaction is in every case represented by the same function of C, that is to say, that the reaction is in all cases affected by the same disturbing influences.

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[1] In practice we do not try to determine these fractions exactly. A series of numbers are obtained in the usual way, and exact values are determined by interpolation. Cf. Mellor's *Higher Mathematics*, § 105.

[2] F. Lengfeld, *Amer. Chem. Journ.*, **11**. 40, 1889.

[3] A. A. Noyes, *Zeit. phys. Chem.*, **19**. 599, 1896.

If k varies with the concentration of the reacting components, the conclusion breaks down. For example, the reaction between potassium ferricyanide and potassium iodide works out to be unimolecular with respect to the former component, whereas at other concentrations it is shown, later on, to be bimolecular. G. Bodländer also obtained unsatisfactory results for the oxidation of sulphur dioxide by free or atmospheric oxygen.[1]

Mittasch's experiments on the formation of nickel carbonyl from its elements may be taken to illustrate the application of equation (8).[2]

Per cent. $Ni(CO)_4$ formed.	t_1	t_2	C_{10}	C_{20}	n
2·24	5·5	11	840	358	1·87
1·65	4·3	21	830	243	2·28
11·7	16·0	60	869	272	2·14
28·7	93·0	260	868	367	2·12

The values of n are sufficiently close to favour the view that the reaction is of the second order.

IV. Ostwald's "method of isolation."—Harcourt and Esson determined the relation between the rate and the concentration of the reacting substances by taking advantage of the fact that if an excess of one of the reacting substances be present, its change of concentration may be neglected; and Ostwald[3] proposed to find the order of each substance taking part in a polymolecular reaction by changing the concentration of the substances individually.

Suppose that three substances, A, B, and C, react together so that—

$$-\frac{dC_1}{dt} = k_0 C_1^{n_1} C_2^{n_2} C_3^{n_3},$$

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[1] F. G. Donnan and R. Le Rossignol, *Journ. Chem. Soc.*, **83.** 703, 1903; G. Bodländer and K. Köppen, *Zeit. Elektrochem.*, **9.** 559, 787, 1903.

[2] A. Mittasch, *Zeit. phys. Chem.*, **40.** 1, 1902; see also J. Brode, *ib.*, **37.** 257, 1901; W. Will and G. Bredig, *Ber.*, **21.** 2785, 1888.

[3] W. Ostwald, *Lehrbuch*, **2.** ii., 238, 1902.

where C_1, C_2, C_3, respectively denote the concentrations of A, B, and C, and n_1, n_2, and n_3 the number of molecules of A, B, and C respectively taking part in the reaction. By keeping an excess of the mixture of B and C, and allowing the amount of A alone to vary, the number of molecules of A taking part in the reaction can be determined from the equation—

$$-\frac{dC_1}{dt} = (k_0 C_2^{n_2} C_3^{n_3}) C_1^{n_1} = k_1 C_1^{n_1},$$

where $k_0 C_2^{n_2} C_3^{n_3} = k_1$. The reaction will therefore be of the n_1th order, and this may be determined by one of the preceding methods. Similar experiments can be made with a constant mixture of A and C with respect to B, since we have—

$$-\frac{dC_2}{dt} = (k_0 C_1^{n_1} C_3^{n_3}) C_2^{n_2} = k_2 C_2^{n_2};$$

similarly, by varying the concentration of C reacting in a mixture containing an excess of A and B, we shall have—

$$-\frac{dC_3}{dt} = (k_0 C_1^{n_1} C_2^{n_2}) C_3^{n_3} = k_3 C_3^{n_3}.$$

The advantage of this method lies in the fact that the mode of action of each component is determined separately, and disturbing effects can be traced to their origin.

Donnan and Le Rossignol's experiments on the reaction between potassium ferricyanide and potassium iodide furnish us with convenient data to illustrate the method. The reaction is provisionally—

$$2KI + 2K_3FeCy_6 = 2K_4FeCy_6 + I_2.$$

The velocity equation is—

$$-\frac{dC_1}{dt} = k_0 C_1^{n_1} C_2^{n_2},$$

where C_1 denotes the concentration, and n_1 the number of molecules of K_3FeCy_6 taking part in the reaction; C_2 and n_2 represent similar magnitudes for molecules of potassium iodide. In one series of experiments the potassium iodide was present in $\frac{1}{2}$N solution, the ferricyanide in $\frac{1}{40}$N solution. Hence—

$$-\frac{dC_2}{dt} = (kC_1^{n_1}) C_2^{n_2} = k_2 C_2^{n_2}.$$

The object of the experiment is to find the order of the reaction n_2. n_2 may now be evaluated by the first method.

If $n_2 = 1$, $k_2 = \frac{1}{t} \log \frac{C_0}{C_2}$; if $n_2 = 2$, $k_2 = \frac{1}{t}\left(\frac{1}{C_2} - \frac{1}{C_0}\right)$, where C_0 denotes the concentration of the potassium iodide, when $t = 0$, and C_2 the concentration at any time t.

t	C_2	$k_2(n_2 = 1)$	$k_2(n_2 = 2)$
0	8·237	—	—
4·72	7·425	0·0219	0·00282
11·00	6·615	0·0198	0·00271
18·97	5·803	0·0185	0·00268
29·21	4·997	0·0171	0·00270
43·18	4·180	0·0158	0·00272
63·55	3·369	0·0149	0·00275

The values of k_2 calculated for a reaction of the second order are so much alike that the reaction may be regarded as bimolecular with respect to potassium ferricyanide.

Subsequent experiments showed that the velocity constant k_2 is greatly dependent upon the initial concentration of the potassium ferricyanide. For example—

Initial concentration of K_4FeCy_6, $\frac{1}{20}$N, $\frac{1}{40}$N, $\frac{1}{80}$N;
k_2 for a bimolecular reaction, 0·00156, 0·00272, 0·00472.

Now let k_2' and k_2'' be values of k_2 obtained in two experiments where the initial concentration of the potassium ferricyanide is kept constant while the concentration of the potassium iodide is respectively C_1' and C_1''. Hence we shall have, by the second method—

$$k' = k_0 C_1'^{n_1};\ k_2'' = k_0 C_1''^{n_1},$$

or—

$$n = \frac{\log k_2' - \log k_2''}{\log C_1' - \log C_1''}.$$

Experiments conducted with mixtures of $\frac{1}{2}$N potassium ferricyanide and $\frac{1}{2}$N, $\frac{3}{8}$N, and $\frac{1}{4}$N potassium iodide, under similar conditions, gave the following results :—

	Initial concentration of KI.	k_2
1	$\frac{1}{2}$N	0·001560
2	$\frac{3}{8}$N	0·000689
3	$\frac{1}{4}$N	0·000228

From 1 and 2—

$$n_2 = \frac{\log 0·00156 - \log 0·000689}{\log \frac{1}{2} - \log \frac{3}{8}} = 2·85.$$

In the same way from 1 and 3, $n_2 = 2·77$; and from 2 and 3, $n_2 = 2·73$. This agrees with the view that the reaction is termolecular with respect to KI. Hence it is concluded that, for these concentrations, the reaction is to be written—

$$2K_3FeCy_6 + 3KI = 2K_4FeCy_6 + KI_3,$$

or as indicated in the preceding section. For other examples, see Price on the action of potassium persulphate upon potassium iodide;[1] Benson on the rate of oxidation of ferrous salts by chromic acid;[2] Delury on the rate of oxidation of potassium iodide by chromic acid;[3] Bray[4] on the reaction which obtains in a mixture of potassium iodide, chloric, and hydrochloric acids; and Forster[5] on the action of iodine on potassium hydroxide.

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[1] T. S. Price, *Zeit. phys. Chem.*, **27**. 481, 1898.

[2] C. C. Benson, *Journ. Phys. Chem.*, **7**. 1, 356, 1903; **8**. 116, 1904.

[3] R. E. Delury, *Journ. Phys. Chem.*, **7**. 239, 1903.

[4] W. C. Bray, *Journ. Phys. Chem.*, **7**. 92, 1903.

[5] E. L. C. Forster, *Journ. Phys. Chem.*, **7**. 640, 1903.

CHAPTER III

HOMOGENEOUS SIDE REACTIONS

§ 22. Side Reactions.

CHEMICAL changes are not in general so simple as those types which precede. The transformation of a substance may be accomplished by a number of independent reactions which furnish different sets of products. For example, although hydroxylamine—NH_2OH—decomposes in aqueous solution according to the equation—

$$3NH_2OH = NH_3 + N_2 + 3H_2O,$$

yet Berthelot[1] has shown that a certain amount of nitrous oxide is invariably present among the products of decomposition. Its formation may be represented symbolically—

$$4NH_2OH = 2NH_3 + N_2O + 3H_2O.$$

Some of the hydroxylamine molecules follow the first, and some the second reaction. Such changes are called **side reactions**. Of two side reactions, the one which predominates is called the **main or principal reaction**. The less obtrusive changes are called **secondary reactions**. Which is the main and which the secondary reaction depends on the conditions of the experiment. Examples are common enough, far more common than is generally supposed. Sulphuric acid and alcohol react with the formation of ethylene and ethyl ether, but which of these compounds predominates depends on the temperature of the reacting mixture. The decomposition of

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[1] M. Berthelot, *Ann. Chim. Phys.* [5], **10.** 433, 1877 ; [6], **21.** 384, 1890 ; S. Tanater, *Zeit. phys. Chem.*, **40.** 475, 1902.

ammonium nitrate,[1] of ammonium nitrite,[2] of glucose,[3] and of ammonium thiocyanate,[4] furnish similar examples.

Another type of side reaction occurs when one of the products of the reaction sets up a secondary reaction with the original substance. Thus, Bugarszky[5] found that the reaction—

$$2KBr + HgO + H_2O = 2KOH + HgBr_2,$$

did not conform with the simple law of mass action because of the probable side reaction—

$$2KBr + HgBr_2 = K_2HgBr_4.$$

Much attention has been directed to the interaction of bromic and hydriodic acids which does not agree with any of the velocity equations set up on the assumption that the reaction is of a simple character. The iodine liberated during the reaction appears to react with the hydriodic acid so as to lower the velocity below the calculated value.[6] Does this mean that the law of mass action breaks down? It is possible to assume that the retardation is proportional to some arbitrary function of the quantity of iodine present.[7] Meyerhoffer tried the hypothesis that the retardation is inversely proportional to the amount of iodine, x, present in the solution at any moment. Assuming, too, that the reaction is of the second order, we obtain—

$$\frac{dx}{dt} = \frac{k(a - x)^2}{x}; \text{ or, } \frac{1}{t}\left(\frac{x}{a - x} - \log \frac{a}{a - x}\right) = k,$$

which gives very fair results when applied to the experimental

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[1] M. Berthelot, *Sur la Force des Materières Explosivs d'après la Thermochemie*, **1.** 20, 1883.

[2] A. A. Blanchard, *Zeit. phys. Chem.*, **41.** 681, 1902; V. H. Veley, *Journ. Chem. Soc.*, **83.** 736, 1903.

[3] L. Pasteur, *Ann. Chim. Phys.* [3], **58.** 330, 1860; *Compt. Rend.*, **48.** 1149, 1859.

[4] F. W. Küster, *Zeit. phys. Chem.*, **18.** 161, 1895.

[5] S. Bugarszky, *Zeit. phys. Chem.*, **11.** 668, 1893; **12.** 223, 1893.

[6] W. Ostwald, *Zeit. phys. Chem.*, **2.** 136, 1888; W. Meyerhoffer, *ib.*, **2.** 585, 1888.

[7] See S. Arrhenius, *Zeit. phys. Chem.*, **1.** 121, 1887.

data.[1] But let us see what can be done by an application of the law of mass action to these complicated reactions without resorting to subsidiary hypotheses.

§ 23. The Mutual Independence of Different Reactions.

In mechanics we are familiar with the fact that when several forces act upon a material particle, each force produces its own motion independent of all the others. The actual velocity of the particle is called the *resultant* velocity, and the several effects produced by the different forces are called the *component* velocities. There is here involved an important principle—the principle of the mutual independence of different reactions; or the principle of the coexistence of different reactions—which lies at the base of chemical dynamics. The principle might be enunciated in the following manner:—

When a number of reactions are simultaneously taking place in any system, each obeys the law of mass action, and each proceeds as if it were independent of the others; the total change is the sum of all the independent changes.

Coppadoro[2] has shown that if a solution of cane sugar and methyl acetate is mixed with hydrochloric acid, each reaction—inversion of cane sugar and hydrolysis of the ester—takes place in the mixture independently of the other.

There are three types of simultaneous reactions—side, opposing, and consecutive. These may be illustrated as follows:—

I. Side reactions.—The actual rate of transformation of a substance is the resultant of the different ways the substance is decomposing. To take a simple analogy, a man can swim at

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[1] There is this objection to Meyerhoffer's formula. At the beginning of the reaction, when x is very small the velocity should be infinitely great. The difficulty is got over by writing the denominator $x + A$, where A is a constant.

[2] A. Coppadoro, *Gazz. Chim. Ital.*, **31.** i., 425, 1901; V. Henri and Larguier des Bancels, *Compt. Rend. Soc. Biol.*, **53.** 784, 1901; **55.** 864, 1903.

the rate of two miles an hour, and a river is flowing at the rate of one mile an hour. If the man swims down-stream, the river will carry him one mile in one hour, and his swimming will carry him two miles in the same time. Hence the man's actual rate of progress down-stream will be three miles an hour.

II. Opposing reactions.—Again, the man might have started to swim up-stream against the current. In that case the actual rate of progress will be the difference between the velocity of the stream and the man's rate of swimming. In short, the man will travel at the rate of 2 – 1, or one mile an hour against the current. This example illustrates a class of chemical reactions in which the products of the reaction re-form the original substance. The direct reaction is opposed by a counter reaction. The actual velocity will then be the difference between the rates of the two opposing reactions.

III. Consecutive reactions.—To carry the analogy one step further, a man might travel a certain distance in different ways, partly by land and partly by sea. So a chemical reaction may first produce a substance—called an **intermediate compound**—which, in turn, decomposes to produce the final products of the reaction. The actual rate of formation of the latter will depend upon the relative rates of the two consecutive reactions. The problem now presents greater difficulties, which will be discussed later on.

§ 24. General Theory of Side Reactions.

Suppose that m_1 molecules of a substance A and m_2 molecules of a substance B react to form p_1 molecules of A_1 and p_2 molecules of A_2, then—

$$m_1 A + m_2 B = p_1 A_1 + p_2 A_2.$$

Let this reaction be accompanied by a side reaction in which n_1 molecules of A and n_2 molecules of B react to form q_1 molecules of B_1 and q_2 molecules of B_2, then—

$$n_1 A + n_2 B = q_1 B_1 + q_2 B_2.$$

Let a denote the amount of A, and b the amount of B expressed in gram-molecules per litre; let x_1 and x_2 respectively denote the amounts of A and B transformed in the time t; y_1 and y_2 the respective amounts of A_1 and A_2 formed in the same time; and z_1 and z_2 similar amounts of B_1 and B_2. It follows directly from the chemical equations that y_1 and y_2 are related to p_1 and p_2, so that—

$$y_1 : y_2 = p_1 : p_2; \text{ or, } \frac{y_1}{p_1} = \frac{y_2}{p_2} = y, \text{ say};$$

and that—

$$z_1 : z_2 = q_1 : q_2; \text{ or, } \frac{z_1}{q_1} = \frac{z_2}{q_2} = z, \text{ say},$$

where y denotes the increase in the concentration of $p_1A_1 + p_2A_2$, or the amount of substance spent in the first side reaction; and z denotes the increase for $q_1B_1 + q_2B_2$ or the amount of the original substance consumed in the second side reaction.

It again follows from the chemical equations that—

$$x_1 = m_1y + n_1z; \text{ and } x_2 = m_2y + n_2z. \quad . \quad . \quad (1)$$

Let x denote the total amount of the original substance consumed by the two side reactions in the time t. The rate of transformation of A and B will then be—

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt},$$

from the principle of the coexistence of different reactions; and the rates of formation of the two products $p_1A_1 + p_2A_2$ and $q_1B_1 + q_2B_2$ will be—

$$\frac{dy}{dt} = k_1(a - x_1)^{m_1}(b - x_2)^{m_2}; \ \frac{dz}{dt} = k_2(a - x_1)^{n_1}(b - x_2)^{n_2}, \ (2)$$

or, by substituting (1) in (2)—

$$\left.\begin{aligned} \frac{dy}{dt} &= k_1(a - m_1y - n_1z)^{m_1}(b - m_2y - n_2z)^{m_2}; \\ \frac{dz}{dt} &= k_2(a - m_1y - n_1z)^{n_1}(b - m_2y - n_2z)^{n_2}, \end{aligned}\right\} \quad . \quad (3)$$

where k_1 and k_2 denote the respective velocities of the two side reactions. By the integration of these equations we get either x or y expressed in terms of t.

If $m_1 = n_1$, and $m_2 = n_2$, we get, on integration—

$$\frac{dy}{dt} = k\frac{dz}{dt};\ \text{or, } y = \frac{k_1}{k_2}z. \quad . \quad . \quad . \quad . \quad (4)$$

This means that *the velocities of two side reactions only differ by a constant factor which is independent of the time.*

By substituting (4) in equation (3) we get two identical equations.

§ 25. Two Unimolecular Side Reactions.

If two side reactions are of the first order, $m_2 = n_2 = 0$; and $m_1 = n_1 = 1$—

$$\therefore \frac{dy}{dt} = k_1(a - x);\ \frac{dz}{dt} = k_2(a - x);$$

$$\therefore \frac{dx}{dt} = k_1(a - x) + k_2(a - x);\ \text{or, } \frac{dx}{dt} = (k_1 + k_2)(a - x)\ (5)$$

by a simple algebraic transposition. By integration, (5) assumes the form—

$$\frac{1}{t}\log\frac{a}{a - x} = k_1 + k_2. \quad . \quad . \quad . \quad . \quad (6)$$

Values of a, x, and t are to be found experimentally, and the results substituted in (6) should give $k_1 + k_2 =$ a constant. How shall we evaluate k_1 and k_2?

It is a well-known rule in algebra that two independent equations are necessary to be able to calculate two unknowns. Some other relation between k_1 and k_2 is therefore required before we can evaluate these constants. The velocity of each side reaction is, at any moment, equal to the product of the amount of the original substance present and the velocity coefficient. But $a-x$ is, at any moment, the same for both reactions. Hence the ratio of the products of each side reaction must be the same as the ratio of the velocity coefficients. Hence from (5)—

$$\frac{k_1(a - x)}{k_2(a - x)} = \frac{k_1}{k_2} = \frac{x_1}{x_2} = K, \text{ say}, \quad . \quad . \quad . \quad (7)$$

where x_1 and x_2 respectively denote the relative quantities of substances formed at any stage, say the end, of the two side reactions. Hence—

$$k_1 + k_2 = \kappa\text{; and } \frac{k_1}{k_2} = K.$$

By an elementary transformation—

$$k_1 = \frac{\kappa K}{K+1}\text{; } k_2 = \frac{\kappa}{K+1}. \quad . \quad . \quad . \quad . \qquad (8)$$

It is easy to get a clear idea of what is taking place in the system by plotting the integrals of equation (4) for each side reaction, and of the resultant reaction (6). For the sake of simplicity, put $k_1 = 0\cdot01$, $k_2 = 0\cdot005$, $a = 1$. Hence $\kappa = 0\cdot015$. The three curves are shown in Fig. 7.

The slope of each curve towards the x-axis represents the relative velocity of the reaction. The curve with the greater slope represents the greater velocity.

The above reasoning may be extended to include three or any number of side reactions. The constants are evaluated from the relations—

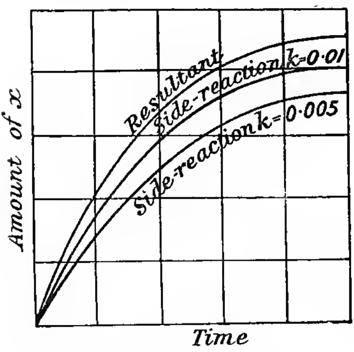

FIG. 7.—Velocity curves.

$$k_1 + k_2 + k_3 + \ldots = \kappa\text{; } \frac{k_1}{k_2} = K_1\text{; } \frac{k_2}{k_3} = K_2\text{; } \ldots$$

Holleman[1] has shown that we have three unimolecular side reactions during the nitration of nitrobenzoic acid in the presence of an excess of the nitrating acid resulting in the formation of the three isomeric *o*-, *m*-, and *p*- nitrobenzoic acids.

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[1] A. F. Holleman, *Zeit. phys. Chem.*, **31**. 79, 1899; *Rec. Trav. Pays-Bas*, **18**. 267, 1899.

§ 26. Two Bimolecular Side Reactions.

A pair of side reactions of the second order may be discussed in the same way. Here m_1, m_2, n_1, n_2, are all unity. The velocity equation is—

$$\frac{dx}{dt} = k_1(a - x)(b - x) + k_2(a - x)(b - x)\,;$$
$$= (k_1 + k_2)(a - x)(b - x)\,; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

the integral of which is—

$$\frac{1}{(a - b)t}\log\frac{b(a - x)}{a(b - x)} = k_1 + k_2. \quad . \quad . \quad (10)$$

The constants are evaluated as before. Side reactions of the third and higher orders are to be treated in a similar manner. Three bimolecular side reactions occur during the nitration of nitrobenzene.[1]

It is interesting to notice that a reaction may be really compounded of two or more side reactions of the same order, and yet have the same formal integrated equation as a normal uni-, bi-, . . . molecular reaction.

We have so far assumed that the side reactions are all of the same order.

§ 27. Mixed Uni- and Bi- molecular Side Reactions.

An infinite number of possible cases could here be discussed. All follow the general rules just laid down. The differential equations are easily set up, but the integration becomes a little more awkward as the reactions become more complex. Let us take the simplest case, a reaction of the first order is accompanied by one of the second. We shall now have $m_1 = 1$, $m_2 = 0$, $n_1 = n_2 = 0$ in our general equation

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[1] A. F. Holleman and B. R. de Bruyn, *Rec. Trav. Pays-Bas*, **19.** 79, 188, 364, 1900; **20.** 206, 352, 1901.

(3). The corresponding differential equation and integral are—

$$\frac{dx}{dt} = k_1(a - x) + k_2(a - x)(b - x);$$

$$= (a - x)(k_1 + k_2b - k_2x); \quad . \quad . \quad . \quad (11)$$

$$\therefore \frac{1}{t} \log \frac{a(K + b - x)}{(K + b)(a - x)} = k_2(b - a), \quad . \quad . \quad . \quad (12)$$

where K has been written in place of the ratio $k_1 \div k_2$, equation (7).

§ 28. Wegscheider's Test for Side Reactions.

R. Wegscheider,[1] in discussing the general theory of side reactions, has pointed out two important characteristics of these reactions.

I. Since the same relative quantities of the reacting substances are always consumed by a given set of side reactions under the same conditions, it follows at once that—

$$\frac{m_1}{n_1} = \frac{m_2}{n_2} = \text{constant} = \alpha, \text{ say.} \quad . \quad . \quad . \quad (13)$$

This relation allows the following simplification of equation (3). From (1)—

$$x_1 = m_1(y + \alpha x); \; x_2 = m_2(y + \alpha z), \quad . \quad . \quad (14)$$

and if we write—

$$y + \alpha z = x, \; \therefore x_1 = m_1x; \; x_2 = m_2x.$$

Also—

$$\frac{dx}{dt} = \frac{dy}{dt} + \alpha\frac{dz}{dt} = k_1(a - m_1x)^{m_1} + k_2(a - m_1x)^{\alpha m_1}. \quad (15)$$

II. Again it follows from (14) that the ratio of the products of the two reactions—

$$x_1 : x_2 = m_1 : m_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

is independent of the time. This is not the case with opposing and consecutive reactions. Hence Wegscheider enunciates

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[1] R. Wegscheider, *Zeit. phys. Chem.*, **30.** 593, 1899.

the principle that *the ratio between the amounts of substances formed in the two side reactions is independent of the time.*

This conclusion may naturally be extended to include three or more side reactions.

$$\therefore x_1 : x_2 : x_3 : \ldots = m_1 : m_2 : m_3 : \ldots \qquad (17)$$

This is in harmony with the fact observed by Holleman[1] during the nitration of nitrobenzene, nitrobenzoic acid, methyl and ethyl benzoates, etc., that, at constant temperatures, "the proportions of the ortho-, meta-, and para- products remain the same during the whole of the reaction." These proportions are indicated in the following table:—

In the nitration of	Temp. 0°			Temp. 30°		
	% ortho	% meta	% para	% ortho	% meta	% para
Nitrobenzoic acid	18·5	80·2	1·3	22·3	76·5	1·2
Methyl benzoate	21·0	73·2	5·8	25·7	69·8	4·5
Ethyl benzoate .	28·3	68·4	3·3	27·7	66·4	5·9
Nitrobenzene .	6·4	93·5	0·1	8·1	90·9	1·0

Skraup[2] has shown that two substances are produced by the action of strong mineral acids upon cinchonine—the one an addition product, and the other an isomeric form of cinchonine—

$$m\overline{\mathrm{C}}.2\mathrm{HCl} + n\mathrm{HCl} \rightarrow n\mathrm{C}_{19}\mathrm{H}_{23}\mathrm{ClN}_2\mathrm{O}.2\mathrm{HCl} + (m - n)\overline{\mathrm{C}}'.2\mathrm{HCl},$$

where $\overline{\mathrm{C}}$ has been written for the cinchonine residue, $\mathrm{C}_{19}\mathrm{H}_{23}\mathrm{N}_2\mathrm{O}$, and $\overline{\mathrm{C}}'$ for the isomeric form of cinchonine. Skraup thought that the addition product was an intermediate stage in the transformation of cinchonine into its isomer. Wegscheider,[3] however, has pointed out that the ratio—

$$\frac{\text{Transformation product}}{\text{Addition product}} = \frac{m - n}{n} = \text{constant},$$

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[1] A. F. Holleman and B. R. de Bruyn, *Rec. Trav. Pays-Bas*, **19.** 79, 1900; A. F. Holleman, *ib.*, **18.** 267, 1899; *Zeit. phys. Chem.*, **31.** 79, 1899; *Koninklijke Akad. van Wetenschappen*, 478, 1900.

[2] Z. H. Skraup, *Monatshefte für Chem.*, **20.** 585. 1899.

[3] R. Wegscheider, *Zeit. phys. Chem.*, **34.** 290, 1900.

was independent of the time, and is virtually the same as equation (16). With hydrochloric acid the constant is nearly 1 : 0·8; for hydrobromic acid, 1 : 3; and for hydroiodic acid, 1 : 8. It is therefore inferred that the addition product is not an "intermediate compound," and that the isomeric cinchonine is derived directly from cinchonine itself. There are thus two side reactions—

$$\bar{C}.2HCl + HCl = C_{19}H_{23}ClN_2O.2HCl;$$

$$\bar{C}.2HCl = \bar{C}'.$$

Wegscheider's principle is thus a valuable aid in the distinction of side reactions from other sources of disturbance—opposing and consecutive reactions.

CHAPTER IV

HOMOGENEOUS OPPOSING REACTIONS

§ 29. Equilibrium.

ANOTHER type of simultaneous reaction occurs when the products of any chemical reaction interact to re-form the original substance. Two independent and antagonistic changes simultaneously take place in the reacting system. Here again the principle of the mutual independence of different reactions holds good. The actual velocity of the reaction will be measured by the difference between the velocities of the two opposing changes. Opposing reactions have been more closely investigated than side reactions, and the literature of chemistry abounds with data supporting the fundamental hypothesis—the law of mass action.

At the outset, when the reaction is just starting, the velocity of the direct change will be a maximum, because the system then contains the greatest amount of reacting substance. From this moment the velocity of the reaction gradually slows down as the concentration of the reacting substance becomes less and less. On the other hand, the velocity of the reverse change will be zero at the commencement, because none of the products of the reaction are then present. The speed of the reverse change will become faster and faster as the products of the direct reaction accumulate in the system. Ultimately a point will be reached where the velocities of the two opposing reactions will be equal. The one will be balanced by the other. The reaction will seem to have stopped, in spite of the fact that more or less of the original substance will still remain untransformed. The system is now said to be in a state of **equilibrium.** Chemical changes of this type are variously styled *incomplete*, *reversible*, *balanced*, *counter*, *or opposing reactions* in contrast with the *complete or irreversible* reactions of Chapter II.

"Equilibrium," says Ostwald,[1] "denotes a state which is independent of time." If, for example, a gram-molecule of ethyl alcohol be mixed with a gram-molecule of acetic acid at the ordinary temperature, never more than two-thirds of the acetic acid will be transformed, however long the reaction may be allowed to continue. This was found to be the case with a mixture that had stood for twenty-five years.[2] In a similar manner, if a gram-molecule of water be mixed with one gram-molecule of ethyl acetate, never more than one-third of the ethyl acetate will suffer hydrolysis. Whichever mixture we start with, the reaction always comes to a "stand-still" when the system contains acetic acid, ethyl alcohol, water, and ethyl acetate distributed in the following proportions :—

$$\tfrac{1}{3}\mathrm{CH_3COOH} + \tfrac{1}{3}\mathrm{C_2H_5OH} + \tfrac{2}{3}\mathrm{H_2O} + \tfrac{2}{3}\mathrm{CH_3COOC_2H_5}.$$[3]

In the same way it is quite immaterial whether we mix, at 2000°, molecular equivalents of carbon monoxide and water, or carbon dioxide and hydrogen, each system will, after the elapse of a certain time, contain all four substances, carbon monoxide, carbon dioxide, water, and hydrogen, distributed in the same proportions.[4] If m and n be whole numbers—

$$(m+n)\mathrm{CO} + (m+n)\mathrm{H_2O} = m\mathrm{CO} + m\mathrm{H_2O} + n\mathrm{CO_2} + n\mathrm{H_2};$$
$$(m+n)\mathrm{CO_2} + (m+n)\mathrm{H_2} = m\mathrm{CO} + m\mathrm{H_2O} + n\mathrm{CO_2} + n\mathrm{H_2},$$

which is more conveniently written—

$$\mathrm{CO} + \mathrm{H_2O} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2O}.$$

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[1] W. Ostwald, *Journ. Chem. Soc.*, **85**. 506, 1904.

[2] A. Villiers, *Compt. Rend.*, **136**. 1452, 1551, 1903; **90**. 1488, 1563, 1880; **91**. 62, 1880; *Ann. Chim. Phys.* [5], **21**. 72, 1881.

[3] M. Berthelot and L. Péan de Saint Gilles, *Ann. Chim. Phys.* [3], **65**. 385, 1862; [3], **66**. 5, 1862; [3], **68**. 225, 1863; *Compt. Rend.*, **53**. 474, 1861; M. Berthelot, *ib.*, **85**. 883, 1877; **86**. 1227, 1296, 1878; **91**. 587, 1880; *Ann. Chim. Phys.* [3], **66**. 110, 1862; [4], **18**. 6, 1869; [5], **14**. 437, 1878; [5], **15**. 238, 1878; *Essai de Mécanique Chimique fondée sur la Thermochemie*, Paris, 1879.

[4] C. Hoitsema, *Zeit. phys. Chem.*, **25**. 686, 1898.

The reversed pointers "⇌" being used in place of the regular symbol "=" when we are dealing with reactions which simultaneously proceed from left to right, and from right to left.[1]

In Fig. 8 corresponding values of x and t are plotted from both ends of the reversible reaction—

$$2HI \rightleftharpoons H_2 + I_2.$$

The slope of the upper curve shows that if we start with pure hydrogen iodide, the velocity diminishes gradually until a state of equilibrium is reached when about 22 per cent. of hydrogen iodide[2] has decomposed; the slope of the lower curve shows the rate of combination of hydrogen and iodine. The reaction comes to a "standstill" when 78 per cent. of hydrogen iodide has been produced. Notice the greater slope of the latter curve, showing that the velocity is greater the further the reacting mixture is from the state of equilibrium.

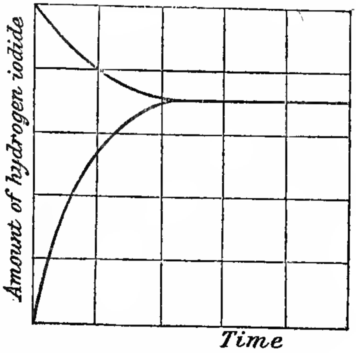

FIG. 8.—Velocity curves.

To summarize, when two reactions mutually oppose one another, the one will have a velocity which is gradually becoming smaller, and the other a velocity which is continually increasing. A state of equilibrium will occur when the rate at which each

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[1] I prefer the symbol "⇌" proposed by H. Marshall (*Proc. Edin. Roy. Soc.*, **24**. 85, 1902; *Zeit. phys. Chem.*, **41**. 103, 1902) in place of van't Hoff's symbol "⇄" in general use. The former is more convenient for blackboard work, and has a more compact appearance on the printed page. Marshall also suggests the symbol "⇛" for irreversible changes, "⥬" for reversible reactions with a negligibly small inverse change, and "⇋" for reversible reactions associated with a definite transition temperature.

[2] M. Bodenstein, *Zeit. phys. Chem.*, **13**. 56, 1893; **22**. 1, 1897.

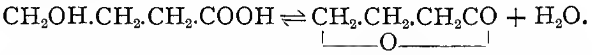
substance is formed is equal to the rate at which it is decomposed. Only then will the quantity of the different substances taking part in the reaction remain unchanged. The study of opposing reactions can thus be attacked from two different standpoints—

1. The resultant velocity of one of the two opposing reactions as the system approaches a state of equilibrium.

2. The distribution of the products of the two reactions when a state of equilibrium is reached.[1]

§ 30. Opposing Unimolecular Reactions.

The simplest case of reversibility occurs when the opposing reactions are both of the same order and unimolecular. In illustration we may take P. Henry's[2] investigation on the reciprocal conversion of γ-oxybutyric acid into γ-butyrolactone, and of γ-oxybutyrolactone into γ-oxybutyric acid, according to the equation—



$$CH_2OH.CH_2.CH_2.COOH \rightleftharpoons \underbrace{CH_2.CH_2.CH_2CO}_{O} + H_2O.$$

Let a_1 and a_2 respectively denote the amounts of γ-oxybutyric acid and of γ-oxybutyrolactone present at the beginning of the reaction, let x gram-molecules of the acid be transformed into the lactone after an interval of time t, then $a_1 - x$ of the acid and $a_2 + x$ of the lactone will be present at the time t. The velocity of transformation of the acid to the lactone will be—

$$\frac{dx_1}{dt} = k_1(a_1 - x);$$

and of lactone to acid—

$$\frac{dx_2}{dt} = k_2(a_2 + x).$$

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[1] J. H. van't Hoff, *Ber.*, **10**. 669, 1877; C. M. Guldberg and P. Waage, *Études*. Christiania, 1867.

[2] P. Henry, *Zeit. phys. Chem.*, **10**. 98, 1892; E. Hjelt, *Ber.*, **29**. 1855, 1861, 1896.

The total velocity of the simultaneous reaction will be—

$$\frac{dx}{dt} = k_1(a_1 - x) - k_2(a_2 + x);$$

or—

$$\frac{dx}{dt} = (k_1a_1 - k_2a_2) \quad (k_1 + k_2)x, \quad . \quad . \quad (1)$$

by a re-arrangement of terms. On integration, we get the expression—

$$\frac{1}{t}\left\{\log\left(\frac{k_1a_1 - k_2a_2}{k_1 + k_2}\right) - \log\left(\frac{k_1a_1 - k_2a_2}{k_1 + k_2} - x\right)\right\} = k_1 + k_2. \quad (2)$$

When the system has come to a stand-still so that the velocity of the reaction in one direction is equal to the velocity in the reverse direction—

$$\frac{dx}{dt} = k_1(a_1 - x) - k_2(a_2 - x) = 0. \quad . \quad . \quad (3)$$

We can calculate the numerical value of the ratio k_1/k_2 by measuring the value of x at the point of equilibrium for—

$$\frac{a_2 + x}{a_1 - x} = \frac{k_1}{k_2} = K, \text{ say.} \quad . \quad . \quad . \quad . \quad (4)$$

Substituting (4) in (2), we get—

$$\frac{1}{t}\log\frac{Ka_1 - a_2}{Ka_1 - a_2 - (K + 1)x} = k_1 + k_2, \quad . \quad . \quad (5)$$

where all the quantities on the left side—K, a_1, a_2, x, and t—can be determined experimentally.

It is interesting to notice the formal resemblance between equations (2) or (5) and the ordinary equation for a direct reaction. Thus, collecting all the constants under the symbol A, we get—

$$\frac{1}{t}\log\frac{A}{A - x} = \text{constant, where } A = \frac{k_1a_1 - k_2a_2}{k_1 + k_2}.$$

Henry worked with $a_1 = 18{\cdot}23$; $a_2 = 0$. Analysis showed that when the reaction had come to a "stand-still," $dx/dt = 0$,

$x = 13{\cdot}28$, hence $a_1 - x = 4{\cdot}95$, $a_2 + x = 13{\cdot}28$. Hence from (4)—

$$K = \frac{k_1}{k_2} = \frac{13{\cdot}28}{18{\cdot}23 - 13{\cdot}28} = 2{\cdot}68.$$

Substituting these numbers in (5), we get—

$$\frac{1}{t} \log \frac{48{\cdot}84}{48{\cdot}84 - 3{\cdot}68x} = k_1 + k_2 \quad . \quad . \quad . \quad (6)$$

The numbers in the third column of the following table were obtained by substituting the observed values of x and t in equation (6).

t	x	$k_1 + k_2$
21	2·41	0·0355
50	4·96	0·0374
100	8·11	0·0384
120	8·90	0·0377
160	10·35	0·0382
220	11·55	0·0370
∞	10·25	—

If we had started the experiment with γ-butyrolactone and measured the rate of formation of γ-oxybutyric acid, we should expect to get the same result for the constant $k_1 + k_2$, if the experiments were conducted under the same conditions, because the point of equilibrium will obviously depend upon the velocity coefficients of the two reactions. Tubandt[1] tested this conclusion for the reciprocal inversion of the two menthones—

$$d\text{-menthone} \rightleftharpoons l\text{-menthone},$$

and found that $k_1 + k_2 = 0{\cdot}016$ for the inversion of the "levo," and of the "dextro" compounds Jungius[2] has also confirmed the deduction for the reciprocal conversion of α- into β- dextromethylglucoside, and of α- into β- pentacetate of d-glucose.

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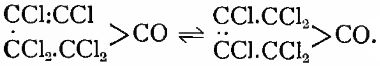
[1] C. Tubandt, *Dissertation*, Halle, 1904; D. Vorländer, *Ber.*, **36**. 268, 1903.

[2] C. L. Jungius, *Koninklijke Akad. van Wetenschappen*, 99, 1903; 779, 1904.

F. W. Küster[1] has also investigated the conversion of hexachloro-α-keto-β-P-pentane into hexachloro-α-keto-γ-R-pentane, and *vice versâ*, in the presence of hydrochloric acid.



$$\begin{matrix}\text{CCl:CCl}\\ \dot{\text{C}}\text{Cl}_2.\text{CCl}_2\end{matrix}\!>\text{CO} \rightleftharpoons \begin{matrix}\text{CCl.CCl}_2\\ \ddot{\text{C}}\text{Cl.CCl}_2\end{matrix}\!>\text{CO}.$$

The constant (0·180) for the conversion of the γ-R-pentane into the β-R-pentane was greater than for the reverse change (0·055). This is said to be due to the accelerating influence of hydrochloric acid upon the velocity of the reaction from one end alone, thus causing the corresponding velocity constant to change from 0·034 to 0·188 in the course of seven minutes. A similar observation was made by J. Wislicenus[2] during the reversible transformation of the two toluene dibromides. Others think that the disturbance is due to the presence of certain impurities contaminating the one compound and not the other.

The effect of referring the "initial concentration" to the concentration of the reacting substances in a state of equilibrium instead of at the beginning of the reaction.

Let us look at the reciprocal transformation of A into B a little more closely. In the first place, let us start with a gram-molecules of A, and let x of A be transformed at any moment, then the velocity of the reaction at any instant will be—

$$\frac{dx}{dt} = k_1(a - x) - k_2x. \quad . \quad . \quad . \quad . \quad (7)$$

Further, let ξ denote the value of x at the point of equilibrium when $dx/dt = 0$, then—

$$k_1(a - \xi) - k_2\xi = 0\text{; or, } k_2 = k_1\frac{a - \xi}{\xi}. \quad . \quad . \quad (8)$$

Substituting this value of k_2 in equation (7), we obtain—

$$\frac{dx}{dt} = k_1(a - x) - k_1\frac{a - \xi}{\xi}x,$$

F. W. Küster, *Zeit. phys. Chem.*, **18**. 161, 1895.

J. Wislicenus, *Dekanatsprogramm*. Leipzig, 1890.

which furnishes, on integration—

$$\frac{1}{t}\log\frac{\xi}{\xi - x} = k_1\frac{a}{\xi};\ \text{or,}\ \frac{1}{t_2 - t_1}\log\frac{\xi - x_1}{\xi - x_2} = k_1\frac{a}{\xi}. \qquad (9)$$

These equations bear a close formal resemblance to those obtained in the treatment of complete reactions, only now we refer the concentration of the changing substance to its concentration at the point of equilibrium instead of at the beginning of the experiment.

In the second place, if instead of starting with A, we start with a gram-molecules of B, then, with the above procedure, we obtain—

$$\frac{dx}{dt} = k_2\frac{a}{a - x}(a - \xi - x). \quad . \quad . \quad . \quad (10)$$

But for equilibrium—

$$k_2\xi = k_1(a - x);\ \text{or,}\ \frac{1}{a - x} = \frac{k_1}{k_2\xi}. \quad . \quad . \quad (11)$$

Whence it follows—

$$\frac{dx}{dt} = k_1\frac{a}{\xi}(a - \xi - x),$$

or—

$$\frac{1}{t}\log\frac{a - \xi}{a - \xi - x} = k_1\frac{a}{\xi};\ \text{or,}\ \frac{1}{t_2 - t_1}\log\frac{a - \xi - x_1}{a - \xi - x_2} = k_1\frac{a}{\xi}. \quad (12)$$

This means that we shall obtain the same velocity coefficient whether we start with a gram-molecules of A or of B.

J. Waddell[1] has verified this deduction for the transformation of solid ammonium thiocyanate into thiourea—

$$NH_4CNS \rightleftharpoons (NH_2)_2CS,$$

as the following table will show. Temp. 152°–3; at equilibrium

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[1] J. Waddell, *Journ. Phys. Chem.*, **2**. 525, 1898. About one gram of not very pure substance was employed in each experiment. The course of the change was followed by Volhard's inexact method for the determination of thiourea by silver nitrate in the presence of excess of ammonia. See J. E. Reynolds and E. A. Werner, *Journ. Chem. Soc.*, **83**. 1, 1903.

there was 21·2 per cent. of thiocyanate, and 78·8 per cent. of thiourea present.

Thiocyanate to thiourea.				Thiourea to thiocyanate.			
t min.	x	$\xi - x$	Const.	t min.	x	$\xi - x$	Const.
0	2·0	19·2	—	0	37·1	47·7	—
5	3·6	17·6	0·00735	15	41·4	37·4	0·00704
10	4·5	16·7	0·00606	27	45·2	33·6	0·00564
15	5·4	15·8	0·00564	38	51·5	27·3	0·00638
46	11·9	9·3	0·00684	68	56·3	22·5	0·00637
71	13·7	7·5	0·00575	90	65·0	13·8	0·00588

The constants obtained with both reactions are said to be sensibly the same within the limits of experimental error.

It follows directly from equation (3) that we can write the first of equations (9) in either of the forms—

$$\frac{1}{t}\cdot\frac{\xi}{a}\log\frac{\xi}{\xi - x} = k_1\,;\ \text{or,}\ \frac{1}{t}\cdot\frac{a - \xi}{a}\log\frac{\xi}{\xi - x} = k_2\,;$$

and—

$$\therefore\ \frac{1}{t}\log\frac{\xi}{\xi - x} = k_1 + k_2.$$

This furnishes an easy means of *evaluating the constants of a reversible reaction.* W. Kistiakowsky[1] applied these equations to the rate of formation of ethyl formate in the presence of an

t	$\xi - x$	$k_1 + k_2$	k_1	k_2
0	19·23	—	—	—
50	16·11	0·00153	0·000939	0·000597
100	13·46	0·00154	0·000952	0·000598
190	9·69	0·00156	0·000988	0·000602
300	6·60	0·00155	0·000952	0·000598
∞	0·0	—	—	—

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[1] W. Kistiakowsky, *Zeit. phys. Chem.*, **27.** 250, 1898; C. S. Hudson, *ib.*, **44.** 487, 1903 (multirotation of lactose hydrate).

excess of alcohol and water so that only the concentration of the acid and ester suffered any change. The reaction is therefore unimolecular with respect to the formic acid on the one hand, and to ethyl formate on the other. The results are shown in the preceding table.

§ 31. Opposing Bimolecular Reactions.

An illustration of two opposing reactions occurs during the esterification of ethyl alcohol—

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

The velocity equation will be—

$$\frac{dx}{dt} = k_1(a - x)(b - x) - k_2(c + x)(d + x), \quad . \quad (1)$$

where a, b, c, and d respectively denote the number of gram-molecules of acetic acid, ethyl alcohol, water, and ethyl acetate present at the beginning of the experiment. By integration—

$$\frac{1}{t} \cdot \frac{1}{P} \log \frac{(Q - P)\{Q + P - 2(K - 1)x\}}{(Q + P)\{Q - P - 2(K - 1)x\}} = k_2, \quad . \quad (2)$$

where, for brevity's sake, $K = k_1/k_2$; $Q = a + b + K(c + d)$; and $P = \sqrt{Q^2 + 4(K - 1)(ab - Kcd)}$. The numerical value of K is obtained from the value of x at equilibrium, when—

$$k_1(a - x)(b - x) = k_2(c + x)(d + x). \quad . \quad . \quad (3)$$

Although the mathematical setting now appears so complicated, the treatment of the experimental results is no more difficult. It will save labour if we suppose the reaction to start from one end so that, at the beginning of the experiment, $c = d = 0$; and if we let $a = b = 1$, we can apply the equation to the universally quoted experiments of Berthelot and Saint Gilles. The rate of formation of ethyl acetate will now be—

$$\frac{dx}{dt} = k_1(1 - x)^2 - k_2x^2.$$

or—

$$\frac{dx}{dt} = (k_1 - k_2)\left(x^2 - 2\frac{k_1}{k_1 - k_2}x + \frac{k_1}{k_1 - k_2}\right); \quad . \quad (4)$$

by putting $m = k_1/(k_1 - k_2)$, we get, on integration—

$$\frac{1}{t}\cdot\frac{1}{2\sqrt{m^2-m}}\log\frac{(m+\sqrt{m^2-m}-x)(m-\sqrt{m^2-m})}{(m-\sqrt{m^2-m}-x)(m+\sqrt{m^2-m})}=k_1-k_2. \quad (5)$$

Berthelot and Saint Gilles found that under these conditions—

$$K=\frac{k_1}{k_2}=4;\ \therefore\ m=\frac{4}{3};\ \text{and}\ m^2-m=\frac{2}{3}.$$

Substituting these values in (5), we obtain the equation—

$$\frac{1}{t}\cdot\frac{3}{4}\log\frac{2-x}{2-3x}=k_1-k_2, \quad . \quad . \quad . \quad (6)$$

for calculating the values shown in the third column of the following table. (Temp. atmospheric.)

t (days)	x	$k_1 - k_2$
41	0·200	0·0045
64	0·250	0·0040
103	0·345	0·0039
137	0·421	0·0041
167	0·474	0·0043
190	0·496	0·0038
∞	0·677	—

"Initial disturbances" of some kind cause certain deviation in the constancy of $k_1 - k_2$ during the earlier stages of the experiment. The coefficients of each reaction can be easily determined, for experiment shows that—

$$\frac{k_1}{k_2}=4;\ k_1-k_2=0{\cdot}004;\ \therefore\ k_1=0{\cdot}0052;\ k_2=0{\cdot}0013.$$

If the "initial disturbances" are small, it may be possible *to evaluate the constants of the reactions in both directions* by measuring the initial velocities of the two reactions, starting from both ends. Each reaction is treated, during the initial stages, as if it were a complete or irreversible reaction.

J. H. van't Hoff[1] has calculated in this way the values of

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[1] J. H. van't Hoff's *Vorlesungen über theoretische und physikalische Chemie*, Braunschweig, **1**. 200, 1898; R. A. Lehfeldt's trans., **1**. 204, 1900.

k_1 and k_2 for the experiments of O. Knoblauch[1] on the velocity of the reaction—

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O,$$

with the following results :—

Formation of ethyl acetate.			Hydrolysis of ethyl acetate.		
t min.	C_{ester}	Velocity.	t min.	C_{acid}	Velocity.
0	0·0	—	0	0·0	—
44	0·1327	0·00302	78	0·0777	0·000966
53	0·1628	0·00307	86	0·0862	0·001003
62	0·1847	0·00298	94	0·0930	0·000989
	Mean .	0·00303		Mean .	0·000996

The solutions contained one gram-molecule of acetic acid and 12·756 gram-molecules of alcohol per litre, and one gram-molecule of ethyl acetate and 12·215 gram-molecules of water per litre respectively.

In the formation of ethyl acetate—

$$\frac{dx}{dt} = k_1(a - x)(b - x)\,;$$

$$\therefore 0{\cdot}00303 = k_1 \times 1 \times 12{\cdot}756\,;\ \therefore 0{\cdot}000238 = k_1.$$

With the hydrolysis of ethyl acetate—

$$k_2 = 0{\cdot}0000815.$$

$$\therefore K = \frac{k_1}{k_2} = 2{\cdot}92 \text{ (calc.)};\ = 2{\cdot}84 \text{ (obs.)}.$$

It follows directly from equations (1) and (2) that we should get the same constant k_2 by starting from either side of the reversible equation—

$$H.OH + CH_3COOC_2H_5 \rightleftharpoons CH_3COOH + C_2H_5OH.$$

This was verified experimentally by O. Knoblauch.[2]

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[1] O. Knoblauch, *Zeit. phys. Chem.*, **22**. 268, 1897.

[2] O. Knoblauch, *Zeit. phys. Chem.*, **22**. 268, 1897 ; A. Bonz, *ib.*, **2**. 865, 1888.

I. The esterification of alcohol.—Starting with $b = 0$, $c = 1$, $a = d = 12\cdot756$, equation (1), K was found from equation (3) to be 2·74. Hence—

$$Q = 12\cdot756 + 2\cdot74(1 + 12\cdot756) = 50\cdot447;$$

$$P = \sqrt{(50\cdot447)^2 - 4 \times 2\cdot74 \times 1\cdot74 \times 12\cdot756} = 47\cdot975;$$

and from (2)—

$$\frac{1}{t} \cdot \frac{1}{47\cdot975} \log \frac{(98\cdot422 - 3\cdot48x)(2\cdot472)}{(2\cdot472 - 3\cdot48x)(98\cdot422)} = k_2. \quad (7)$$

Corresponding values of x, t, and k_2 are shown in the subjoined table.

II. Hydrolysis of ethyl acetate.—Starting with $a = 12\cdot215$, $b = 1$, $c = 0$, $d = 12\cdot215$, K was found to be 2·74. Hence (2) reduces to—

$$\frac{1}{t} \cdot \frac{1}{47\cdot585} \log \frac{(9\cdot268 + 3\cdot48x)(0\cdot902)}{(0\cdot902 - 3\cdot48x)(94\cdot268)} = k_2. \quad . \quad (8)$$

The experimental data used for calculating the constant k_2 are shown in the following table:—

Esterification of alcohol.			Hydrolysis of ester.		
t min.	x	$k_2 10^4$	t min.	x	$k_2 10^4$
0	0·0	—	0	0·0	—
53	2·06	1·00	86	1·41	1·00
108	4·87	1·02	138	2·04	1·01
155	6·27	1·03	348	3·42	1·00
322	9·29	1·03	405	3·64	1·02
442	10·28	1·01	464	3·80	1·03
∞	11·69	—	∞	4·32	—

The effect of referring the "initial concentration" to the concentration of the reacting substances at equilibrium instead of at the beginning of the reaction.

We may write the reversible bimolecular equation—

$$\frac{dx}{dt} = k_1(a - x)^2 - k_2 x^2, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in the form—

$$\frac{dx}{dt} = (k_1 - k_2)\left(\frac{k_1}{k_1 - k_2}a^2 - \frac{2k_1}{k_1 - k_2}x + x^2\right), \qquad (10)$$

by multiplying out and arranging the terms. If we put—

$$K = \frac{k_2}{k_1};\ k_1 - k_2 = k_1(1 - K), \quad . \quad . \quad . \qquad (11)$$

we get—

$$\frac{dx}{dt} = (k_1 - k_2)\left(\frac{a}{1 + \sqrt{K}} - x\right)\left(\frac{a}{1 - \sqrt{K}} - x\right). \qquad (12)$$

This bears a close formal analogy with the regular equation for an irreversible bimolecular reaction, and reminds one of that employed by Muller[1] for calculating up the constants of reversible reactions.

When the system is in a state of equilibrium, we write ξ in place of x, and—

$$K = \frac{k_2}{k_1} = \frac{(a - \xi)^2}{\xi^2};\ \therefore \frac{a - \xi}{\xi} = \pm\sqrt{K}; \quad . \qquad (13)$$

$$\therefore \xi = \frac{a}{1 \pm \sqrt{K}};\ \xi_1 = \frac{a}{1 - \sqrt{K}},\ \xi_2 = \frac{a}{1 + \sqrt{K}}; \qquad (14)$$

or—

$$\frac{dx}{dt} = (k_1 - k_2)(\xi_1 - x)(\xi_2 - x); \quad . \quad . \qquad (15)$$

hence, by integration—

$$\frac{1}{t} \cdot \frac{1}{\xi_2 - \xi_1} \log \frac{\xi_1(\xi_2 - x)}{\xi_2(\xi_1 - x)} = k. \quad . \quad . \quad . \qquad (16)$$

If—

$$\xi_1 = \xi_2,$$

then, from (14), $\sqrt{K}$ must be zero, and both ξ_1 and ξ_2 must be equal to a. This means that the reaction is not reversible. For this reason, Waddell[2] points out that we may not

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[1] P. T. Muller, *Bull. Soc. Chim.* [3], **19**. 337, 1898.

[2] J. Waddell, *Journ. Phys. Chem.*, **3**. 41, 1899; W. Ostwald's *Lehrbuch*, **2**. ii., 257, 1902.

assume, as Walker and Hambly[1] have done, that the equations —

$$\frac{dx}{dt} = k_1(\xi - x)^2 ; \ \frac{1}{t} \cdot \frac{x}{\xi - x} = k, \quad . \quad . \quad (17)$$

are true for reversible reactions, even though fairly constant values of k be obtained.

Two opposing side reactions occur in the reaction between hydrogen peroxide and hydriodic acid,[2] thus Harcourt and Esson state that—

$$H_2O_2 + 2HI \rightleftharpoons I_2 + 2H_2O ; \ H_2O_2 + I_2 \rightleftharpoons 2HI + O_2.$$

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[1] J. Walker and F. J. Hambly, *Journ. Chem. Soc.*, **67**. 746, 1895; ammonium cyanate to urea. For the reversible transformation of alkyl-ammonium cyanates into their corresponding ureas, which J. Walker and J. R. Appleyard (*Journ. Chem. Soc.*, **67**. 193, 1896) consider to be unimolecular in the one direction and bimolecular in the other, see J. Waddell, *l.c.*; J. Walker and J. Henderson, *Journ. Chem. Soc.*, **69**. 748, 1896.

[2] A. V. Harcourt and W. Esson, *Phil. Trans.*, **186**. 817, 1895. See M. Delépine, *Bull. Soc. Chim.* [3], **25**. 364, 1904 (methyal).

CHAPTER V

HOMOGENEOUS CONSECUTIVE REACTIONS

§ 32. "Abnormal" Reactions.

According to the current mode of representing chemical reactions, only the initial and the final states of the process are indicated. The symbol " = " linking these two stages together gives no indication of the true character of the change. In the interval between the initial and the final stages there may be a number of intermediate states of which the chemistry of to-day has no inkling. The formation of a chemical compound is the concluding act of a complex series of changes which begin the moment the reacting substances are brought into contact, and cease only when the products of the reaction appear in their final state. "And it appears to me," said Schönbein[1] in 1852, "that those states which exist before the so-called chemical combination has taken place constitute the most important part of chemistry, the peculiar dynamics of our science."

By way of illustration, the reaction between ferric chloride and potassium iodide appears to be unimolecular with respect to the former constituent.[2] Consequently, one of the three following formulæ is at our disposal:—

$$\text{(i.)}\ FeCl_3 + 3KI = FeI_2 + 3KCl + I;$$
$$\text{(ii.)}\ FeCl_3 + 2KI = FeI_2 + 2KCl + Cl;$$
$$\text{(iii.)}\ FeCl_3 + KI = FeCl_2 + KCl + I.$$

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[1] C. F. Schönbein, *Journ. prakt. Chem.* [2], **55**. 1, 1852.

[2] A. Schükarew, *Zeit. phys. Chem.*, **38**. 353, 1901.

It was then found that the reaction is bimolecular with respect to potassium iodide; and also that one atom of iodine is liberated for every molecule of ferric chloride reduced. It is therefore inferred that (ii.) represents the first stage of the reaction, and that this is followed by another change—

$$\text{(iv.)}\ 2KI + 2Cl = 2KCl + I_2.$$

The reaction thus consists of two distinct processes:—(ii.) and (iv.).

What will be the effect of the former reaction upon the measured speed of the change? Suppose, for the sake of simplicity, that a substance A forms an intermediate compound M, and this, in turn, forms a final product B. If one gram-molecule of A is transformed into M in the ten-thousandth part of a second, while M is transformed into B at the rate of one gram-molecule per hour, the observed order of the whole reaction—

$$A = B,$$

will be solely fixed by the order of the slower reaction $M = B$, because the methods in use for measuring the rates of chemical reactions are not sensitive to changes so rapid as the assumed rate of transformation of A into M. Whatever the order of the first reaction, $M = B$ is alone accessible to measurement. If, therefore, $A = B$ appears to be a reaction of the first, second, or nth order, we must understand that *one* of the subsidiary reactions ($A = M$, or $M = B$) may be—

(1) an immeasurably fast reaction, accompanied by

(2) a slower measurable change of the first, second, or nth order.

This may be illustrated by the following analogy: "The time occupied in the transmission of a telegraphic message depends both on the rate of transmission along the conducting wire, and on the rate of progress of the messenger who delivers the telegram; but it is obviously this last, slower rate that is of really practical importance in determining the time of transmission."[1] Hence we have the following rule:—*If a chemical*

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[1] J. Walker, *Proc. Roy. Soc. Edin.*, **22**. 22, 1898.

reaction takes place in two stages, one of which is considerably faster than the other, the observed order of the whole reaction will be determined by the order of the slower change.

The same reasoning applies to a slow reaction accompanied by any number of fast reactions.

When the velocities of the consecutive reactions are of the same order of magnitude, the complete reaction cannot be represented by the simple velocity equations hitherto considered. Some changes have to be made in the mode of treatment, although we still follow the fundamental law of mass action. We now enter into one of the most difficult departments of chemical dynamics.

Harcourt and Esson (1864) were the first to attempt to cope with the difficulties which beset this subject. Since then the problem has only been treated in a desultory way. Although Harcourt and Esson's work is so often cited, yet this phase of their work is generally overlooked. The neglect is surprising. But the combination of mathematical dexterity with the chemical astuteness necessary for the treatment of consecutive chemical reactions is not particularly common. It is only within recent years that anything beyond the routine "school mathematics" has been thought necessary for the equipment of the chemist.

§ 33. Two Consecutive Unimolecular Reactions.

Let us now study a special case. A substance A forms an intermediate compound M, which finally forms a third substance B. There are two consecutive reactions—

$$A = M; \ M = B.$$

Harcourt and Esson [1] found that when potassium permanganate in a solution of dilute sulphuric acid acts upon a great excess

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[1] A. V. Harcourt and W. Esson, *Chem. News*, **10**. 171, 1864; *B. A. Reports*, 29, 1865; *Proc. Roy. Soc.*, **14**. 470, 1865; *Phil. Trans.*, **156**. 193, 1866; R. Ehrenfeld, *Zeit. anorg. Chem.*, **33**. 117, 1903; N. Schilow, *Ber.*, **36**. 2735, 1903 (oxalic and formic acids).

of oxalic acid and of manganese sulphate, so that the original mixture contains—

$$2KMnO_4 + 14MnSO_4 + 108H_2C_2O_4 + 760H_2SO_4,$$

manganese dioxide is formed with very great velocity, so quickly, in fact, that we may suppose the solution to contain manganese dioxide at the beginning of the experiment.

$$2KMnO_4 + 3MnSO_4 = K_2SO_4 + 2H_2SO_4 + 5MnO_2.$$

Three reactions now set in—

First, a slight reduction of oxalic acid by the manganese dioxide;

Second, the formation of an intermediate manganese oxide, possibly Mn_2O_7, by the interaction of the manganese dioxide with the excess of manganese sulphate still present;

Third, the reduction of the oxalic acid by this intermediate oxide.

Everything but the manganese dioxide is in great excess, so that we are only concerned with the change in the concentration of the manganese dioxide. Let us neglect the direct reduction of the oxalic acid by the manganese dioxide (side reaction), and confine our attention to the formation of the hypothetical intermediate compound and the subsequent reduction of oxalic acid. The complete reaction may be written—

$$MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2H_2O + 2CO_2;$$

and this takes place in the stages—

$$MnO_2 \rightarrow Mn_2O_7;\ Mn_2O_7 \rightarrow MnO.$$

Let us start with *a* gram-molecules of manganese dioxide. At the end of a certain time, *t*, the solution will contain, say, *x* of manganese dioxide (A), *y* of the intermediate oxide (M), and *z* of the product remaining after reduction (B). Hence—

$$x + y + z = a. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The rate of diminution of A is—

$$-\frac{dx}{dt} = k_1x, \text{ or, } x = ae^{-k_1t}, \quad . \quad . \quad . \quad (2)$$

where k_1, as usual, denotes the velocity coefficient of the transformation of A into M. The rate of formation of B is—

$$\frac{dz}{dt} = k_2 y, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k_2 is the velocity coefficient for the transformation of M into B. Again, the rate at which M accumulates in the system is evidently the difference in the rate of diminution of A and the rate of increase of B. Consequently—

$$\frac{dy}{dt} = -\frac{dx}{dt} - \frac{dz}{dt} = k_1 x - k_2 y. \quad . \quad . \quad . \quad (4)$$

By the integration of these four relations—(1), (2), (3), (4)—it is found that—

$$x + y = a - z = a\left(\frac{k_2}{k_1 - k_2}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}e^{-k_2 t}\right). \quad (5)$$

Here, then, we have a relation between $x + y$, t, a, and two constants, which permits our theory to be tested. The reaction can be stopped at any time, t, by the addition of potassium iodide, and the amount of MnO_2 and Mn_2O_7—*i.e.* of $x + y$—determined by titrating the liberated iodine with a standard solution of sodium thiosulphate in the usual manner. In this way Harcourt and Esson found a series of corresponding values of $x + y$ and t. The constants were then collected together so that—

$$\frac{ak_2}{k_1 - k_2} = A; \ \frac{ak_1}{k_2 - k_1} = B; \ e^{-k_1} = C; \ e^{-k_2} = D. \quad (6)$$

Hence—

$$x + y = A(B)^t + C(D)^t. \quad . \quad . \quad . \quad . \quad (7)$$

An infinite number of values of A, B, C, D might be found, by simple mathematical processes,[1] to satisfy the experimental data. In this way Harcourt and Esson obtained the following set of empirical values—

$$A = 28{\cdot}5; \ B = 0{\cdot}82; \ C = 2{\cdot}7; \ D = 0{\cdot}98,$$

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[1] For methods, see J. W. Mellor's *Higher Mathematics*, §§ 105, 106.

which, when substituted in equation (7), gave an expression which permits us to calculate the value of $x + y$ for corresponding values of t. The results are shown in the following table:—

$$x + y = 28{\cdot}5(0{\cdot}82)^t + 2{\cdot}7(0{\cdot}98)^t.$$

t min.	$x + y$		t min.	$x + y$	
	Found.	Calc.		Found.	Calc.
0·5	25·85	25·9	3·0	10·45	10·4
1·0	21·55	21·4	3·5	8·95	9·0
1·5	17·90	17·8	4·0	7·7	7·8
2·0	14·90	14·9	4·5	6·65	6·6
2·5	12·55	12·5	5·0	5·7	5·8

The agreement between the observed and calculated values of $x + y$ is exceedingly good. Still, we must remember that the problem is not completely solved. Empirical values of A, B, C, and D in equation (7) might be calculated for a great number of chemical equations, whose intermediate states do not proceed as indicated above. The "agreement between the observed and calculated values" is therefore illusory, and of little theoretical importance,[1] until we have learned to evaluate k_1 and k_2.

Consecutive reactions may be expressed mathematically in many different forms; for example, let y denote the amount of A which has been transformed into M at the time t, and z the amount of M which has been transformed into B at the time t, then—

$$\frac{dy}{dt} = k_1(a - y); \quad \frac{dz}{dt} = k_2(y - z). \quad . \quad . \quad . \quad (8)$$

By integration, z assumes the form expressed in equation (5). It will generally be found that one setting can be integrated

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[1] See also Mills' application of Harcourt and Esson's formula (5) to Gladstone's experiments. E. J. Mills, *Phil. Mag.* [4], **48**. 241, 1874.

more readily than another. The choice of setting is therefore soon decided.

The inversion of gentianose[1] in the presence of a mixture of invertase and emulsin appears to be the resultant of two unimolecular consecutive reactions. With invertase alone, the gentianose is transformed into a mixture of levulose and gentiobiose; while the latter, in the presence of emulsin, is resolved into dextrose. The two reactions can be studied separately. k_1 and k_2 can thus be evaluated altogether apart from the main reaction.

We also find from the experiments of Rutherford and Soddy,[2] that the rate of decay of the excited radioactivity produced in bodies exposed to thorium or radium emanations follows the law for a pair of unimolecular consecutive reactions.

§ 34. Two Consecutive Bimolecular Reactions.

In some cases it is possible to get an approximate idea of the values of k_1 and k_2 from measurements made near the beginning and end of the reaction. Take, for example, Reicher's[3] investigation "on the hydrolysis of ethyl succinate by sodium hydroxide"—

$$C_2\dot{H}_4(COOC_2H_5)_2 + 2NaOH = C_2H_4(COONa)_2 + 2C_2H_5OH.$$

Measurements were made immediately after the mixing of the ethyl succinate with the sodium hydroxide, as well as 15, 45, and 120 minutes after mixing. The following values of k were

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[1] E. Bourquelot and H. Hérissey, *Ann. Chim. Phys.* [7], **27**. 397, 1902; E. Bourquelot, *Journ. Pharm. Chim.* [6], **16**. 598, 1902; [6], **17**. 409, 1903; *Compt. Rend.*, **136**. 762, 1903.

[2] E. Rutherford and F. Soddy, *Journ. Chem. Soc.*, **81**. 321, 837, 1902; P. Curie and J. Danne, *Compt. Rend.*, **136**. 346, 1903; E. Rutherford's *Radioactivity*, Cambridge, 268, 295, 1904.

[3] L. T. Reicher, *Maandblad voor natuurwetenschappen*, **12**. 105, 1885; or *Recueil des Trav. chim. des Pays-Bas.*, **4**. 350, 1885; O. Knoblausch, *Zeit. phys. Chem.*, **26**. 96, 1898; H. Imbert and E. Hjelt, *Ber.*, **29**. 1864, 1867, 1896.

obtained on the assumption that the reaction is of the simple bimolecular type:—

Stage I.—Immediately after mixing—
t = 1·5, 3·2, 5·3, 7·1 hours;
k = 1·56, 1·38, 1·33, 1·24.
Stage II.—15 minutes after mixing—
t = 9·9, 17·2, 23·6 hours;
k = 0·75, 0·73, 0·73.
Stage III.—45 minutes after mixing—
t = 15·3, 24·3, 43·2 hours;
k = 0·65, 0·63, 0·65.
Stage IV.—120 minutes after mixing—
t = 16·0 33·2, 41·0, 46·1 hours;
k = 0·63, 0·62, 0·59, 0·62.

If the reaction really takes place in the two stages (p. 50)—

(i.) The formation of ethyl sodium succinate;
(ii.) The hydrolysis of sodium ethyl succinate,

the decrease in the values of k during the earlier stages of the reaction shows that the velocity of the first reaction is much faster than the second, and the constancy of the values of k during the later stages of the reaction shows that the formation of ethyl sodium succinate is practically complete. The velocity constant of the second reaction will be about 0·6, and the constant for the first reaction will be a little greater than 1·6.

The velocity equations for the hydrolysis of ethyl succinate have not yet been fully investigated on the experimental side, although this reaction offers a typical example of two consecutive bimolecular changes. Ostwald[1] gives one setting of the equations in his *Lehrbuch*, but the following method of treating bimolecular consecutive reactions is to be preferred.

Let x denote the amount of ethyl succinate which has been transformed at the time t; $a - x$ will then denote the amount remaining in the solution at the same time. Similarly, if the system contains b of sodium hydroxide at the beginning of the reaction, x of this will have been consumed in the

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[1] W. Ostwald's *Lehrbuch*, 2. ii., 278, 1902.

formation of sodium ethyl succinate at the time t, and y in the formation of sodium succinate, hence, $b - x - y$ of sodium hydroxide, and $x - y$ of sodium ethyl succinate will be present in the system at the time t. The rate of formation of sodium ethyl succinate is, therefore—

$$\frac{dx}{dt} = k_1(a - x)(b - x - y) \; ; \quad . \quad . \quad . \qquad (1)$$

and the rate of formation of sodium succinate will be—

$$\frac{dy}{dt} = k_2(x - y)(b - x - y). \quad . \quad . \qquad (2)$$

By integration, we get—

$$y = \frac{Kx}{K - 1} - \frac{a}{K - 1} + C(a - x)^K \; ; \quad . \quad . \qquad (3)$$

and therefore, from (1)—

$$\frac{dx}{dt} = k_1\{A(a - x) + B(a - x)^2 - C(a - x)^{K + 1}\}, \quad (4)$$

where we have written, for the sake of brevity—

$$b - 2a = A \; ; \; \frac{2K - 1}{K - 1} = B \; ; \; \frac{1}{(K - 1)a^{K - 1}} = C \; ; \; \frac{k_2}{k_1} = K. \; (5)$$

In order to compare expressions (3) and (4) with the experimental results, it will be found most convenient to use the methods of § 15, since the integration of (4) is usually impracticable.

By way of illustration, let us apply this equation to Reicher's experiments (*l.c.*), where $k_1 = 1{\cdot}6$, and $k_2 = 0{\cdot}6$; $\therefore K = 0{\cdot}375$. Assume[1] that the experiments were started with $a = b = 1$. Then, $A = -1$; $B = 0{\cdot}4$; $C = -1{\cdot}6$, from (5). Hence, from (4), and the method of § 15, where $\Delta t = 1$, and the mean value of x for the first interval is $\frac{1}{2}\Delta x$—

$$\Delta x = 1{\cdot}6\{ - (1 - \tfrac{1}{2}\Delta x) + 0{\cdot}4(1 - \tfrac{1}{2}\Delta x)^2 + 1{\cdot}6(1 - \tfrac{1}{2}\Delta x)^{1{\cdot}375}\}. \; (6)$$

Now expand each term by the binomial theorem[2] neglecting

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[1] The experiments of Reicher were obviously not designed for use with equation (4), but they might be repeated with this end in view.

[2] J. W. Mellor's *Higher Mathematics*, § 98. For integration (3), see also §§ 122 and 74.

powers of Δx higher than the third because of their smallness; collect like terms together, and we get—

$$1{\cdot}6 - 2{\cdot}6\Delta x + 0{\cdot}32(\Delta x)^2 = 0.$$

We can solve this equation for Δx in the usual way, or, if the unit of time be taken small enough, $(\Delta x)^2$ will be so small that it will have no influence on the calculated result. In that case $(\Delta x)^2$ might be neglected, and—

$$\Delta x = 0{\cdot}62\,;\ \therefore 1 - x = 1 - 0{\cdot}62 = 0{\cdot}38$$

should represent the amount of ethyl succinate present in the system at the end of the first unit of time. Now calculate y by substituting the value of x just determined in (3).

The new value of a for the next interval will be 0·38, and instead of b we use $1 - x - y$. Thus we get, step by step, a series of values of x and y which can be compared with those determined by experiment.

Among other consecutive reactions we have the action of potassium hydroxide upon chloral hydrate,[1] and upon chloroform;[2] the hydrolysis of methyl oxalate;[3] the esterification of phosphoric acid by glycerol;[4] the oxidation of arsenious acid by iodine, and the reduction of arsenic acid by hydrogen iodide;[5] the action of bromine upon oxalic acid,[6] and upon phenyl sulphonacetic acid;[7] and the hydrolysis of carbonic and sulphonic esters.[8] The course of the oxidation of hydriodic acid, sulphurous acid, or ferrous sulphate by the oxyacids of the halogens, appears to be so intricate that "a satisfactory

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[1] L. T. Reicher, *Rec. Trav. Chim. Pays-Bas*, **4**. 347, 1885; C. M. van Deventer, *ib.*, **4**. 353, 1885.

[2] A. P. Saunders, *Journ. Phys. Chem.*, **4**. 660, 1900.

[3] A. Quartaroli, *Gazz. Chim. Ital.*, **33**. i., 497, 1903.

[4] H. Imbert and G. Belugon, *Bull. Soc. Chim.* [3], **21**. 166, 1899; P. Carré, *Compt. Rend.*, **137**. 1070, 1903.

[5] T. R. Roebuck, *Journ. Phys. Chem.*, **6**. 365, 1902.

[6] T. W. Richards and W. N. Stull, *Proc. Amer. Acad.*, **38**. 321, 1902; *Zeit. phys. Chem.*, **41**. 544, 1902.

[7] L. Ramberg, *Zeit. phys. Chem.*, **34**. 561, 1900.

[8] J. H. Kastle, J. Murrill, and J. C. Frazer, *Amer. Chem. Journ.*, **19**. 894, 1899; R. Wegscheider, *Zeit. phys. Chem.*, **41**. 62, 1902; with M. Furcht, *Monatshefte für Chem.*, **23**. 1093, 1902; with P. von Rušnov, *ib.*, **24**. 375, 1903; with J. Hecht, *ib.*, **24**. 413, 1903.

application of the law of mass has not yet been made."[1] In some cases formulæ have been suggested which have no connection with the law of mass action. The trouble, in many cases, arises from the fact that the mere presence of the products of the reaction may hasten or retard the progress of the change.

The reaction between potassium persulphate and phosphorous acid—

$$H_3PO_3 + K_2S_2O_8 + H_2O = K_2SO_4 + H_2SO_4 + H_3PO_4,$$

is, theoretically, a reaction of the second order, but the reaction is too slow for measurement unless hydriodic acid be also present. A mixture of potassium persulphate, hydriodic acid and phosphorous acid first turns brown, showing that iodine is liberated during the earlier stages of the reaction; the coloration then slowly disappears, owing to the reformation of hydriodic acid. The complete reaction is thus compounded of two consecutive changes. There is first a bimolecular reaction between potassium persulphate and hydriodic acid—

$$K_2S_2O_8 + 2HI = K_2SO_4 + H_2SO_4 + I_2,$$

which was investigated by Price[2] in the usual manner. If a and b respectively denote the initial concentrations of hydriodic acid and of potassium persulphate, x the amount transformed, then $a-x$ of hydriodic acid and $b-x$ of the

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[1] The more interesting attempts are: W. Ostwald, *Zeit. phys. Chem.*, **2**. 127, 1888; W. Meyerhoffer, *ib.*, **2**. 585, 1888; O. Burchard, *ib.*, **2**, 823, 1888; N. Schilow, *ib.*, **27**. 513, 1899; A. A. Noyes and W. O. Scott, *ib.*, **18**. 122, 1895; A. A. Noyes, *ib.*, **19**. 599, 1896; W. H. Pendlebury and M. Seward, *Proc. Roy. Soc.*, **45**. 396, 1899; G. Magnanini, *Gazz. Chim. Ital.*, **20**. 377, 1890; **21**. 476, 1891; H. Schlundt, *Bull. Wisconsin Univ.*, **1**. 1, 1894; H. Schlundt and R. Warder, *Amer. Chem. Journ.*, **17**. 754, 1895; **18**. 23, 1896; W. Judson and J. W. Walker, *Journ. Chem. Soc.*, **73**. 410, 1898; W. C. Bray, *Journ. Phys. Chem.*, **7**. 92, 1903; H. Landolt, *Berlin Akad. Ber.*, 249, 1885; 193, 1886; 21, 1887; *Ber.*, **19**. 1317, 1886; **20**. 745, 1887; F. Selmons, *Chem. Central.* [3], **18**. 502, 1887; *Inaug. Dissert.*, Berlin, 1887; J. J. Hood, *Phil. Mag.* [5], **6**. 371, 1878; **8**. 121, 1879; **13**. 419, 1882; J. McCrae, *Proc. Chem. Soc.*, **19**. 225, 1903.

[2] T. S. Price, *Zeit. phys. Chem.*, **27**. 476, 1898.

persulphate will remain in the solution at the time *t*. Federlin[1] finds that if $a = 500$, $b = 28{\cdot}45$—

$$\frac{dx}{dt} = k_1(a - x)(b - x)\text{; and } k_1 = 0{\cdot}0065. \quad . \quad (7)$$

Second, the above reaction appears to be followed by another bimolecular reaction between the iodine so liberated and the phosphorous acid—

$$H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI.$$

If c denotes the initial concentration of the phosphorous acid, and x the amount of iodine liberated from the 28·45 grams of potassium iodide at the time t; and y the amount transformed at that instant—

$$\frac{dy}{dt} = k_2(c - y)(x - y)\text{, and } k_2 = 0{\cdot}157, \quad . \quad . \quad (8)$$

when $c = 500$. The hydriodic acid formed in the second reaction reacts again as in the preceding equation.

Federlin has closely investigated the course of the complete reaction—

$$H_3PO_3 + K_2S_2O_8 + H_2O = K_2O_4 + H_2SO_4 + H_3PO_4,$$

by measuring the amount of free iodine in the solution by titration with a centinormal solution of sodium thiosulphate; then, by adding an excess of potassium iodide to the solution along with a few drops of a mixture of copper and ferrous sulphates so as to decompose the persulphate, and again titrating the liberated iodine with standard "thio," the amount of persulphate unchanged at the time *t* can be readily calculated.

It is rather fortunate that the intermediate stages of the complete reaction can be studied separately, and the velocity constants evaluated in the usual way; but, unfortunately, the integration of equations (7) and (8) in a form suitable for the experimental material presents some difficulties. Federlin found it most convenient to work by the method of

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[1] W. Federlin, *Zeit. phys. Chem.*, **41**. 565, 1902.

approximation indicated above. A selection from the results obtained are shown in the following table:—

t hours.	Iodine.		Persulphate.	
	Obs.	Calc.	Obs.	Calc.
0·5	4·55	3·44	8·08	9·13
1·0	5·39	4·58	4·89	6·72
1·5	5·05	4·84	3·13	4·98
2·0	4·18	4·64	2·17	3·64
2·5	3·38	4·22	1·49	2·68
3·0	2·59	3·68	1·01	1·94

When we take into consideration the approximate nature of the "method of integration," the agreement between the observed and calculated results is as close as we could expect. Consequently, it is inferred that the reaction indicated in the last equation is really compounded of the two intermediate reactions just indicated.

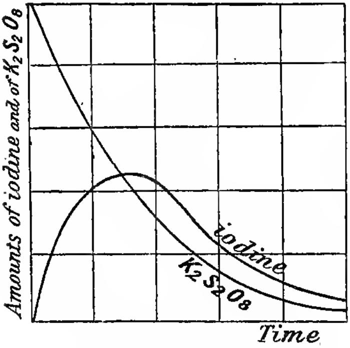

FIG. 9.—Velocity curves.

It is now interesting to plot the found and calculated values of iodine and persulphate present in the solution at different intervals of time. The observed values are shown in Fig. 9.

§ 35. Mixed Uni- and Bi-molecular Consecutive Reactions.

When potassium permanganate, manganese sulphate, oxalic acid, and sulphuric acid are mixed together in the following proportions—

$$2KMnO_4 + 15MnSO_4 + 5H_2C_2O_4 + 3H_2SO_4,$$

Harcourt and Esson (*l.c.*) have shown that very probably the two reactions which take place with a measurable velocity are—

(i.) *The formation of manganese dioxide* by the action of potassium permanganate on manganese sulphate—

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

Since there is an excess of managanese sulphate present, the potassium permanganate alone changes concentration. Let x denote the concentration of the potassium permanganate after the elapse of an interval of time t, the rate of diminution of the permanganate will be in accord with the unimolecular equation—

$$-\frac{dx}{dt} = k_1x. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(ii.) *The reduction of manganese dioxide*[1] by the oxalic acid—

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2.$$

The sulphuric acid being in great excess, we may confine our attention to the changes in the concentration of the manganese dioxide and oxalic acid. Let y and z respectively denote the concentration of the manganese dioxide and oxalic acid in the solution at the time t, then the rate of diminution of oxalic acid (or of manganese dioxide) will be proportional to the amounts of manganese dioxide and oxalic acid present in the solution at the time t, and we have the bimolecular equation—

$$-\frac{dz}{dt} = k_2yz. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But the rate of formation of manganese dioxide is equal to the difference in the rate of reduction of manganese dioxide by the oxalic acid, and the rate of formation of manganese dioxide by the first reaction, or—

$$\frac{dy}{dt} = k_1x - k_2yz. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[1] For the reduction of potassium permanganate by manganese dioxide (side reaction), see H. N. Morse, A. J. Hopkins, and M. S. Walker, *Amer. Chem. Journ.*, **18**. 401, 1896; J. C. Olsen, *ib.*, **29**. 242, 1903; with F. S. White, *ib.*, **29**. 246, 1903.

Measurements of the resultant velocity of the reaction are made by finding the amount of $x + y$ in the solution at the time t. Remembering that there are a equivalents of oxalic acid and of potassium permanganate originally present, it will be obvious that $a - x$ and $a - z$ respectively denote the number of equivalents of potassium permanganate and of oxalic acid transformed at the time t, hence—

$$a - x = a - z + y; \therefore z = x + y. \quad . \quad . \quad (4)$$

A set of equations which furnish, on integration—

$$\frac{k_2}{k_1}e^{\frac{k_2}{k_1}x}\left\{C - \log x + \frac{k_2}{k_1}x - \frac{1}{4}\left(\frac{k_2}{k_1}\right)^2 x^2 + \ldots\right\}z = 1. \quad (5)$$

C is a constant. By the integration of (1) we obtain—

$$x = ae^{-k_1 t},$$

which, when substituted in the preceding equation, furnishes a relation between z, or $x + y$, t, and constants. The following values for the latter were computed from the experimental data—

$$C = 4{\cdot}68 ; k_1 = 0{\cdot}69 ; k_2 = 0{\cdot}006364.$$

The values of z and t shown in the following table were calculated from equation (5) :—

t min.	z	
	Obs.	Calc.
2	51·9	51·6
3	42·4	42·9
4	35·4	35·4
5	29·8	29·7

After five minutes had elapsed, it was found that the quantity of potassium permanganate present in the solution was negligibly small. The terms succeeding x in (5) were accordingly neglected, and—

$$\frac{k_2}{k_1}(C - \log a + k_1 t)z = 1$$

remained. Collecting together the constants—

$$(C' + t)z = \frac{1}{k_2},$$

Harcourt and Esson found that if $C' = 0{\cdot}1$, and $k_2 = 0{\cdot}006364$, the agreement between the observed and calculated values of z was remarkably close. Thus—

t min.	z		t min.	z	
	Obs.	Calc.		Obs.	Calc.
6	25·7	25·7	10	15·5	15·5
7	22·2	22·1	15	10·4	10·4
8	19·4	19·4	20	7·8	7·8
9	17·3	17·3	30	5·5	5·2

§ 36. Three Bimolecular Consecutive Reactions.

In the hydrolysis of triacetin, $C_3H_5(CH_3COO)_3$—

$$C_3H_5(CH_3COO)_3 + 3H_2O = 3CH_3COOH + C_3H_5(OH)_3,$$

there is every reason to suppose that the reaction takes place in three consecutive stages—

Triacetin → diacetin → monacetin → glycerol.

These reactions are interdependent. The rate of formation of diacetin conditions the rate of formation of monacetin, and this, in turn, determines the rate of formation of glycerol. There are, therefore, three consecutive reactions of the second order taking place in the system at the same time. Let us write, for the sake of brevity, $\bar{A}$ instead of CH_3COO.

$$C_3H_5.\bar{A}_3 + H_2O = \bar{A}.H + C_3H_5.\bar{A}_2.OH;$$

$$C_3H_5.\bar{A}_2.OH + H_2O = \bar{A}.H + C_3H_5.\bar{A}(OH)_2;$$

$$C_3H_5.\bar{A}(OH)_2 + H_2O = \bar{A}.H + C_3H_5(OH)_3.$$

If a and b respectively denote the number of gram-molecules of triacetin and of water used at the beginning of the experiment, and x, y, z the respective number of molecules of mono-, di-, and tri- acetin hydrolyzed at the end of t minutes, the system will contain $a - z$ gram-molecules of triacetin, $z - y$ molecules of diacetin, $y - x$ of monacetin, and $b - (x + y + z)$ of water. The rate of hydrolysis will be completely determined by the equations—

$$\frac{dx}{dt} = k_1(y - x)(b - x - y - z);$$

$$\frac{dy}{dt} = k_2(z - y)(b - x - y - z);$$

$$\frac{dz}{dt} = k_3(a - z)(b - x - y - z).$$

Geitel[1] has partly investigated these reactions, but the velocity constants for each individual reaction have not yet been determined. The experiments went far enough to show that the saponification of fats is a complicated process, taking place in the series of stages indicated above.[2]

§ 37. Abnormal Velocities with Opposing Reactions.

It is sometimes thought that reactions of a lower order than that deduced from the chemical equation describing the reaction cannot be reversible "because differences between the

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[1] A. C. Geitel, *Journ. prakt. Chem.* [2], **55.** 429, 1897 ; **57.** 113, 1898 ; A. Wogrinz, *Zeit. phys. Chem.*, **44.** 571, 1903.

[2] J. Lewkowitsch, *Ber.*, **33.** 89, 1900 ; **36.** 175, 3766, 1903 ; **37.** 884, 1904 ; *Journ. Soc. Chem. Ind.*, **17.** 474, 1898 ; L. Balbiano, *Ber.*, **36.** 1571, 1903 ; **37.** 155, 1904 ; *Gazz. Chim. Ital.*, **32.** i., 265, 1902. See R. Wegscheider, *Zeit. phys. Chem.*, **30.** 593, 1899 ; **34.** 290, 1900 ; **35.** 513, 1900 ; *Monatshefte Chem.*, **22.** 849, 1901, for a discussion "Über die allgemeinste Form der Gesetze der chemischen Kinetik homogener Systeme" ; G. Lemoine, *Ann. Chim. Phys.* [4], **27.** 289, 1872 (transformation of yellow to red phosphorus) ; J. W. Mellor and L. Bradshaw, *Zeit. phys. Chem.*, **48.** 353, 1904 (a unimolecular reaction followed by two unimolecular side reactions) ; see also "The Kinetics of Catalytic Reactions," § 110.

order of a reaction and the number of molecules taking part in the reaction should only be possible when the process is not reversible; the number of molecules and the order of a reaction should agree in processes where the original substance can be reformed from the products of the reaction."[1] W. Bancroft,[2] however, has pointed out that "the intermediate compound theory" is quite compatible with the view that abnormal velocities can occur in the case of reversible reactions, and the reversible reaction—

$$\mathrm{Ni} + 4\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)_4},$$

which Mittasch[3] found to be of the second order, appears to be a case in point. The explanation is not difficult to follow.

Suppose the reaction takes place in two stages—

$$\mathrm{Ni} + 2\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)_2};\ \mathrm{Ni(CO)_2} + 2\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)_4},$$

so that the intermediate compound $\mathrm{Ni(CO)_2}$ is used up as fast as it is formed, and that y denotes the infinitesimal concentration of the nickel dicarbonyl $\mathrm{Ni(CO)_2}$ at any moment; further, let x denote the concentration of the carbon monoxide, and a the initial concentration of the nickel tetracarbonyl $\mathrm{Ni(CO)_4}$. Then $a - x - y$ will be the concentration of the nickel tetracarbonyl at any moment t. The velocity of the two reactions will therefore be respectively—

$$\frac{dy}{dt} = k_1x^2 - k_2'y;\ \frac{dx}{dt} = k_1'x^2y - k_2'(a - x - y).$$

For equilibrium—

$$K_1 = \frac{x^2}{y};\ K_2 = \frac{x^4}{a - x - y}.$$

Multiply these two equations together and write $K = K_1K_2$, then—

$$\frac{x^4}{a - x - y} = K;\ \text{or,}\ \frac{x^4}{a - x} = K,$$

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[1] W. Ostwald, *Lehrbuch*, **2**. ii., 243, 1897-1902; A. Colson, *Compt. Rend.*, **125**. 945, 1897.

[2] W. D. Bancroft, *Journ. Phys. Chem.*, **4**. 705, 1900.

[3] A. Mittasch, *Zeit. phys. Chem.*, **40**. 1, 1902.

since, by hypothesis, y is vanishingly small. This equation is identical with the equilibrium equation deduced on the assumption that the reaction is quadri-molecular with respect to carbon monoxide, namely—

$$\mathrm{Ni} + 4\mathrm{CO} = \mathrm{Ni(CO)_4},$$

and it agrees with the experimental data which show that the formation of nickel carbonyl $Ni(CO)_4$ is a reaction of the second order.

CHAPTER VI

THE BEGINNING OF A CHEMICAL REACTION

§ 38. Initial Stages of Consecutive Reactions.

RETURNING once more to the transformation of A into B, § 33, *viâ* the intermediate stages—

$$A = M ; M = B.$$

At the beginning of the reaction the rate of transformation of A will be a maximum, while the rate of formation of B will be zero. From that moment the rate of formation of the intermediate compound M will be equal to the difference in the rates of diminution of A and the rate of formation of B, or—

$$-\frac{dy}{dt} = -\frac{dx}{dt} - \frac{dz}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where x, y, and z denote the respective amounts of A, M, and B in the system at the time t.

During the first period of the reaction the amount of M is continually increasing, and the rate of formation of B will increase in a corresponding way. The rate of formation of B will be greatest when the system contains a maximum amount of M, and this will occur when the rate of formation of B is equal to the rate of formation of M, *i.e.* to the rate of diminution of A. The rate of formation of B will gradually increase from zero at the beginning of the reaction when $y = 0$ up to a maximum when y is a maximum; at this moment M will cease to accumulate in the system and begin to diminish. Hence—

$$\frac{dy}{dt} = 0; \text{ and } -\frac{dx}{dt} = \frac{dz}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Suppose, for the moment, that the constants k_1 and k_2 of equation (5), p. 98, have been found to be respectively—

$$a = 10·02\,;\ k_1 = 0·0035\,;\ k_2 = 0·007.$$

The following table shows the relative amounts of A, B, and C which would be present in the system at the time t, calculated from equations (1), (2), and (5), § 33:—

t	x of A	y of M	z of B
0	10·02	0	0
30	9·02	0·90	0·10
60	8·19	1·60	0·23
90	7·31	1·97	0·74
180	5·44	2·54	1·99
240	4·32	2·44	3·26
360	2·84	2·00	5·16
600	1·22	0·83	7·93

By plotting corresponding values of t with x, y, and with z, the relative amounts of A, M, and B in the system at any moment is brought out very clearly. In Fig. 10 curve 1 represents the rate of diminution of the original substance, curve 2 the rate of formation of the intermediate compound, and curve 3 the rate of formation of the product of the reaction at different intervals of time. The gradual accumulation of M up to a maximum, and its subsequent diminution, is shown in an interesting manner.

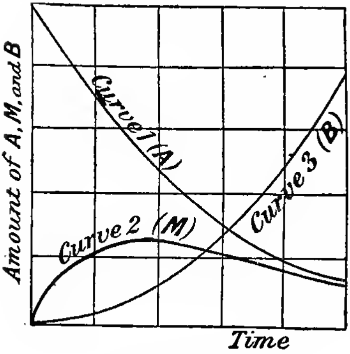

FIG. 10.—Velocity curves.

Let x_1, y_1, and z_1 denote values of x, y, z, and t when y is a maximum. From equation (4), § 33—

$$k_1x_1 = k_2y_1, \ . \ . \ .$$

and from (3) and (5), § 33, the value of y is greatest when—

$$y_1 = a\left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_2 - k_1}}.$$

The time required for y to attain its maximum value thus depends on the relative magnitudes of k_1 and k_2. With the above-mentioned values of k_1 and k_2—

$$y_1 = 10{\cdot}02 \times (\tfrac{1}{2})^2 = 2{\cdot}5,$$

as shown in the preceding table.

If we now plot the rate of formation of B at different intervals of time, we get a curve resembling Fig. 11. There is a well-defined period of acceleration (increasing velocity) during which the velocity of the reaction gradually increases up to a maximum. This is followed by the usual curve of diminishing velocity characteristic of chemical reactions in general.

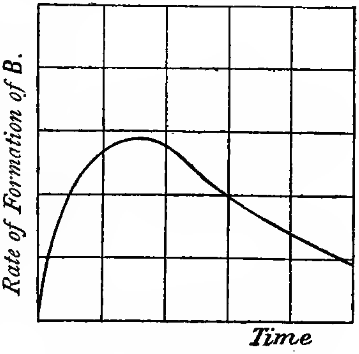

FIG. 11.—Acceleration curve.

The existence of such a period has been recognized since the beginning of the nineteenth century,[1] when W. Cruickshank [2] (1801) observed that the combination of hydrogen and chlorine did not proceed very rapidly until the mixture had been exposed to the light for some time. Dalton (1811) and Draper (1843) independently rediscovered the period of

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[1] For historical details, see J. W. Mellor, *Journ. Chem. Soc.*, **79**. 216, 1901.

[2] W. Cruickshank, *Nicholson's Journal* [1], **5**. 202, 1801 ; J. Dalton's *A New System of Chemical Philosophy*, Manchester, **2**. 189, 1811 ; J. W. Draper, *Phil. Mag.* [3], **23**. 401, 1843 ; *Scientific Memoirs*, London, 1878.

acceleration with a mixture of hydrogen and chlorine gases, and Bunsen and Roscoe named it the **period of induction.**[1]

There is a pleasing "lecture experiment" for illustrating the "period of induction." A very dilute solution of sulphurous acid and iodic acid (one gram, *e.g.*, in 600 litres of water) is mixed with starch. The appearance of a visible blue colour occupies a measurable time, which may be extended by using more dilute solutions.

It is sometimes said that the period of induction consists of two distinct parts: (1) *a period of inertness* during which no chemical action occurs; (2) *a period of gradually increasing rate of chemical transformation.*[2] In the case of hydrogen and chlorine there is yet no experimental evidence of a period of inertness, for when a mixture of hydrogen and chlorine is exposed to a momentary flash of light there is a momentary expansion, and an immediate contraction of the mixed gases to the original volume.

I have named this phenomenon,[3] after its discoverer, "the Draper effect." The expansion is a secondary effect arising from chemical action. Chemical combination takes place even when the mixture of hydrogen and chlorine is exposed to light for a small fraction of a second. Instantaneous photography also illustrates how quickly chemical action sets in when the proper conditions are satisfied.

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[1] With reactions induced by exposure to light, Bunsen and Roscoe employed the term, the "period of photo-chemical induction." R. Bunsen and H. E. Roscoe, *Pogg. Ann.*, **96**. 373, 1855; **100**. 43, 481, 1857; **101**. 235, 1857; **108**. 193, 1859; **117**. 529, 1862; *Phil. Trans.*, **147**. 355, 601, 1857; **148**. 879, 1859; W. Ostwald's *Klassiker*, Nos. 34 and 38; "preliminary actinization," J. W. Draper, *Phil. Mag.* [4], **44**. 422, 1872.

[2] V. H. Veley, *Phil. Mag.* [5], **37**. 165, 1894; E. J. Mills and W. McD. Mackey, *ib.* [5], **16**. 429, 1883; H. von Oettingen, *Zeit. phys. Chem.*, **33**. 1, 1900 (clouding of sodium thiosulphate in the presence of acids); A. F. Holleman, *Rec. Trav. Pays-Bas*, **14**. 71, 1895; *Zeit. phys. Chem.*, **33**. 500, 1900; W. Ostwald, *ib.*, **22**. 302, 1897.

[3] J. W. Draper, *Phil. Mag.* [3], **23**. 403, 415, 1843; J. W. Mellor *Journ. Chem. Soc.*, **79**. 216, 1901; J. W. Mellor and W. R. Anderson, *ib.*, **81**. 414, 1902; P. V. Bevan, *Proc. Camb. Phil. Soc.*, **11**. 380, 1902; *Phil. Trans.*, **202**. 71, 1903.

Bunsen and Roscoe once thought that the period of induction could be explained by assuming that when light first acts upon a mixture of hydrogen and chlorine gases, the light which is absorbed produces a dislocation of the molecules, which must reach a certain magnitude before chemical change can begin. This idea, however, was abandoned[1] when the same writers discovered a period of induction during the action of bromine upon tartaric acid,[2] and it was suggested that the phenomenon depended upon "the mode of action of affinity itself." Berthelot and Gilles[3] also noticed a similar period during the action of acids upon alcohols, and they considered *l'acceleration initiale* to be due to a kind of inertia or resistance, which had to be overcome before combination could proceed. See p. 414.

According to these ideas the period of acceleration is characteristic of chemical changes in general. In 1884, however, van't Hoff[4] seems to have thought that the phenomenon was "quite incompatible with the law of mass action because, in that case, the maximum velocity must occur at the beginning

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[1] Of course there is the possibility that the mechanism of the union of hydrogen and chlorine, in light, is quite different from that of other reactions which proceed in darkness. The "dislocation hypothesis" is not disproved by the tartaric acid experiment, and recent work may lead us to revive a simple modification of the hypothesis.

[2] R. Bunsen and H. E. Roscoe, *Pogg. Ann.*, **100**. 513, 1855; *Phil. Trans.*, **147**. 355, 601, 1857. See also A. von Baeyer, *Liebig's Ann.*, **103**. 178, 1857 (bromination of lactic acid); C. Hell and F. Urech, *Ber.*, **13**. 531, 1880 (bromination of fatty acids); W. Müller, *Zeit. phys. Chem.*, **41**. 483, 1902 (decomposition of bromosuccinic acid).

[3] M. Berthelot and Péan de Saint Gilles, *Ann. Chim. Phys.* [3], **66**. 26, 1862; N. Menschutkin, *Ber.*, **15**. 2512, 1882; D. Konowalow, *Zeit. phys. Chem.*, **1**. 63, 1887; C. R. A. Wright with A. P. Luff, *Journ. Chem. Soc.*, **33**. 1, 509, 1878; with A. P. Luff and E. H. Rennie, *ib.*, **35**. 475, 1879; with E. H. Rennie and A. C. Menke, *ib.*, **37**. 757, 1880 (reduction of metallic oxides by carbon monoxide and hydrogen); G. Dyson and A. Harden, *Proc. Chem. Soc.*, **10**. 165, 1894; *Journ. Chem. Soc.*, **83**. 201, 1903; M. Wilderman, *Phil. Trans.*, **199**. 337, 1902; *Proc. Roy. Soc.*, **70**. 166, 1902 (union of chlorine and carbon monoxide gases); J. W. Draper, *Phil. Mag.* [3], **27**. 327, 1845 (decomposition of chlorine water).

[4] J. H. van't Hoff, *Études*, 74, 1884 ("absolument incompatible"); T Ewan's trans., 91, 98, 1896.

of the reaction." We have just seen that the delay occasioned by the formation of "an intermediate product" is a necessary consequence of the law of mass action, and we can enunciate the law: *the period of induction is characteristic of chemical reactions which take place in a series of intermediate stages.*[1]

Harcourt and Esson[2] explain the period of induction by assuming that "chemical change consists in the gradual formation of a substance which at the same time slowly disappears by reason of its reaction with a proportional quantity of a third substance;" Hell and Urech[3] attribute the initial period of acceleration observed during the bromination of organic acids to the intermediate formation of an unstable addition product of the acid with the bromine. It was formerly thought that the period of induction observed when a mixture of hydrogen and chlorine is exposed to light is due to the preliminary formation of hydrogen hypochlorite or of chlorine monoxide,[4] but since the addition of either of these compounds to a mixture of hydrogen and chlorine just before illumination does not produce any measurable effect, the hypothesis has been rejected and the preliminary formation of the complex, $x\mathrm{Cl}_2.y\mathrm{H}_2\mathrm{O}.z\mathrm{H}_2$, has been suggested as a temporary hypothesis to explain the period of acceleration.[5]

§ 39. Initial Disturbances.

What would be the effect of applying the velocity equation of a unimolecular equation to a chemical transformation which

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[1] J. W. Mellor, *Journ. Chem. Soc.*, **81**. 1280, 1902.

[2] A. V. Harcourt and W. Esson, *Phil. Trans.*, **156**. 193, 1866.

[3] C. Hell and F. Urech, *Ber.*, **13**. 531, 1880.

[4] E. Becquerel and E. Frémy, *Wurtz's Dict. de Chimie*, Paris, **2**. 255, 1879; E. Pringsheim, *Wied. Ann.*, **32**. 384, 1887; J. W. Mellor, *Journ. Chem. Soc.*, **81**. 1280, 1902; P. V. Bevan, *Phil. Trans.*, **202**. 71, 1903.

[5] The two consecutive reactions: (1) action of Cl_2 on water with liberation of nascent oxygen, (2) action of nascent oxygen on hydrogen, explain the experimental work just as well as the assumption of an intermediate compound. See p. 414.

is really compounded of two chemical reactions of the first order—

$$A = M;\ M = B?$$

It is easy to show that the complex nature of the reaction would become less and less apparent as the difference between the values of the velocity coefficients k_1 and k_2 of the two reactions increases in magnitude.

First find corresponding values of z and t for pairs of imaginary reactions, in which $k_1 = 0{\cdot}01$, and k_2 is made successively equal to 0·01, 0·1, 1·0, and 10·0; and $a = 1$. (5), § 33.

$$z = 1 + \frac{k_2}{k_1 - k_2}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}e^{-k_2 t}.$$

The values of z so obtained are to be regarded as the quantities of substance actually produced in the time t. Now suppose that we seek the order of the reaction which furnished these values of z and t, under the belief that the double reaction is simple. We naturally substitute these values of z in the regular equation for unimolecular reactions—

$$\frac{dz}{dt} = k(1 - z);\ \frac{1}{t}\log\frac{1}{1 - z} = k.$$

The following table shows the values of $k \times 10^3$ obtained for the intervals of time indicated :—

I. $k_1 = 0{\cdot}01$; $k_2 = 0{\cdot}01$		II. $k_1 = 0{\cdot}01$; $k_2 = 0{\cdot}1$		III. $k_1 = 0{\cdot}01$; $k_2 = 1{\cdot}0$		IV. $k_1 = 0{\cdot}01$; $k_2 = 100$	
t	$k \times 10^3$	t	$k \times 10^3$	t	$k \times 10^3$	t	$k \times 10^3$
10	1	10	4	5	6	5	9
40	2	40	7	10	9	10	9
100	3	100	9	20	9	20	9
400	6	200	9	40	9	40	9
1000	8	400	9	100	9	100	9

In I. the disturbance is very marked; in II. the disturbance resembles that which occurs in the experiments of Berthelot and Gilles; in III. the disturbance is negligible; and in IV. it is completely masked.

Thus it is obvious that the coefficient k would be considered to be in agreement with that required for a simple unimolecular change when the ratio of the coefficients of the two intermediate reactions is greater than 1 : 100. After the so-called "initial disturbances" the numbers are quite regular, when $k_1 : k_2 = 1 : 1000$; when this ratio has got to 1 : 10,000 the initial disturbances have disappeared altogether, and the complex character of the reaction is completely masked. Many initial disturbances can thus be traced to the fact that a series of consecutive reactions have been assumed to consist of one simple and direct change. The existence of the initial disturbances might lead us to suspect the presence of consecutive reactions of the type under consideration. For example, the disturbance in the velocity coefficient for the hydrolysis of ethyl succinate by sodium hydroxide led Reicher[1] to assume that the reaction took place in two stages—

Ethyl succinate → ethyl sodium succinate → sodium succinate;

similar perturbations observed during the action of sodium hydroxide upon chloral hydrate led to the view that the reaction is essentially—

$$CCl_3.COH.H_2O \rightarrow CCl_3.CONa.H_2O \rightarrow CHCl_3.$$

§ 40. The Period of Induction.

J. H. van't Hoff[2] seems to have thought that the initial acceleration should always be referred to *secondary* reactions, due to the presence of foreign substances, which interfere with the normal course of the reaction. We exclude effects arising from the imperfect mixing of the reacting substances, the initial disturbance arising from the heat[3] of the reaction, etc.

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[1] L. T. Reicher, *Maandblad voor Naturweten.*, **12.** 105, 1885; **12.** 78, 1885; C. M. van Deventer, *ib.*, **12.** 108, 1885; *Rec. Trav. Pays-Bas*, **4.** 353, 1885; L. T. Reicher, *ib.*, **4.** 350, 1885; **4.** 347, 1885.

[2] J. H. van't Hoff, *Études*, 82, 1884; T. Ewan's trans., 98, 1896.

[3] S. Brussoff, *Zeit. phys. Chem.*, **34.** 129, 1900.

Periods of induction can be traced to five different causes.

I. The main reaction is compounded of a number of consecutive reactions.—The initial period is then, as we have just seen, a necessary consequence of the law of mass action. The duration of the period depends on the relative magnitude of the velocity constants of the intermediate reactions.

II. The overcoming of passive resistance.—See p. 414.

III. The presence of catalytic agents.—A slowly progressing reaction might be accelerated by the presence of the products of the main reaction or of a side reaction. For example, Harcourt and Esson[2] observed that the manganese sulphate produced during the reaction between potassium permanganate and oxalic acid in presence of sulphuric acid accelerates the reaction. Schilow[3] has shown that if oxalic acid be in great excess the reaction proceeds according to the equation—

$$\frac{dx}{dt} = kx(a - x); \text{ or, } \frac{dx}{dt} = k(b + x)(a - x),$$

where a denotes the initial concentration of the permanganate, x the amount of permanganate converted into maganese sulphate, and b the amount of manganese sulphate present at the beginning of the reaction. By purely mathematical calculation it follows that the velocity of the reaction will have a maximum value when—

$$x = \tfrac{1}{2}a; \text{ or, } x = \tfrac{1}{2}(a - b),$$

respectively. The permanganate was estimated by adding potassium iodide, and then titrating the liberated iodine with sodium thiosulphate. The permanganate is expressed in terms of "thiosulphate" in the following table, $b = 0$; when—

$t = 0,\ 40,\ 60,\ 70,\ 75,\ 80,\ 85,\ 100,\ 110;$

$x = 20,\ 17{\cdot}02,\ 14{\cdot}05,\ 12{\cdot}42,\ 11{\cdot}75,\ 9{\cdot}95,\ 8{\cdot}70,\ 5{\cdot}90,\ 4{\cdot}98;$

$dx/dt = -,\ 0{\cdot}08,\ 0{\cdot}15,\ 0{\cdot}21,\ 0{\cdot}23,\ 0{\cdot}26,\ 0{\cdot}25,\ 0{\cdot}17,\ 0{\cdot}09.$

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[1] V. H. Veley, *Phil. Mag.* [6], **6.** 271, 1903.

[2] A. V. Harcourt and W. Esson, *Phil. Trans.*, **156.** 201, 1866. This explains why the pink colour of the permanganate is discharged very slowly during the earlier stages of the titration of oxalic acid with potassium permanganate, and more rapidly later on.

[3] N. Schilow, *Ber.*, **36.** 2735, 1903.

Here $a = 20$. Hence the calculated maximum velocity occurs when $x = 10$, a result very nearly that which would be obtained by plotting the observed values of x and t. Satisfactory results were also obtained when some manganese sulphate was present at the beginning of the reaction. By plotting corresponding values of x and of dx/dt we get an "acceleration curve" resembling Fig. 11, p. 115.

The monosymmetric sulphur produced during the transformation of rhombic sulphur into the monosymmetric form accelerates the change;[1] and the cyamelide produced during the polymerization of cyanic acid modifies the velocity of the transformation.[2] Changes of this kind will subsequently be studied in the section on "Autocatalysis." Van't Hoff has also noticed that there is a well-defined period of acceleration during the slow union of hydrogen and oxygen at 440°, provided nitrogen be present, not if nitrogen be absent, and the suggestion is made that the acceleration is due to the production of nitrogen oxides, which act as catalytic agents.

Dilute nitric acid acts upon copper with extreme slowness. As the action progresses the process of dissolution becomes more and more rapid. This goes on for a certain time and then the reaction continually slows down. It is supposed that the nitrous acid produced in the direct action of the acid on copper accelerates the action at a rate proportional with the amount present. When a certain maximum amount of the acid has accumulated in the system, it begins to decompose according to the equation—

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$[3]

In consequence the acceleration cannot proceed beyond a certain limit. Nitric acid in which a little copper has been previously dissolved, vigorously attacks a new piece of copper

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[1] T. L. Reicher, *Inaug. Dissert.*, Amsterdam, 45, 1883.

[2] J. H. van't Hoff, *Études*, 82, 1884.

[3] A. Millon, *Compt. Rend.*, **14**. 904, 1842; V. H. Veley, *Phil. Trans.*, **182**. 279, 1891; C. Montemartini, *Gazz. Chim. Ital.*, **22**. i., 250, 277, 397, 1892; *Accad. Lincei Rendiconti*, **6**. 264, 1890; G. O. Higley and P. C. Freer, *Amer. Chem. Journ.*, **15**. 71, 1893; G. O. Higley, *ib.*, **17**. 18, 1895.

at once, whereas a similar piece of copper placed in fresh nitric acid is but slowly acted upon.[1] Induction phenomena have also been observed during the action of acids upon metallic zinc.[2] This suggests a fourth source of disturbance—

IV. The retention of gas by the liquid.—This gives rise to an "apparent" period of induction, *q.v.*

V. Negative catalysis.—See p. 371.

§ 41. Apparent Periods of Induction.

In heterogeneous systems, when the speed of the reaction is measured by the rate of evolution of a gas from a liquid, a kind of "pseudo" or apparent period of acceleration is frequently observed. This is due to the retention of the gas by the liquid. Such is the period of acceleration observed by Veley[3] during the action of sulphuric acid upon formic acid, oxalic acid, or potassium ferrocyanide; the decomposition of ammonium nitrate into nitrous oxide and steam; of an aqueous solution of ammonium nitrite into nitrogen and water; of a mixture of oxalic acid and ferric chloride into carbon dioxide and ferrous chloride in light;[4] and during the evolution of oxygen from solutions of the peroxides.

The rate of evolution of carbon monoxide from a mixture of formic and sulphuric acids, after the expiration of the period of acceleration, agrees with the regular bimolecular equation—

$$\frac{dx}{dt} = k(a - x)^2; \quad \frac{1}{t} \cdot \frac{x}{a(a - x)} = k;$$

or, solving for x—

$$\therefore x = \frac{a^2kt}{1 + akt}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where x denotes the amount of carbon monoxide produced in

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[1] W. Ostwald (*Ueber Katalyse*, Leipzig, 23, 1902) likens this to the psychological phenomenon of "habit" or "memory."

[2] E. J. Mills and W. J. Mackey, *Phil. Mag.* [5], **16**. 429, 1883; W. Spring and E. van Aubel, *Ann. Chim. Phys.* [6], **11**. 505, 1887; *Zeit. phys. Chem.*, **1**. 465, 1887.

[3] V. H. Veley, *Phil. Mag.* [6], **6**. 271, 1903.

[4] E. Marchand, *Ann. Chim. Phys.* [4], **4**. 30, 302, 1873; G. Lemoine, *ib.* [7], **6**. 433, 1895.

the time t; a the original amount of carbon monoxide available; and k is the velocity coefficient found to be $k = 0{\cdot}00001$.

Let z denote the amount of carbon monoxide retained by the solution at the time t, and let dy denote the amount evolved from the solution in the time dt; further, let s denote the amount of carbon monoxide retained by a saturated solution at the temperature of the experiment. Experiment shows that $s = 4{\cdot}95$. Esson has suggested the plausible hypothesis that the relative amounts of gas absorbed (dz) and evolved (dy) by the solution in the time dt is proportional to the total amount of carbon monoxide which the solution can hold, and inversely proportional to the amount of gas evolved.

$$\therefore \frac{dz}{dt} = nse^{-ny}\frac{dy}{dt}; \text{ or, } z = s(1 - e^{-ny}),$$

where n is the constant of proportion. In place of the last equation Veley writes—

$$z = s(1 - m^{-y}), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where m is a constant to be evaluated from the experimental data. In this way it is found that $m = 2$.

Starting with the original concentration of the formic acid $= a = 165{\cdot}5$; and remembering that $s = 4{\cdot}95$; $m = 2$, $k = 0{\cdot}00001$, we get from equations (3) and (4)—

$$x = \frac{(165{\cdot}5)^2 \times 0{\cdot}00001 \times t}{1 + 165{\cdot}5 \times 0{\cdot}00001 \times t}; \quad z = 4{\cdot}95(1 - 2^{-y}).$$

A comparison of the observed and calculated values of z in the following table gives numbers in harmony with Esson's hypothesis within the limits of experimental error:—

t	x	y	$z = x - y$	z
	Calc.	Obs.		Calc.
13·37	3·61	1	2·61	2·48
21·59	5·73	2	3·73	3·71
27·89	7·32	3	4·32	4·33
33·27	8·66	4	4·66	4·63
42·45	10·87	6	4·87	4·87
51·16	12·94	8	4·94	4·93

CHAPTER VII

HETEROGENEOUS REACTIONS

§ 42. Reactions between Liquids and Solids.

HETEROGENEOUS chemical changes in which the reacting substances are not all in the same state of aggregation next claim our attention. Examples are common enough: the solution of solids or of gases in liquids; the crystallization of saturated solutions; the dissolution of metals in acids; the oxidation of metals in air; and the dissociation of calcium carbonate under the influence of heat.

These reactions are, in general, more prone to disturbing influences than those which take place in homogeneous systems. Consider the dissolution of zinc in dilute sulphuric acid. The measured rate of dissolution is dependent not only on the surface exposed to attack and upon the *local* rise of temperature due to the chemical action, but it also depends upon the rate of diffusion of the metallic salt in the acid liquid, the disengagement of the gas bubbles from the surface of the metal, and the rate of removal of these bubbles from the solution in the vicinity of the dissolving metal. It is also necessary to keep the surface of the metal constant, or else to allow for the variation of the surface during the attack.[1]

It is exceedingly difficult, if not impossible, to allow for the variation of the surface, because the latter is not uniformly attacked by the acid. If a smooth plate of metal be dipped in the acid, the surface of the metal is quickly corroded, and

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[1] For a general discussion on the variation of the surface of a dissolving solid, see J. Bottomley, *Manchester Memoirs* [4], **2**. 154, 1889; G. Cesaro, *Ann. Chim. Phys.* [6], **17**. 1, 1889.

hence the surface exposed to the acid suffers considerable change during the dissolution of the metal. As a first approximation we shall assume that the surface itself remains uniform.

In order to eliminate some of these disturbances, Veley[1] has devised a method of measuring the rate of dissolution of metals in acids by rotating balls of the dissolving metal in the acid, so that not only is a fresh spherical surface continually exposed to the acid, but the products of the action are continually removed from the vicinity of the dissolving metal.

I. Constant surface.—If the surface of the metal exposed to the action of the acid be kept constant, and if the products of the action be removed as fast as they are formed, the velocity of the reaction will be simply—

$$\frac{dx}{dt} = k; \text{ or, } \frac{x}{t} = k, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant.

Among reactions which have been studied in this connection may be mentioned the decomposition of solid pinene hydrochloride by boiling water,[2] which takes place with the formation of hydrochloric acid. The rate of formation of the acid is in agreement with the equation—

$$x = 0{\cdot}000813t,$$

but when over 6 per cent. of acid has accumulated in the system, secondary reactions set in. The hydrolysis of methyl benzoyl sulphonate;[3] the action of yeast on glucose;[4] of diastase upon sugar or starch;[5] and of colloidal platinum on solutions of hydrogen peroxide[6] of a certain concentration, also follow (1).

II. Variable surface.—In order to allow for the variation

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[1] V. H. Veley, *Journ. Chem. Soc.*, **55**. 361, 1889; *Phil. Trans.*, **182**. 279, 1891.

[2] J. Riban, *Ann. Chim. Phys.* [5], **6**. 51, 1875.

[3] R. Wegscheider and M. Furcht, *Monatshefte für Chem.*, **23**. 1093, 1902.

[4] G. Tammann, *Zeit. phys. Chem.*, **3**. 25, 1889.

[5] E. Duclaux' *Traité de Microbiologie*, Paris, **2**. 137, 1898–1901.

[6] G. Bredig and R. Müller von Berneck, *Zeit. phys. Chem.*, **31**. 258, 1899.

of the surface of the solid during the chemical action, let us assume that the rate of dissolution of the metal, say, in acid is proportional to the surface s exposed, then—

$$\frac{dx}{dt} = ks. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

There is no particular difficulty in integrating this equation,[1] but it has been found simpler to verify the assumption by letting dx denote the amount of metal which has disappeared in the finite interval[2] of time dt—

$$\frac{dx}{dt} = ks; \text{ or, } \frac{1}{s} \cdot \frac{dx}{dt} = k. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Veley's experiments on the rate of dissolution of metallic copper in dilute nitric acid (sp. gr. 1·71) will serve to test the hypothesis. In the following table x denotes the weight of the copper sphere after the elapse of unit interval of time, so that $dt = 1$; s denotes the mean area of the surface of the copper sphere:—

x	dx	s	k
4·3465	—	—	—
4·0463	0·3002	289·93	10·35
3·7673	0·2790	276·40	10·10
3·5035	0·2638	263·40	10·00
3·2458	0·2577	250·63	10·28
3·0045	0·2413	237·61	10·15
2·7713	0·2332	225·15	10·33
2·5511	0·2202	213·34	10·32

The numbers in the last column are in harmony with the assumption that the speed of the reaction is proportional to the surface of the metal. The concentration of the acid was practically uniform during the time of the experiment.

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[1] For a general discussion, see J. Bottomley, *Manchester Memoirs* [4], **2.** 154, 1889 (parallelopiped, cylinder, cube, sphere); W. Ostwald, *Lehrbuch*, **2.** ii., 289, 1897-1902 (sphere).

[2] If we are going to use *finite* intervals, "Δx" is often used, as in § 15.

III. Nature of solid.—The rate of dissolution is dependent on the structure of the dissolving substance.

Iceland spar dissolves at a different rate, according as the attack of the acid is directed parallel with or perpendicular to its principal crystallographic axis. The velocity coefficient is about 1·15 times greater when the surface exposed to the action of the acid is perpendicular to the principal axis.[1] Carbonelli's experiments seem to show that the rate of dissolution of the different forms of the same solid is nearly proportional to the density of the solid.

IV. Change in the concentration of the reacting acid.—Wenzel[2] first measured the time required to dissolve metals in acids of varying strength, and he found that "if an acid dissolves one part of copper in one hour, an acid half as strong will take two hours to dissolve the same amount of copper (or zinc), provided that the surface exposed and the temperature remain constant." W. Spring's[3] experiments may be employed to test the effect of keeping the surface constant and varying the concentration of the acid. In these experiments calcspar ($CaCO_3$) was dissolved in dilute hydrochloric acid of varying strengths—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

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[1] W. Spring, *Zeit. phys. Chem.*, **2**. 13, 1888; C. E. Carbonelli, *ib.*, **10**. 287, 1892, Abs.; J. Schürr, *Journ. Chim. Phys.*, **2**. 245, 1904.

[2] C. F. Wenzel's *Lehre von der Verwandtschaft*, Dresden, 28, 1777.

[3] W. Spring, *Zeit. phys. Chem.*, **2**. 13, 1888. See also E. J. Mills, *Journ. Chem. Soc.*, **37**. 453, 1880; J. G. Boguski, *Ber.*, **9**. 1646, 1876; J. G. Boguski and N. Kajander, *ib.*, **9**. 1809, 1876; **10**. 34, 1877; N. Kajander, *ib.*, **13**. 2387, 1880; **14**. 2050, 2676, 1881; B. Pawlewski, *ib.*, **10**. 34, 1880; F. Hurtur, *Chem. News*, **22**. 193, 1870; J. T. Conroy, *Journ. Soc. Chem. Ind.*, **20**. 316, 1901; T. Ericson-Aúren and W. Palmaer, *Zeit. phys. Chem.*, **39**. 1, 1902; **45**. 182, 1903; T. Ericson-Aúren, *Zeit. anorg. Chem.*, **27**. 209, 1901; E. Divers and T. Shimidzu, *Journ. Chem. Soc.*, **47**. 597, 1885. For theoretical discussion, see M. Wilderman, *Phil. Mag.* [6], **4**. 468, 1902; R. B. Warder, *Science*, **2**. 176, 1883 (dissolution of brass); *Proc. Ohio Mech. Inst.*, **2**. 134, 1883 (dissolution of phosphoric acid from commercial fertilizers); J. F. Caleb, *Amer. Chem. Journ.*, **11**. 31, 1889 (dissolution of anhydrite and gypsum from fertilizers); M. Geiger, *Gazz. Chim. Ital.*, **30**. i, 225, 1900 (action of acids in alcoholic solution upon marble).

The concentration of the acid, at any moment, can be readily calculated from the amount of carbon dioxide developed. In this case we have—

$$\frac{dx}{dt} = ks(a - x), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where x denotes the concentration of the acid at the time t. a $(=1)$ denotes the initial concentration. Instead of integrating, let us put—

$$\frac{1}{1 - x} \cdot \frac{dx}{dt} = \text{constant.} \quad . \quad . \quad . \quad . \quad (5)$$

In the following table dx/dt denotes the rate of solution of one sq. mm. of surface, x the concentration of the hydrochloric acid calculated from the volume of carbon dioxide evolved :—

dx/dt	x	Constant.
0·00115	0·0625	0·00123
0·00106	0·1250	0·00115
0·00098	0·1875	0·00120
0·00091	0·2500	0·00120
0.00082	0·3125	0·00120
0·00074	0·3750	0·00118
0·00067	0·4375	0·00118
0·00061	0·5000	0·00122

Equivalent solutions of hydrochloric, hydrobromic, and of nitric acids acted upon the carbonate with the same velocity.

V. Dissolution of a solid in its own solution.—The rate of solution of arsenious acid in dilute acids and bases does not depend upon the amount of the arsenic trioxide already in solution,[1] but the rate of dissolution of many solids is actually proportional to the amount of solid already present in the solution. This was suspected by Berthollet in 1803.[2] Noyes

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[1] K. Drucker, *Zeit. phys. Chem.*, **36**. 693, 1901.

[2] C. L. Berthollet's *Essai de Statique Chimique*, Paris, **1**. 65, 1803; B. Lambert's trans., **1**. 39, 1804.

and Whitney[1] found that the rate of solution of benzoic acid and of lead chloride in water was proportional to the difference between the concentration of the film in immediate contact with the solid and the more dilute layers. If a denotes the concentration of the saturated solution in immediate contact with the solid, x the concentration of the rest of the solution at any time t—

$$\frac{dx}{dt} = ks(a - x)\,; \;\therefore\; \frac{1}{t} \log \frac{a}{a - x} = sk$$

provided the area s of the surface is kept constant. The following table illustrates the experimental results for a constant surface of benzoic acid dissolving in water. $a = 27{\cdot}93$.

t	x	Constant.
10	6·38	112·7
30	15·51	117·4
60	21·89	110·9

Bruner and Tolloczko[2] have confirmed the conclusion of Noyes and Whitney. It is interesting to notice that the surface exposed to the solvent is much eroded after the action; s cannot, therefore, be constant. Hence it is inferred that the constancy of the product sk means that the process of dissolution is really between the film of saturated solution between the solid and the surrounding medium, and not directly between the solvent and the surface of the solid. The thicker this "film of saturated solution," the slower the rate of dissolution. If the solvent be kept in motion by means of a rotatory stirrer, the effect will

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[1] A. A. Noyes and W. R. Whitney, *Zeit. phys. Chem.*, **23**. 689, 1897; *Journ. Amer. Chem. Soc.*, **19**. 930, 1897.

[2] L. Bruner and S. Tolloczko, *Zeit. phys. Chem.*, **35**. 283, 1900; *Zeit. anorg. Chem.*, **28**. 314, 1901; **35**. 23, 1903; **37**. 455, 1903; K. Druckeř, *ib.*, **29**, 459, 1902; De Heens, *Bull. de l'Akad. Roy. de Belgique* [3], **23**. 235, 1892.

be to diminish the thickness (l) of this film of liquid. Hence—

$$\frac{dx}{dt} = \frac{ks}{l}(a - x); \ \frac{1}{t}\log\frac{a}{a - x} = \frac{ks}{l} = A,$$

where A is a constant. l, and hence also A, obviously depend upon the number of revolutions (n) of the stirrer per minute, as well as upon the temperature of the experiment. For the solution of benzoic acid, and of magnesium benzoate in water, Brunner[1] found that—

$$A = Bn^{\frac{2}{3}},$$

where B is a constant.

The dissolution of a solid thus consists of two distinct processes—

(1) A reaction between the solid and solvent.

(2) The diffusion of the products of the action away from the seat of the reaction.

There are, therefore, two limiting cases. (i.) If the first process is very slow in comparison with the second, the rate of dissolution will not depend upon the amount of solid already present in the solution. This is the case with Drucker's observation on the dissolution of arsenic trioxide; Manchot and Herzog's[2] work on the oxidation of cobaltous cyanide and of ferrous salts; and with Meyer and Saam's[3] work on the oxidation of hydrogen, carbon monoxide, and the hydrocarbons by solutions of potassium permanganate.

(ii.) On the other hand, if the chemical action is very rapid in comparison with the rate of diffusion, Noyes and Whitney's observations hold good. The rate of diffusion (Fick's law),[4] and hence also the rate of dissolution of the solid (Noyes and Whitney's law), will be proportional to the amount of solid already present in the solution. In illustration, Brunner found

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[1] E. Brunner, *Dissertation*, Göttingen, 1903; *Zeit. phys. Chem.*, **47.** 56, 1904; H. Danneel, *Zeit. Elektrochem.*, **10.** 41, 1904.

[2] W. Manchot and J. Herzog, *Zeit. anorg. Chem.*, **27.** 357, 1901; *Ber.*, **33.** 1742, 1900.

[3] V. Meyer and E. Saam, *Ber.*, **30.** 1935, 1897.

[4] A. Fick, *Pogg. Ann.*, **94.** 59, 1855; *Phil. Mag.* [4], **10.** 30, 1855.

that magnesium oxide dissolves faster in acetic acid than in benzoic acid, because the products of the action in the former case diffuse more rapidly away from the seat of the reaction, and this in spite of the fact that the "strength" of the acetic acid is but one-third that of the benzoic acid.[1]

Since the rate of diffusion depends upon the motion of the stirrer, the stirring of the liquid will make very little difference to the rate of dissolution of the solid when the reaction between the solid and solvent is very slow in comparison with the rate of diffusion of the products of the action; but when the reaction is very fast in comparison with the rate of diffusion, the rate of dissolution of the solid will be very sensitive to the motion of the solvent. This fact also explains Bigelow's[2] observations on the rate of oxidation of sodium sulphite in the presence of various catalytic agents. With some, the rate of oxidation was found to depend upon the concentration of the sodium sulphite, and not upon the motion of the fluid; while with others, the rate of oxidation was found to be independent of the concentration of the sulphite, but dependent upon the movements of the fluid. So too the "order" of many gaseous reactions, which are determined by the presence of solid catalytic agents, really depends upon the rate of diffusion of the reacting substances to and from the catalytic agent, and not upon the number of molecules which take part in the reaction.[3]

VI. The rate of precipitation of a solid from a solution.—Gladstone and Tribe[4] investigated the relation between the number of y gram-molecules of metal displaced by zinc from solutions of copper salts, of lead by zinc in lead nitrate, etc., in ten minutes, and the concentration x of the solution. They found that by doubling the concentration of the solution, three

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[1] See R. Abegg and E. Bose, *Zeit. phys. Chem.*, **30.** 511, 1899; S. Arrhenius, *ib.*, **10.** 51, 1892.

[2] S. L. Bigelow, *Zeit. phys. Chem.*, **26.** 493, 1898.

[3] See p. 57; W. Nernst, *Zeit. phys. Chem.*, **47.** 52, 1904.

[4] J. H. Gladstone and A. Tribe, *Proc. Roy. Soc.*, **19.** 498, 1871; *Journ. Chem. Soc.*, **24.** 1123, 1871; *Chem. News*, **24.** 4, 63, 1871; *Journ. prakt. Chem.* [1], **67.** 1, 1856; **69.** 257, 1856; J. W. Langley, *Journ. Chem. Soc.*, **45.** 633, 1884. See "note," p. 140.

times the amount of metal was precipitated. Expressed algebraically, when—

$$x = 1, 2, 4, 8, \ldots, 2^n;\ y = 1, 3, 9, 27, \ldots, 3^n.$$

Or, summing the progressions—

$$n \log 2 = \log x;\ n \log 3 = \log y;$$

$$\therefore y = kx^{\frac{\log 3}{\log 2}};\ \text{or, } y = kx^{1\cdot585}.$$

Langley has verified these conclusions and shown that the results are modified by currents set up in the solution by the change in the density during the action. If the solution were kept at a uniform density, Langley thinks that the rate of action would be proportional to the amount of salt in the solution.

VII. Rate of electrochemical action.—This subject has recently attracted a good deal of attention owing to the fact that many of the reactions in technical electrochemistry take place in heterogeneous systems—liquid electrolyte, and solid electrode.

If an electric current be sent through an electrolyte, decomposition takes place when the difference of potential at the electrodes exceeds a certain value called the **decomposition voltage**. The decomposition voltage for different solutions varies with the nature of the acid and base. It is possible to range the salts of the different metals with the same acid in the order of their decomposition voltages. The difference in the decomposition voltages of the different metals renders their electrochemical separation possible. Two metals can be separated electrolytically when the difference of potential required for the precipitation of the one metal is not sufficient for the precipitation of the other.

The rate of precipitation of the metal is given by Faraday's law: "the quantity of liquid decomposed is proportional to the quantity of electricity in circulation." The rate of precipitation of copper, for instance, from a concentrated solution of copper sulphate, when a constant current is passing, is—

$$\frac{dx}{dt} = k(= \text{electrochemical equivalent of copper}). \quad . \quad (6)$$

If the solution be sufficiently diluted, hydrogen as well as copper will separate,[1] and it is found that the rate of precipitation of copper is then—

$$\frac{dx}{dt} = k(a - x)^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where n increases in value from zero to unity with increasing dilution. When the solution has attained a certain dilution—

$$\frac{dx}{dt} = k(a - x). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The velocity of the reaction is also approximately proportional to the strength, E, of the current, hence—

$$\frac{dx}{dt} = k'E, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where k' is a constant. Hence, from equations (8) and (9)—

$$k'E = k(a - x)\,; \; \therefore \frac{E}{a - x} = \frac{k}{k'} = \text{constant, say, } K. \quad (10)$$

A result known as Haber's equation.[2] For the electrolysis of dilute hydrochloric acid, E. Brunner (*l.c.*) finds—

E	$a - x$	Const.
192	7·5	25·5
147	6·8	21·6
130	5·7	22·8
114	4·6	24·8
98	4·2	23·3
79	3·5	22·6

During electrolysis, the liquid which has undergone chemical change in the neighbourhood of the electrodes must be renewed by diffusion from the more concentrated parts

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[1] A. Schrader, *Zeit. Elektrochem.*, **3.** 489, 1897; H. J. S. Sand, *Zeit. phys. Chem.*, **35.** 641, 1900; J. Siegrist, *Zeit. anorg. Chem.*, **26.** 273, 1901.

[2] F. Haber, *Zeit. phys. Chem.*, **32.** 193, 1900; *Zeit. angew. Chem.*, **14.** 133, 1900; *Zeit. Elektrochem.*, **10.** 156, 1904.

of the solution, the value of n will, therefore, be connected with the rate of diffusion of the reacting liquid. In the reduction of nitrobenzene by hydrogen liberated at the cathode when an alkaline solution of this substance is subjected to electrolysis, Goldschmidt[1] finds that equation (7) assumes the form—

$$\frac{dx}{dt} = k(a - x)^{\frac{2}{3}}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

VIII. The velocity of crystallization.—Some interesting work has been done on the rate of crystallization of supersaturated solutions and of supercooled liquids.[2]

§ 43. Reactions between Liquids which do not mix.

The velocity of the chemical action between liquids which do not mix has been studied by Carrara and Zoppellari.[3] They find that the decomposition of mixtures of water and sulphuryl chloride, SO_2Cl_2; thionyl chloride, $SOCl_2$; disulphuryl chloride, $S_2O_5Cl_2$; phosphorus trichloride, PCl_3; phosphorus tribromide, PBr_3; phosphorus oxychloride, $POCl_3$; phosphorus sulphochloride, $PSCl_3$, give numbers which agree with one of the two formulæ—

$$\frac{dx}{dt} = k; \text{ or, } \frac{dx}{dt} = k(a - x).$$

The velocity of transformation of a substance in an aqueous solution in contact with another solution of the same substance which does not mix with the former, has also been investigated.[4] If a gram-molecules of ethyl acetate are dissolved in two immiscible solvents, v_1 volumes of dilute hydrochloric acid,

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[1] H. Goldschmidt, *Zeit. Elektrochem.*, **7**. 263, 1901; for the oxidation of oxalic acid, see T. Åkerberg, *Zeit. anorg. Chem.*, **31**. 161, 1902.

[2] See A. Findlay's *The Phase Rule and its Applications*, London, 70, 1904.

[3] G. Carrara and I. Zoppellari, *Gazz. Chim. Ital.*, **25**. i., 1, 1894; **26**. i., 483, 1896.

[4] H. Goldschmidt and A. Messerschmitt, *Zeit. phys. Chem.*, **31**. 235, 1899.

and v_2 volumes of benzene, the ester is hydrolyzed in the former solution, not in the latter. As fast as the ester is hydrolyzed, more ester passes in from the benzene solution. Let α denote the number of gram-molecules of ester present in the dilute hydrochloric acid at any moment t. The velocity of hydrolysis will then be—

$$\frac{dx}{dt} = k\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

To find the value of α at any moment we must remember that the amount of—

$$\text{Ester in dil. HCl} = \frac{\alpha}{v_1}; \ \text{Ester in } C_6H_6 = \frac{a - \alpha - x}{v_2},$$

where x denotes the number of gram-molecules of ester saponified at the time t. From Nernst's partition law (§ 71)—

$$\alpha v_2 = \kappa(a - \alpha - x); \ \kappa = \frac{\alpha v_2}{a - \alpha - x}; \ \text{and } \alpha = \frac{v_1\kappa}{v_2 + v_1\kappa}(a - x); \quad (2)$$

$$\therefore \frac{dx}{dt} = k\frac{v_1\kappa}{v_2 + v_1\kappa}(a - x); \ k = \frac{1}{t} \cdot \frac{v_2 + v_1\kappa}{v_1\kappa}\log\frac{a}{a - x}. \quad (3)$$

This expression closely resembles that for unimolecular reactions in homogeneous systems. The new equation contains the partition constant κ. Consequently, reactions in heterogeneous systems must be slower than in homogeneous systems; the less the value of κ the slower the reaction, because less ester passes from the benzene to the hydrochloric acid in a given interval of time. It also follows that the velocity of a fast homogeneous reaction can be reduced by adding a sufficiently great volume of a second solvent, and the velocity of many reactions, too fast for measurement in the ordinary way, can be readily followed.

The experimental data has been worked out on the hypothesis that the above reaction is reversible. When the dilute hydrochloric acid was replaced by a dilute solution of barium hydroxide, the reaction is bimolecular. The corresponding equation is—

$$\frac{dx}{dt} = k\alpha(b - x), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where b denotes the initial concentration of the baryta solution. Let a denote the total quantity of ester. As before—

$$\frac{dx}{dt} = k\frac{\kappa}{1+\kappa}(a-x)(b-x);\ k = \frac{1}{t}\cdot\frac{\kappa+1}{\kappa}\cdot\frac{1}{a+b}\log\frac{b(a-x)}{a(b-x)}. \quad (5)$$

If $a = b$—

$$k = \frac{1}{t}\cdot\frac{\kappa+1}{\kappa}\cdot\frac{x}{a(a-x)}. \quad . \quad . \quad . \quad . \quad (6)$$

No other experimental work has yet been done on this subject.

§ 44. Reactions between Liquids and Gases.

We have the well-known laws of Dalton and of Henry for the solubility of gases in liquids.[1] Very few measurements have been made upon the rate of chemical action between gases and liquids. Hood [2] has investigated the rate of absorption of chlorine, carbon dioxide, sulphur dioxide, and of hydrogen sulphide in the presence of air or hydrogen, by an aqueous solution of potassium hydrate. Owing to the magnitude of the perturbing influences, downward currents of gas, etc., the results were not very satisfactory. The rate of absorption was not found to be proportional to the partial pressure of the gas.

From some of my own experiments, it appears that the rate of absorption of a gas, kept at constant pressure, by a liquid at rest, depends principally on the rate of diffusion of the gas in the liquid. The rate of absorption may almost be taken as a measure of the rate of diffusion of the gas in the liquid.

Perman [3] found the rate of evolution of ammonia from aqueous solutions to be proportional to the partial pressure of the ammonia vapour (Henry's law), and his experimental

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[1] For full details, see the work dealing with solutions in this series of Text-books; also O. W. Richardson, *Phil. Mag.* [6], **7.** 266, 1904.

[2] J. J. Hood, *Phil. Mag.* [5], **17.** 352, 1884; W. J. Busnikoff, *Journ. Russ. Chem. Soc.*, **29.** 488, 1897; **30.** 418, 1898; C. Bohr, *Wied. Ann.*, **62.** 644, 1897; **68.** 500, 1899; *Drude's Ann.*, **1.** 244, 1900; J. A. Wanklyn, *Phil. Mag.* [6], **3.** 347, 498, 1902.

[3] E. P. Perman, *Journ. Chem. Soc.*, **73.** 515, 1898; **83.** 1168, 1903.

results can be referred to formulæ (1) and (2), § 11. For example, Perman expresses the relation between the amount q of ammonia in the solution at the time t, and the volume v of dry air which has been bubbled through the solution, by the formula—

$$\log q = A - Bv, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where A and B are constants. Obviously, if we write $A = \log a$, $q = a - x$; and if a denotes the concentration of the solution at the beginning of the experiment, while $a - x$ denotes the concentration of the solution at the time t, hence—

$$\frac{1}{t}\log\frac{a}{a-x} = k; \quad \therefore \frac{dx}{dt} = k(a - x), \quad . \quad . \quad (8)$$

where k has been written in place of B. See (1), p. 30.

If v c.c. of liquid which has a surface s, be exposed to a gas, the rates of evolution ("evasion") of the gas from the liquid, and of absorption ("invasion") of the gas by the liquid, will be respectively—

$$-\frac{dx}{dt} = \frac{\beta s}{v}(a - x_1); \quad \frac{dx}{dt} = \frac{\gamma s}{v}(a + x_2), \quad . \quad . \quad (9)$$

where a denotes the amount of gas dissolved in the liquid at the beginning of the experiment; x the amount which has entered or left the liquid at the time t; β is a constant whose meaning can be obtained by making s and v unity, in other words, β denotes the number of cubic centimetres of gas at 0° and 760 mm. given off per minute from one square centimetre of the surface. Bohr calls β the **evasion coefficient.** When we are dealing with the rate of absorption of a gas, the corresponding constant, γ, is called the **invasion coefficient.** The system is in a state of equilibrium when the rates at which the gas enters and leaves the liquid are equal, as with opposing chemical reactions—

$$\beta(a - x_1) = \gamma(a + x_2); \quad \therefore \frac{\beta}{\gamma} = \text{constant, say, } \alpha. \quad (10)$$

Now α is nothing more than the coefficient of absorption of the gas in the given liquid. Bohr finds that the effect of temperature on the coefficients of invasion and evasion is not the same. Whereas γ is almost unaffected by variations of temperature, T, between 5° and 30°, $\beta = c(T - n)$, where c and n are constants to be evaluated from the experimental data. Hence it follows that $a(T - n) =$ constant, a result in harmony with Bohr's experiments.

Trautz[1] measured the rate of decomposition of nitrosulphonic acid in aqueous solutions of sulphuric acid by the rate of evolution of nitric oxide; but the hydrolysis of nitrosulphonic acid is so rapid that what is actually measured is the rate of evolution of nitric oxide.

Meyer[2] has measured the rate of oxidization of various gases: carbon monoxide, hydrogen, ethylene, etc., by aqueous solutions of potassium permanganate, without coming to any very definite conclusions.

§ 45. Reactions between Solids and Gases.

As shown in § 21, the velocity of a great many reactions between gases which take place in the presence of solids is proportional to the pressure of the gas.

Hurter[3] found that the rate of absorption of carbon dioxide and chlorine by calcium monoxide was proportional to the pressure of the gas; Ikeda and Ewan[4] have obtained a similar result for the rate of oxidation of phosphorus and of sulphur in moist oxygen. The proportionality does not hold if the measurements be extended over a wide range. Only during the earlier stages of the oxidation of phosphorus is the velocity proportional to the pressure of the gas.

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[1] M. Trautz, *Zeit. phys. Chem.*, **47**. 513, 1904.

[2] V. Meyer with E. Saam, *Ber.*, **30**. 1935, 1897; with M. von Recklinghausen, *ib.*, **29**. 2549, 1896; with H. Hirtz, *ib.*, **29**. 2828, 1896; H. N. Morse with C. L. Reese, *Amer. Chem. Journ.*, **20**. 521, 1898; with H. G. Byers, *ib.*, **23**. 313, 1900. For oxidations with chromic acid, C. L. Reese, *ib.*, **22**. 158, 1899; E. Ludwig, *Liebig's Ann.*, **162**. 47, 1872.

[3] J. Hurter, *Moniteur scientifique* [3], **8**. 1075, 1878.

[4] T. Ewan, *Zeit. phys. Chem.*, **16**. 315, 1895; *Phil. Mag.* [5], **38**. 512, 1894; K. Ikeda, *Journ. Coll. Sci. Imperial Univ. Japan*, **6**. 43, 1893; E. J. Russell, *Journ. Chem. Soc.*, **83**. 1263, 1903.

A few moments' reflection will show that the oxidation of the phosphorus is a very complicated operation, involving the formation of various side products—ozone, hydrogen, peroxide, etc. We do not know what surface changes take place during the oxidation; nor do we know what part the vapour of phosphorus plays in the process. It is therefore not surprising that all attempts to obtain a theoretical expression for the rate of oxidation through a wide range of pressure have proved nugatory.

Thorpe[1] has studied the rate of reduction of acidulated solutions of ferric salts by metallic zinc, iron, and magnesium. The maximum reducing action is obtained by diminishing the concentration of the free acid and increasing the concentration of the ferric salt.

Cantor[2] measured the pressure produced upon a copper plate exposed on one side to the action of chlorine gas, by means of a torsion balance. The copper plate tends to move towards the partial vacuum created at the absorbing surface of the copper. The results are said to be in harmony with the kinetic theory.

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[1] T. E. Thorpe, *Journ. Chem. Soc.*, **41**. 287, 1882.

[2] M. Cantor, *Wied. Ann.*, **62**. 482, 1897.

NOTE TO FACE PAGE 133.

The rate of precipitation of a number of salts has just been measured (S. Liesegang, *Ueber chemische Reaktionen in Gallerten*, Düsseldorf, 1898; J. Hausman, *Zeit. anorg. Chem.*, **40**. 110, 1904; J. Traube, *ib.*, **40**. 145, 1904) by mixing a 10 per cent. solution of gelatine with, say, $AgNO_3$ and allowing the whole to solidify in a tube. The gelatine was then placed in contact with, say, an aq. NaCl-sol. The rate of formation of AgCl was found to be nearly proportional to the rate of diffusion of the ions of the salts concerned—so much so that the rate of precipitation has been proposed as a measure of the speed of migration of the ions. J. Traube also suggests that the velocity coefficient, k, in homogeneous reactions may be simply the coefficient of diffusion of the reacting substances. R. B. Warder (*Proc. Amer. Assoc. Sci.*, **30**. 1, 1881) abandoned a similar hypothesis in 1881. The precipitate forms a series of laminæ at right angles to the axis of the tube. This has not been explained. W. Ostwald (*Zeit. phys. Chem.*, **22**. 302, 1897; **23**. 365, 1898) thinks that it is a supersaturation phenomenon.

CHAPTER VIII

EQUILIBRIUM AND DISSOCIATION

§ 46. Unimolecular Homogeneous Equilibria.

THE velocity of the reversible reaction of the first order—

$$A_1 \rightleftharpoons A_2,$$

is represented by the equation—

$$\frac{dx}{dt} = k_1\frac{a_1 - x}{v} - k_2\frac{a_2 + x}{v};$$

while the condition of equilibrium is that—

$$\frac{dx}{dt} = 0; \text{ or, } \frac{a_2 + \xi}{a_1 - \xi} = \frac{k_1}{k_2} = K, \text{ say} \quad . \quad . \quad . \quad (1)$$

where a_1 and a_2 respectively denote the number of gram-molecules of A_1 and A_2 present in v litres, x is the number of gram-molecules of A_1 decomposed at the time t, and ξ is the value of x when equilibrium has set in.

Equation (1) means that when one substance is converted into another, by a reversible reaction, the system will be in equilibrium when the quantities of the two substances are in a definite ratio which is equal to the ratio of the velocity coefficients of the opposing reactions. The value of this ratio does not depend upon the initial concentration of A_1 or A_2. We only obtain the relative, not the absolute, values of the velocity coefficients in this manner. If we know the velocity coefficients of the two opposing reactions, we can obviously calculate how much of each substance will be present when equilibrium is established. The conclusions are in full agreement with the experimental work given in Chapter IV., provided all the substances taking part in the reaction are in the same state of aggregation, liquid or gaseous. Examples: the transformation of ammonium thiocyanate into thiourea; of γ-oxybutyric acid into γ-oxybutyrolactone; and of hexachloro-α-keto-γ-R-pentane into hexachloro-α-keto-β-P-pentane.

Solid ammonium thiocyanate or solid thiourea may be kept an indefinite time at ordinary temperatures, but if either of these substances is fused, a reversible "isomeric" change sets in until about 80 per cent. of the former and 20 per cent. of the latter has been formed. This illustrates the phenomenon of **dynamic isomerism.**[1] Tautomeric (C. Laar), pseudomeric (A. Baeyer), and desmotropic (O. Jacobsen) liquids are no doubt mixtures of two isomerides in a state of equilibrium. Further examples are—

Normal π-bromonitrocamphor $\rightleftharpoons$ pseudo π-bromonitrocamphor;
Cis-dibromotoluene $\rightleftharpoons$ trans-dibromotoluene;
Enolic α-benzylcamphor $\rightleftharpoons$ ketonic α-benzylcamphor.

§ 47. Unimolecular Heterogeneous Equilibria.

Unimolecular heterogeneous equilibria may be set up when matter passes from one state of aggregation to another—say, of ice to water, or of water to steam. A general discussion of his subject belongs to the chapter of chemistry dealing with the "Phase Rule."[2] Let us take the reciprocal transformation of gaseous cyanogen into solid paracyanogen—

Paracyanogen (solid) $\rightleftharpoons$ cyanogen (gas).

Equilibrium always occurs at any given temperature when the vapour pressure has attained a certain fixed value. This value increases with rise of temperature. According to Troost and Hautefeuille[3] the following relations hold:—

Temperature.	Pressure at equilibrium.
502°	5·4 cms. of mercury
559°	12·3 ,, ,,
599°	27·5 ,, ,,
640°	131·0 ,, ,,

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[1] T. M. Lowry, *Journ. Chem. Soc.*, **75**. 211, 1899; *B. A. Reports*, 1904.
[2] A. Findlay's *The Phase Rule and its Applications*, London, 1904.
[3] L. Troost and P. Hautefeuille, *Compt. Rend.*, **66**. 795, 1868.

We have abundant evidence to show that *at any definite temperature there is one and only one pressure at equilibrium.*[1] This pressure is called the **dissociation-pressure.**

Before we can apply the law of mass action it is necessary to find the concentration of the substances concerned in the reaction. It is easy to see that the concentration of the gaseous cyanogen is directly proportional to the pressure, but the concentration of the solid paracyanogen is not so easy to determine. Indeed, it is found experimentally that the pressure of the gaseous cyanogen, at equilibrium, is independent of the quantity of paracyanogen present. Let us turn to a more familiar analogy.

If a sufficient quantity of water be put into a closed vessel, part of it will be vaporized and part of it will remain liquid.

$$\text{Liquid water} \rightleftharpoons \text{Water vapour.}$$

The amount of water vaporized depends principally on the temperature, and it is not governed by the amount of liquid present. The vapour pressure of a large quantity of liquid is the same as that of a small quantity of liquid. The same thing applies to the vapour pressure of benzoic acid, naphthalene, etc. We may, indeed, assume that all solids exert a small but real vapour pressure. This pressure is, in general, too small to come within the range of the instruments employed for the measurement of vapour pressures. We naturally assume, further, that the small sublimation pressures of solids obey the same laws as the vapour pressures of substances which are accessible to measurement. The sublimation pressure of a solid in a state of equilibrium will remain constant so long as the temperature remains constant. The sublimation pressure will also be unaffected by the quantity of the solid. Hence the concentration of a solid will be proportional to its vapour pressure, and the vapour pressure will have a constant value at a definite temperature. It is therefore concluded that at any definite temperature the "active mass" or concentration

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[1] The evidence or states of "false equilibria" will be discussed in a later chapter.

of a solid substance is independent of its quantity, a fact first noticed by Guldberg and Waage in 1867.[1]

Of course, the *rate* at which a system assumes a state of equilibrium will depend on the surface of the solid. It is sometimes stated that the extent of surface of a solid in a gas-solid or in a gas-liquid reaction should affect the final state of equilibrium if the assumption be made that the latter state occurs when the number of molecules which enter is equal to the number which leave the boundary surface of the solid in a given time.[2] Thus, in the dissociation of solid calcium carbonate into solid calcium oxide and carbon dioxide equilibrium occurs when the number of molecules of carbon dioxide given off by the carbonate is equal to the number absorbed by the calcium oxide. Hence at first sight the equilibrium appears to depend upon the ratio of the surface of the oxide and carbonate. A few moments' reflection, however, will show that this conclusion is erroneous.[3]

The state of equilibrium may be modified by the physical condition of the solid, whether it be crystalline or amorphous, precipitated from hot or cold solutions, whether it be previously dried or kept moist.[4] But this wants looking into.

If, now, a certain amount of solid paracyanogen be introduced into a closed vessel at 599°, gaseous cyanogen will be formed until the pressure of its vapour has attained the value 27·5 cms. Equilibrium then sets in, and the system undergoes no further change.

Now let the pressure of the cyanogen be increased while the temperature is kept constant (599°), cyanogen will be reconverted into paracyanogen until the pressure of the cyanogen

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[1] A. Ponsot, *Compt. Rend.*, **130**. 829, 1900.

[2] A. Horstmann, *Liebig's Ann.*, **170**. 192, 1873; W. Ostwald's *Klassiker*, No. 137. For a theoretical treatment, see M. Wilderman, *Phil. Mag.* [6], **2**. 50, 1901; **4**. 270, 468, 1902.

[3] W. Ostwald's *Grundriss der allgemeinen Chemie*, Leipzig, 349, 1899; J. Walker's trans., 320, 1895.

[4] L. Meyer's *Die Modernen Theorien der Chemie*, Breslau, 525, 1884; P. P. Bedson and W. P. Williams' trans., 495, 1888; H. W. Foote, *Zeit. phys. Chem.*, **33**. 740, 1900; A. Colson, *Compt. Rend.*, **132**. 467, 1901.

has fallen to 27·5 cms.; on the other hand, if the pressure of the cyanogen be reduced by the removal of a certain amount of the gas from the system, fresh quantities of paracyanogen will pass into cyanogen until the former pressure, 27·5 cms., is attained. It follows directly from this that if some substance be present which is capable of absorbing the cyanogen as fast as it is formed, the reaction will go on until all the paracyanogen has been converted into cyanogen.

Let us now apply equation (1) to this reaction. Let A_1 denote the solid component, whose concentration $a_1 - x$ has some constant value, say c_1; we shall have—

$$\frac{k_1}{k_2} = \frac{a_2 + \xi}{c_1} = \frac{p}{c_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where p denotes that the concentration of the cyanogen $a_2 + x$ is measured in terms of the pressure of the gas. Hence—

$$p = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

since c_1, k_1, and k_2 are all constant. This result is in agreement with Troost and Hautefeuille's experiments on the mutual transformation of cyanogen into paracyanogen; of cyanic acid into cyamelide;[1] of red into yellow phosphorus;[2] the conversion of styrol into metastyrol;[3] of acetaldehyde into paraldehyde,[4] etc.

What has been said of solid-gas systems applies equally well to all cases of heterogeneous equilibria. If both substances have a constant active mass, they need never be in equilibrium, because the ratio of the active masses of the two substances need not be the ratio of their rates of transformation; and when equilibrium does occur, certain definite conditions must be

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[1] L. Troost and P. Hautefeuille, *Compt. Rend.*, **67**. 1345, 1868; *Annales scientifique de l'École normale* [2], **2**. 261, 1868.

[2] W. Hittorf, *Pogg. Ann.*, **126**. 193, 1865; G. Lemoine, *Ann. Chim. Phys.* [5], **2**. 153, 1874; [4], **24**. 129, 1871; L. Troost and P. Hautefeuille, *Ann. Phys. Chem.* [5], **2**. 145, 1874.

[3] G. Lemoine, *Comp. Rend.*, **125**. 520, 1897; **129**. 719, 1899.

[4] R. F. Hollmann, *Zeit. phys. Chem.*, **43**. 129, 1903; see also G. Bodländer, *Chem. Zeitschrift*, **3**. 102, 1903.

satisfied. Water and ice, for example, can only exist together at one definite temperature; the same thing might be said of rhombic and monoclinic sulphur; and of red and yellow mercuric iodides. The equation of equilibrium—

$$\frac{k_1}{k_2} = \frac{c_2}{c_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it will be observed, contains no variable magnitude at all.

§ 48. Bimolecular Homogeneous Equilibria.

From our previous work, § 31, we deduce the condition of equilibrium—

$$K = \frac{k_1}{k_2} = \frac{(c + \xi)(d + \xi)}{(a - \xi)(b - \xi)}, \quad . \quad . \quad . \quad . \quad (5)$$

provided all the substances taking part in the reaction are in the same state of aggregation, liquid or gaseous. It is more convenient to make the original quantities of the two substances equal to unity, and let there be no products of the reaction present at the start. In that case—

$$K = \frac{k_1}{k_2} = \left(\frac{\xi}{1 - \xi}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In other words, *the condition of equilibrium of a homogeneous reaction of the second order is, that the velocity constants be proportional to the squares of the concentrations of the substances undergoing transformation.*

The truth of the law of mass action is brought out in a striking manner from the oft-quoted experiments of Berthelot and Gilles (see p. 80).[1] One molecule of acetic acid was mixed with *b* molecules of alcohol, and the quantity of ethyl alcohol formed when the system is in a state of equilibrium is indicated in the second column of the following table. As

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[1] M. Berthelot and L. Péan de St. Gilles, *l.c.*; N. Menschutkin, *Ann. Chim. Phys.* [5], **20.** 289, 1880; **23.** 14, 1881; **30.** 81, 1885; *Liebig's Ann.*, **195.** 334, 1879; **197.** 193, 1879; *Bull. Soc. Chim.* [2], **28**, 563, 1877; H. Euler, *Zeit. phys. Chem.*, **36.** 405, 1901.

previously mentioned, § 31, $K = 4$, $a = 1$, $c = d = 0$. From (5)—

$$\therefore \xi = \tfrac{1}{2}(b + 1 \pm \sqrt{b^2 - b + 1}).$$

This expression was used to calculate the numbers given in the last column of the table.

Alcohol. b	ξ = Ethyl acetate produced.	
	Obs.	Calc.
0·05	0·050	0·049
0·18	0·171	0·171
0·50	0·414	0·423
1·00	0·667	0·667
2·00	0·858	0·845
8·00	0·966	0·945

When one-fifth of an equivalent of alcohol is used, only about 17 per cent. of ester is formed; when one equivalent of alcohol is used, 66·7 per cent. of ester is formed; and when fifty equivalents of alcohol are employed, practically all the acid present is transformed into ester.

The oft-quoted reaction—

$$H_2 + I_2 \rightleftharpoons 2HI,$$

studied by Hautefeuille, Lemoine, and Bodenstein,[1] furnishes another example. Here the reacting substances are all gaseous. The condition of equilibrium is—

$$\frac{p_1 p_2}{p^2} = K,$$

where p_1, p_2, and p respectively denote the partial pressures of the hydrogen, iodine, and hydrogen iodide.

Zaitschek[2] has tried to solve the disputed question of the existence of hydrates of sulphuric acid in aqueous solutions by

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[1] P. Hautefeuille, *Compt. Rend.*, **64.** 608, 1867; G. Lemoine, *ib.*, **80.** 792, 1875; **85.** 144, 1877; *Ann. Phys. Chim.* [5], **12.** 145, 1877; V. Meyer and M. Bodenstein, *Ber.*, **26.** 1146, 2603, 1893; M. Bodenstein, *Zeit. phys. Chem.*, **22.** 1, 1897.

[2] A. Zaitschek, *Zeit. phys. Chem.*, **24.** 1, 1897.

measuring the equilibrium constants for various mixtures of sulphuric acid, water, and alcohol, at 45°, and titrating the solution with normal sodium hydroxide for ethylsulphuric acid—

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O.$$

The results are said to be in harmony with theory, when it is assumed that the mixture contains the hydrate $H_2SO_4.2H_2O$. We are told that "K remains constant only under the assumption that sulphuric acid exists in solution as orthosulphuric acid, H_6SO_6. . . . The two molecules of water united with the H_2SO_4 are subtracted from the total water, and the free water remaining is employed to calculate the active mass of the water." No indication of the existence of other hydrates of sulphuric acid or of alcohol was obtained. The reaction, however, appears to be too complicated to be dismissed in this way.

Another interesting application of the law of mass action to the partition of an acid between two alkaloids was made a few years later than the work of Guldberg and Waage, but yet independently. J. H. Jellet[1] investigated the distribution of hydrochloric acid between quinine and codeïne in alcoholic solution, when the acid was not present in sufficient quantity to saturate all the alkaloids present. When the system is in a state of equilibrium, the free alkaloids and their hydrochlorides will be present. Hence—

$$\text{Quinine} + \text{Codeïne hydrochloride} \rightleftharpoons \text{Codeïne} + \text{Quinine hydrochloride}.$$

Let a, b, and c respectively denote the original quantities of quinine, codeïne, and hydrochloric acid present at the beginning of the reaction, let ξ denote the quantity of quinine hydrochloride present when the system is in a state of equilibrium, then $c - \xi$ will denote the quantity of codeïne hydrochloride, $a - \xi$ the quantity of quinine, and $b - (c - \xi)$ the quantity of codeïne present at the same time. Hence, from (5)—

$$\frac{\{b - (c - \xi)\}}{(a - \xi)(b - \xi)} = K.$$

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[1] J. H. Jellet, *Trans. Irish. Acad.*, **25.** 371, 1875.

A comparison of this equation with Jellet's experimental results is shown in the following table :—

a	b	c	ξ	K
100	104	70·7	42·7	1·91
100	104	91·9	55·0	2·08
100	104	112·4	66·0	2·10
100	104	130·3	73·0	2·02

Experiments on the partition of an acid between codeïne and brucine, and between quinine and brucine, gave similar results.

This simple application of the law of mass action presupposes that no disturbing side reactions occur. Bonz[1] has shown that the equilibrium constant for the reversible reaction between acetamide and ethyl alcohol is not so simple as the equation—

$$NH_3 + CH_3COOC_2H_5 \rightleftharpoons CH_3.CO.NH_2 + C_2H_5OH,$$

would lead one to expect. Among the bye-products Bonz found ethyl ammonium acetate, ethyl acetamide, and water.

The equilibria of fused mixtures of potassium or sodium chloride with either sodium carbonate or lithium carbonate; and of sodium carbonate with either titanium dioxide or zirconium dioxide, have also been studied. The results are in agreement with the law of mass action.[2]

§ 49. Heterogeneous Bimolecular Equilibria.

Let us now apply the condition of equilibrium—

$$k_1(a_1 - \xi)(b_1 - \xi) = k_2(a_2 + \xi)(b_2 + \xi),$$

for the bimolecular reaction—

$$A_1 + B_1 \rightleftharpoons A_2 + B_2,$$

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[1] A. Bonz, *Zeit. phys. Chem.*, **2**. 865, 1888.

[2] E. Brunner, *Zeit. anorg. Chem.*, **38**. 350, 1904; D. P. Smith, *ib.*, **37**. 332, 1903.

to heterogeneous systems. Four cases arise according as the active masses of A_1, B_1, A_2, and B_2 are in succession made constant.

CASE I.—*The active mass of one substance is made constant.* One of the commonest reactions of this type occurs when barium chloride reacts with sulphuric acid, producing insoluble barium sulphate and hydrochloric acid; the action of steam upon carbon producing a mixture of hydrogen and carbon monoxide[1]—"water gas," and of ammonium chloride upon manganese hydroxide.[2]

Let A_1 and B_1 both in solution react to form soluble A_2 and insoluble B_2. The active mass of B_2 will therefore be constant, say c_4. In this case the equation becomes—

$$k_1(a_1 - \xi)(b_1 - \xi) = k_2(a_2 + \xi)c_4,$$

$$\therefore \frac{(a_1 - \xi)(b_1 - \xi)}{\xi} = \text{Constant} = c, \text{ say.} \quad (7)$$

The truth of this equation has been tested by a series of experiments on the precipitation of solutions of calcium chloride (A_1) by oxalic acid (B_1), and the action of hydrochloric acid (A_2) upon calcium oxalate (B_2).[3] By solving equation (7) for ξ, we obtain—

$$\xi = \tfrac{1}{2}\{a_1 + b_1 + c - \sqrt{(a_1 + b_1 + c)^2 + 4a_1b_1}\}, \quad (8)$$

where ξ denotes the number of gram-molecules of calcium oxalate precipitated, or of hydrochloric acid set at liberty when the system is in a state of equilibrium. By substituting the experimental values of a_1, b_1, and of ξ in (7), we get $c = 0{\cdot}0215$. Again, when a_1 ($CaCl_2$) = 1; a_2 (HCl) = 0, and b_1 (oxalic acid) had the values represented in the first column of the following table, S. Wleugel found the corresponding values ξ

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[1] J. Lang, *Zeit. phys. Chem.*, **2**. 173, 1888.

[2] W. Hertz, *Zeit. anorg. Chem.*, **21**. 243, 1899; **22**. 279, 1899.

[3] W. Ostwald, *Journ. prakt. Chem.* [2], **16**. 385, 1877; [2], **19**. 468, 1879; [2], **22**. 251, 1880; **24**. 486, 1881; S. Wleugel's experiments quoted by C. M. Guldberg and P. Waage, *ib.* [2], **19**. 69, 1879.

(the amount of calcium oxalate precipitated) represented in the second column. The calculated values of ξ are from formula (8).

b_1	ξ (Calcium oxalate).	
	Obs.	Calc.
0·398	0·385	0·385
0·596	0·596	0·568
0·994	0·873	0·863
1·491	0·957	0·961
1·988	0·973	0·979

In spite of the agreement between the calculated and observed values of the calcium oxalate present when the system is in equilibrium, W. Ostwald (*l.c.*) has pointed out two objections to the method of verification.

(i.) On account of the small value of c this quantity can have but little influence on the results of the calculation. If $c = 0$, ξ is either equal to unity or to b. This can only be the case if either A_1 or A_2 are zero, that is, when either all the calcium chloride or all the oxalic acid is precipitated from the solution. This is so nearly what really happens that it is not possible to determine correctly the value of c. Indeed the experimental data furnish values of c varying from 1·0176 to 0·0386.

(ii.) The question might also be raised, are we justified in assuming that the term $b_2 + \xi$ is really constant? The equation as it stands tells us that the amount of calcium oxalate formed in unit time is proportional to the amount of calcium chloride (A_1), and of oxalic acid (B_1) present in the solution; and also that if we assume $b_2 + \xi$ to be constant, the decomposition of calcium oxalate by the hydrochloric acid is proportional to the amount of this acid present in the solution. Experiment shows that the action of hydrochloric acid upon calcium oxalate increases more rapidly than the concentration of the acid, and this action is also affected by temperature to a greater extent than the action of the other substances present in the solution.

These influences, and possibly others, interfere with the regular course of the law of mass action; $b_2 + \xi$ is no longer constant, but rather is equal some unknown function of the amount of hydrochloric acid present in the solution, say, $f(A_2)$; hence—

$$K(a - \xi)(b - \xi) = f(A_2),$$

an expression symmetrical with respect to the concentrations of A_1 and B_1. This means that the presence of an excess of calcium chloride will affect the condition of equilibrium in precisely the same way as an excess of oxalic acid. This is in agreement with observed facts.

The reaction of potassium bromide upon mercuric oxide in the presence of a great excess of water—

$$4KBr + HgO + H_2O \rightleftharpoons 2KOH + K_2HgBr_4,$$

is in agreement with the formula—

$$\frac{(a - 2\xi)^2}{\xi\sqrt{\frac{1}{2}\xi}} = \text{const.}; \text{ not } \frac{(a - 2\xi)^4}{\xi^2 \cdot \xi} = \text{const.},$$

where a denotes the original concentration of the potassium bromide, ξ the number of gram-molecules present when equilibrium has set in. The active masses of the water and of the mercuric oxide are constant.[1] Muir[2] has also investigated the conditions affecting chemical equilibria when water acts upon bismuth chloride; and a soluble carbonate upon calcium chloride.

CASE 2.—*The active mass of two substances is made constant.* For example, the interaction of barium carbonate and potassium sulphate—

$$K_2SO_4 + BaCO_3 \rightleftharpoons K_2CO_4 + BaSO_4,$$

tested by Guldberg and Waage,[3] and a similar reaction in

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[1] S. Bugarszky, *Zeit. phys. Chem.*, **11.** 668, 1893; **12.** 223, 1893.

[2] M. M. P. Muir, *Journ. Chem. Soc.*, **33.** 27, 1878; **35.** 311, 1879.

[3] C. M. Guldberg and P. Waage, *Journ. prakt. Chem.* [2], **19.** 89, 1879; *Études*, 18, 1867.

which the potassium salt was replaced by sodium,[1] tested by Ostwald.

The condition of equilibrium is—

$$\frac{k_1c_1}{k_2c_3} = \frac{a_2 + \xi}{a_1 - \xi}; \text{ or, } \frac{a_1 - \xi}{a_2 + \xi} = \text{const., say, } c, \quad . \quad (9)$$

where c_1 and c_2 respectively denote the constant active masses of the solids B_1 and B_2; $a_1 + \xi$ and $a_2 + \xi$ respectively denote the concentrations of sulphate and carbonate of potassium. Equation (9) shows that the relation between the concentrations of the two substances in solution is always the same when equilibrium has been established. Experiment shows that $c = \frac{1}{4}$, hence there will always be four times as much potassium carbonate in solution as potassium sulphate. This means that insoluble barium carbonate will be decomposed by potassium sulphate four times as fast as barium sulphate is decomposed by potassium carbonate. This view is in harmony with experiment. The long period of time which must elapse before equilibrium sets in frequently makes it uncertain, in any particular experiment, whether equilibrium has really been established. In one series of Guldberg and Waage's experiments, for example, equilibrium was not established after the mixture had stood a year at 3°.[2] Increase of temperature or diminution of the solvent generally hastens the process, but the precipitation of barium as chromate was found to be more rapid in dilute solutions.[3]

Solving (9) for ξ, we get—

$$\xi = \frac{a_1 - ca_2}{1 + c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which has been used in the comparison of the experimental values of ξ, with theory for different values of a_1 and a_2. The following is one of the first tables published by Guldberg and

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[1] W. Ostwald, *Journ. prakt. Chem.* [2], 22. 251, 1880.

[2] In some cases van't Hoff thinks that "geological periods" of time are required before the state of true equilibrium sets in (J. H. van't Hoff, *Arch. néerlandaises des Sciences exactes et naturelles* [2], 6. 489, 1901).

[3] W. Ostwald, *Journ. prakt. Chem.* [2], 22. 259, 1880.

Waage in support of the law of mass action. The agreement between theory and experiment is very good.

Original concentration.		Amount transformed.	
K_2SO_4 a_1	K_2CO_3 a_2	Observed.	Calculated.
0·0	3·5	0·719	0·700
0·0	2·0	0·395	0·400
0·0	1·0	0·176	0·200
0·25	3·8	0·593	0·560
0·25	3·0	0·408	0·400
0·50	2·0	trace	0·000

J. Morris[1] has investigated the mutual action of the carbonates and chromates of barium and potassium, as well as the mutual action of potassium and barium carbonates and sulphates, by analysis of the precipitates produced when barium chloride is added to a mixture of potassium carbonate and chromate; W. Smith,[2] the mutual action of carbonates and oxalates of the alkaline earths with carbonate and oxalate of sodium, from which it appears that the alkaline earths form more "carbonate" than either "oxalate" or "chromate;" Ogg,[3] the mutual reaction between mercury and silver nitrate on the one hand, and mercuric nitrate and metallic silver on the other. It is necessary to allow for the secondary action—combination of silver with the mercury; Pélabon,[4] the action of hydrogen on antimony, bismuth, mercury, and arsenic sulphides.

Jaeger[5] has made an interesting application of the theory to determine the constitution of hydrofluoric acid. He found that the solubility of mercuric oxide in hydrofluoric acid was

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[1] J. Morris, *Inaug. Dissert.*, Tübingen, 1879; *Liebig's Ann.*, **213.** 253, 1882.

[2] W. Smith, *Journ. Chem. Soc.*, **31.** 245, 1877.

[3] A. Ogg, *Zeit. phys. Chem.*, **22.** 536, 1897; **27.** 285, 1898.

[4] H. Pélabon, *Compt. Rend.*, **130.** 911, 1900; **132.** 78, 774, 1411, 1901.

[5] A. Jaeger, *Zeit. anorg. Chem.*, **27.** 22, 1901.

proportional to the concentration of the acid. The action may be represented by, say, one of two equations—

$$HgO + 2HF \rightleftharpoons HgF_2 + H_2O; \text{ or, } HgO + H_2F_2 \rightleftharpoons HgF_2 + H_2O.$$

The concentration of the insoluble oxide and of the excess of water may be regarded as constant. Hence, for equilibrium, we have either—

$$C_{HgF_2} = KC^2_{HF}; \text{ or, } C_{HgF_2} = KC_{H_2F_2}.$$

The formula H_2F_2 is alone in agreement with the experimental result that the solubility of mercuric fluoride is directly proportional to the concentration of the acid, and not proportional to the square of the concentration of the acid. In this way Bodländer[1] has also shown that the cuprous salts have the formulæ CuBr, and not Cu_2Br_2...

We have no experimental data at hand for reactions in which two substances on one side of the equation have a constant mass. The condition of equilibrium is—

$$\frac{k_1}{k_2c_3c_4} = (a_2 + \xi)(b_2 + \xi) = c, \text{ say.} \quad . \quad . \quad (11)$$

Or, if $a_2 = b_2 =$ unity, or zero,

$$\xi = \text{constant.}$$

CASE 3.—*The active mass of three substances is constant.* The reaction—

$$PbO + NH_4Cl \rightleftharpoons Pb(OH)Cl + NH_3 \text{ (gas)},$$

studied by Isambert,[2] was found to give results in agreement with the condition of equilibrium—

$$\xi = \frac{k_1c_2c_3}{k_2c_3} = \text{constant.} \quad . \quad . \quad . \quad . \quad (12)$$

Here ξ is proportional to the pressure p of the gaseous ammonia, so that—

$$p = \text{constant.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

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[1] G. Bodländer and O. Storbech, *Ziet. anorg. Chem.*, **31**. 458, 1902; *Festschrift*, Braunschweig, 1901; *Zeit. phys. Chem.*, **9**. 730, 1892; **39**. 597, 1902.

[2] F. Isambert, *Compt. Rend.*, **102**. 1313, 1886.

At any particular temperature the pressure of the ammonia was found to be independent of the relative amounts of solids present.

CASE 4.—*The active mass of all four substances is constant.* The conditions of equilibrium resemble those already discussed for unimolecular heterogeneous reactions.

§ 50. Mixed Uni- and Bi-molecular Homogeneous Equilibria.

The study of mixed equilibria is nothing more than a further application of the principles which precede. Examples are familiar to every student of chemistry: The dissociation of nitrogen peroxide;[1] of phosphorus pentachloride;[2] of iodine, bromine, and chlorine;[3] of amyl chloride, bromide, and iodide;[4]

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[1] E. Mitscherlich, *Pogg. Ann.*, **29**. 220, 1883; P. A. Müller, *Liebig's Ann.*, **122**. 15, 1862; L. Playfair and J. A. Wanklyn, *Trans. Roy. Soc. Edin.*, **22**. 463, 1861; H. St. Claire Deville and L. Troost, *Compt. Rend.*, **64**. 237, 1867; G. Salet, *ib.*, **67**. 488, 1868; A. Naumann, *Ber.*, **11**. 2045, 1878; L. Troost, *Compt. Rend.*, **86**. 1394, 1878; E. and L. Natanson, *Wied. Ann.*, **24**. 454, 1885; **27**. 606, 1886.

[2] A. Cahours, *Ann. Chim. Phys.* [3], **20**. 369, 1847; *Compt. Rend.*, **21**. 625, 1845; **63**. 14, 1866; J. A. Wanklyn and A. Robinson, *ib.*, **56**. 547, 1237, 1863; *Phil. Mag.* [4], **26**. 545, 1863; H. St. Claire Deville, *Compt. Rend.*, **56**. 195, 322, 1863; **62**. 1157, 1866; **64**. 713, 1867; A. Wurtz, *ib.*, **76**. 601, 1873; *Bull. Soc. Chim.* [2], **19**. 451, 1873; *Association française pour l'advancement des sciences*, Bordeaux, 42, 1872; Lyon, 292, 1873; H. Debray, *Compt. Rend.*, **77**. 123, 1873; L. Troost and P. Hautefeuille, *ib.*, **83**. 220, 333, 975, 1876; R. Wegscheider, *Monatshefte für Chem.*, **20**. 307, 1899.

[3] V. Meyer, *Ber.*, **12**. 2202, 1879; A. Lieben, *Compt. Rend.*, **89**. 353, 1879; V. Meyer and J. M. Crafts, *Ber.*, **13**. 1018, 1880; *Compt. Rend.*, **92**. 39, 1881; V. Meyer and J. Züblin, *Ber.*, **13**. 405, 1880; V. Meyer, *ib.*, **13**. 394, 1721, 1880; V. Meyer and C. Langer, *ib.*, **15**. 2769, 1882; *Pyrochemische Untersuchungen*, Braunschweig, 1885; A. P. Smith and W. B. Lowe, *Chem. News*, **45**. 226, 1882; J. M. Crafts, *Ber.*, **16**. 457, 1883; *Compt. Rend.*, **90**. 183, 1880; A. Leduc, *Compt. Rend.*, **125**. 937, 1897.

[4] A. Wurtz, *Compt. Rend.*, **60**. 728, 1865; **62**. 1182, 1866; M. Berthelot, *Ann. Chim. Phys.* [5], **22**. 456, 1881.

of hydrogen fluoride,[1] etc. In solution we have the "reversible hydrolysis" of maltose,[2] etc.

Consider the dissociation of nitrogen tetroxide into the simple molecules—

$$N_2O_4 \rightleftharpoons 2NO_2.$$

The composition of the dissociating gas, at equilibrium, can be calculated from vapour density determinations. Let ρ denote the theoretical vapour density of the undissociated nitrogen peroxide calculated from the theoretical formula, N_2O_4; let D denote the observed vapour density of the partially dissociated gas; let α denote the fraction of the gas dissociated, then $1-\alpha$ will denote the undissociated part, that is to say, if there are 100 molecules of the undissociated gas, 100α will be dissociated, and produce 200α new molecules, while $100(1-\alpha)$ will remain undecomposed. The number of molecules thus increases from 100 to $200\alpha + 100(1-\alpha)$, that is, to $100(1+\alpha)$.

$$\therefore \text{Total number of molecules} = 100(1+\alpha), \quad . \quad (1)$$

at equilibrium, when the density of the gas had decreased from ρ to D.

$$\therefore \frac{100}{100(1+\alpha)} = \frac{D}{\rho}; \text{ or, } \alpha = \frac{\rho - D}{D}. \quad . \quad . \quad (2)$$

Let p_1 and p_2 respectively denote the partial pressures of the undissociated and dissociated molecules, P the total pressure. By Dalton's law—

$$P = p_1 + p_2.$$

But the partial pressure, p_1, of the undissociated molecules is to the total pressure, P, as the number of undissociated molecules, $100(1-\alpha)$, is to the total number of molecules, $100(1+\alpha)$.

$$\therefore p_1 = P\frac{100(1-\alpha)}{100(1+\alpha)} = P\left(2\frac{D}{\rho} - 1\right), \quad . \quad . \quad (3)$$

from (2). Similarly the partial pressure, p_2, of the dissociated

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[1] T. E. Thorpe and F. J. Hambly, *Journ. Chem. Soc.*, **53**. 765, 1888; **55**. 163, 1889.

[2] A. C. Hill, *Journ. Chem. Soc.*, **73**. 634, 1898.

molecules is to the total pressure, P, as the number of dissociated molecules, 100α, is to the total number of molecules, $100(1 + \alpha)$:

$$\therefore p_2 = P\frac{100\alpha}{100(1 + \alpha)} = 2P\left(1 - \frac{D}{\rho}\right). \quad . \quad . \quad (4)$$

But the condition of equilibrium of the dissociated nitrogen peroxide is—

$$\frac{p_2^2}{p_1} = K; \; \therefore K = \frac{4(\rho - D)^2P}{(2D - \rho)\rho}, \quad . \quad . \quad (5)$$

from (3) and (4).

In verification, we may take some of E. and L. Natanson's (*l.c.*) measurements, and compare them with the results calculated from the preceding formula.

Temperature = 49·7°.

P mm.	D		α
	Obs.	Calc.	
0·0	—	1·590	1·000
26·80	1·663	1·665	0·930
93·75	1·788	1·782	0·789
182·69	1·894	1·901	0·690
261·37	1·993	1·977	0·630
497·75	2·144	2·143	0·493

The result is very satisfactory. The last column shows what fraction of the N_2O_4 is dissociated at the corresponding pressure. At a pressure of 497·75 mm. of mercury, for example, about 50 per cent. will be dissociated.

Salet (*l.c.*) has obtained similar results by observations of the colour of the dissociating gas, and Cundall[1] has also verified the law from the colour of dissociating nitrogen peroxide dissolved in chloroform. It is assumed that N_2O_4 is colourless,

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[1] J. T. Cundall, *Journ. Chem. Soc.*, **59**. 1076, 1891; **67**. 794, 1895; W. Ostwald, *ib.*, **61**. 242, 1892.

and that NO_2 is coloured. Berthelot and Ogier[1] have also confirmed the law by observations on the specific heat of the dissociating gas.

By raising the temperature the coefficient of dissociation of gaseous nitrogen peroxide also increases, and at 500° the NO_2 begins to dissociate into nitric oxide and oxygen.[2]

Similar results were obtained by Nernst and Hohmann[3] for the dissociation of amyl acetate in sealed tubes at 100°.

$$CH_3COOC_2H_5 \rightleftharpoons CH_3COOH + C_5H_{10}.$$

On mixing together one molecule of acetic acid and a molecules of amylene we have, according to the law of mass action, the following condition of equilibrium—

$$\left(\frac{a-\xi}{v}\right)\left(\frac{1-\xi}{v}\right) = K\frac{\xi}{v}; \text{ or, } \frac{(a-\xi)(1-\xi)}{\xi v} = K, \quad (6)$$

where v denotes the volume of the reacting mixture, and ξ the number of gram-molecules of amyl ester produced when the system is in a state of equilibrium. The following experimental results were obtained :—

a	v	ξ	K
2·15	361	0·762	0·00120
4·48	638	0·820	0·00126
6·80	915	0·839	0·00125
7·67	1018	0·855	0·00113
9·51	1237	0·863	0·00111
14·15	1787	0·873	0·00107

When the reaction took place in v litres of benzene, K was no longer in agreement with equation (6). The disturbance

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[1] M. Berthelot and J. Ogier, *Compt. Rend.*, **94**. 916, 1882 ; *Bull. Soc. Chim.* [2], **37**. 434, 1882 ; **38**. 60, 1882.

[2] A. Richardson, *Journ. Chem. Soc.*, **51**. 397, 1887.

[3] W. Nernst and A. Hohmann, *Zeit. phys. Chem.*, **11**. 345, 352, 1893. The reaction had been previously studied by D. Konowalow (*Zeit. phys. Chem.*, **1**. 63, 1887 ; **2**. 380, 1888), but not accurately formulated.

was traced to the fact that the molecule of acetic acid is doubled in benzene solutions. In this case we have—

$$(CH_3COOH)_2 + 2C_5H_{10} \rightleftharpoons 2CH_3COOC_5H_{11},$$

with the condition of equilibrium—

$$\left(\frac{1-\xi}{v}\right)\left(\frac{a-\xi}{v}\right)^2 = K\left(\frac{\xi}{v}\right)^2; \ \therefore \frac{a-\xi}{\xi}\sqrt{\frac{1-\xi}{v}} = K_1. \quad (7)$$

The values of K_1, calculated from the experimental data, are now in harmony with theory.

a	v	x	K_1
0·481	3·00	0·181	0·87
0·963	4·00	0·298	0·94
0·481	7·77	0·135	0·85
0·963	13·54	0·197	0·94

The behaviour of a solution of phenanthrene picrate in pure alcoholic solution presents a still more complicated example, but an instructive one. In alcoholic solution the salt dissociates as follows:—

Phenanthrene picrate $\rightleftharpoons$ phenanthrene + picric acid.

Let C, C_1, and C_2 respectively denote the number of grams of phenanthrene picrate, $C_{14}H_{10} \cdot C_6H_2(HO_2)_3OH$, picric acid, $C_6H_2(NO_2)_3OH$, and phenanthrene, $C_{14}H_{10}$, dissolved in 100 grams of solution. The condition of equilibrium is—

$$KC = C_1C_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If the solution is kept saturated with phenanthrene, C may be regarded as constant, and, from (8)—

$$K_1 = C_1C_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The result is not satisfactory. R. Behrend[1] has shown that the trouble arises from the fact that although the molecular weight of picric acid in alcoholic solution is normal, yet phenanthrene seems to be partially polymerized into triple molecular

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[1] R. Behrend, *Zeit. phys. Chem.*, **9**. 405, 1892; **10**. 265, 1892.

complexes which do not react with picric acid. The "inactive" trimolecular phenanthrene must be subtracted from the free phenanthrene present in the solution in order to obtain the concentration of the molecular phenanthrene which takes part in the reaction.

The condition of equilibrium of the phenanthrene in alcoholic solution is—

$$(C_{14}H_{10})_3 \rightleftharpoons 3C_{14}H_{10}\,; \text{ or, } C_3K_2 = C_2^3. \quad . \quad (10)$$

where C_2 denotes the concentration of the monomolecular and C_3 the concentration of the trimolecular phenanthrene. Boiling-point determinations show that $K_2 = 10{\cdot}26$. Solubility determinations show that at 12·3°, $C = 0{\cdot}173$. In one experiment the total quantity of phenanthrene (free and combined) in the solution was 2·141 grams, and picric acid 0·409 grams. In 0·173 grams of phenanthrene picrate there are 0·097 grams of picric acid and 0·076 grams of phenanthrene. Hence the solution contains 0·257 grams of free picric acid (C_1) and 2·044 grams of phenanthrene. But C_2 denotes the amount of monomolecular phenanthrene in the solution, and $2{\cdot}044 - C_2$ denotes the concentration of the trimolecular phenanthrene. Hence, from (10)—

$$\frac{C_2^3}{2{\cdot}044 - C_2} = 10{\cdot}36\,; \text{ or, } C_2 = 1{\cdot}635.$$

$$\therefore K_1 = 1{\cdot}635 \times 0{\cdot}257 = 0{\cdot}516.$$

The constant calculated from the experimental data in this manner is fairly satisfactory, as shown in the last column of the subjoined table.

Picric acid.	Phenanthrene.	Picrate. C	Picric acid.		Phenanthrene.				K_1
			Combined.	Free. C_1	Combined.	Free.	Trimolecular. C_3	Monomolecular. C_2	
0·354	2·770	0·093	0·097	0·257	0·076	2·695	0·688	2·007	0·516
0·409	2·141	0·173	0·097	0·312	0·076	0·065	0·430	1·635	0·516
0·534	1·413	0·173	0·097	0·437	0·076	0·430	0·457	1·180	0·516
0·912	0·709	0·173	0·097	0·815	0·076	0·633	0·022	0·611	0·498

From the experiments of Biltz[1] we infer that the complex molecule of sulphur, S_8, gradually dissociates when heated, until, at high temperatures, simple molecules, S_2, predominate. Riecke[2] has pointed out that the experimental numbers indicate that the decomposition takes places in a series of stages—

$$S_8 \rightleftharpoons S_6 + S_2;\ S_6 \rightleftharpoons 3S_2,$$

and not directly—

$$S_8 \rightleftharpoons 4S_2.$$

Sulphur vapour, in general, contains all three kinds of molecules: S_8, S_6, and S_2; at the higher temperatures the latter predominate, at lower temperatures the former prevail.

To find the conditions of equilibrium, write—

$$S_8 \rightleftharpoons S_6 + S_2 \rightleftharpoons 4S_2.$$

It follows that—

$$\frac{C_{S_8}}{C_{S_6}C_{S_2}} = K_{12};\ \frac{C_{S_6}C_{S_2}}{C^4_{S_2}} = K_{23};\ \frac{C_{S_8}}{C^4_{S_2}} = K_{13}. \quad . \quad (11)$$

Hence it follows that—

$$K_{12}K_{23} = K_{13}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Now let—

$$\frac{k_1}{k_2} = K_{12};\ \frac{k_2}{k_3} = K_{23};\ \frac{k_1}{k_3} = K_{13}, \quad . \quad . \quad . \quad (13)$$

where k_1, k_2, . . . depend upon the nature of the substance undergoing decomposition, and not upon the nature of the product of the action. The condition of equilibrium is—

$$\frac{C_{S_8}}{k_1} = \frac{C_{S_4}C_{S_2}}{k_2} = \frac{C^4_{S_2}}{k_3}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The absolute values of the constants k_1, k_2, . . . cannot be determined, but sufficient data can be obtained to calculate the relative magnitudes of these constants.[3]

Owing to the symmetry of equations (14), it is easy to

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[1] H. Biltz, *Zeit. phys. Chem.*, **2**. 920, 1888.

[2] E. Riecke, *Zeit. phys. Chem.*, **6**. 430, 1890.

[3] H. N. McCoy, *Amer. Chem. Journ.*, **29**. 437, 1903 (hydrolysis of sodium bicarbonate in aqueous solutions); E. Abel, *Zeit. anorg. Chem.*, **26**. 361, 1901 (different stages of oxidation of metals).

write the conditions of equilibrium of any number of dependent reactions very quickly.

§ 51. Mixed Uni- and Bi-molecular Heterogeneous Equilibria.

CASE I.—*A solid decomposes into two gaseous products.* The condition of equilibrium will be—

$$k_1(a_1 - \xi) = k_2(a_2 + \xi)(b_2 + \xi) . \quad . \quad . \quad . \qquad (1)$$

As an example, take the dissociation of solid ammonium hydrosulphide[1] into equal volumes of ammonia and hydrogen sulphide gases.

$$\mathrm{NH_4HS} \rightleftharpoons \mathrm{H_2S} + \mathrm{NH_3}.$$

The active mass of the solid ammonium hydrosulphide, $a_1 - \xi$, will be constant, say, c_1, and the concentration of the ammonia, $a_2 + \xi$, and of hydrogen sulphide, $b_2 + \xi$, when the system is in equilibrium, will be proportional to the respective partial pressures of these gases, say, p_1 and p_2. Hence—

$$p_1 \times p_2 = \text{constant} = c. \quad . \quad . \quad . \quad . \qquad (2)$$

Isambert's experiments are usually quoted in illustration of this formula. The experiments were performed by adding one of the products of dissociation to the dissociating ammonium hydrosulphide. The total pressure always remained constant for a definite temperature, as the following results show:—

$p_1(\mathrm{NH_3})$	$p_2(\mathrm{H_2S})$	Constant.
208	294	61,152
138	450	63,204
417	146	60,882
452	143	64,779

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[1] A. Bineau, *Ann. Chim. Phys.* [2], **64**. 416, 1838; H. St. Claire Deville and L. Troost, *Compt. Rend.*, **56**. 891, 1863; **88**. 1239, 1879; A. Horstmann, *Liebig's Ann. Suppl.*, **6**. 51, 1868; G. Salet, *Compt. Rend.*, **86**. 1080, 1878; A. Moitessier and R. Engel, *ib.*, **88**. 1201, 1353, 1879; F. Isambert, *ib.*, **92**. 919, 1881; **93**. 731, 1881; **94**. 958, 1882.

These results are affected by a small error arising from the presence of the vapour of undissociated ammonium sulphide. This exerts a small measurable pressure which has been neglected.

At 25·1° the total pressure exerted by the dissociating ammonium sulphide is 501 mm. This is the sum of the partial pressures exerted by the ammonia and the hydrogen sulphide. But equal volumes of these gases are present, and each gas contributes half of the total pressure, 501 mm. Hence—

$$p_1 \times p_2 = \tfrac{1}{4}(501)^2 = 62{,}700 \text{ mm.}$$

A result in close agreement with the mean—62,504—of the observed values of this constant.

These results hold good provided the ammonium sulphide is heated in an exhausted vessel or in a vessel filled with a gas which exerts no chemical action upon the products of dissociation.

If one of the dissociating gases be present in excess, the product of the two partial pressures must still have the same constant value as before, and therefore a much smaller amount of ammonium hydrosulphide will dissociate. This is shown in the fourth column of the following table due to Isambert:—

Pressure before dissociation.		Total pressure at equilibrium.	Pressure due to gases from NH_4HS.	At equilibrium.		Constant.
NH_3	H_2S			p_1	p_2	
0	0·0	50·1	50·1	25·05	25·05	627
0	8·6	50·4	41·8	20·09	29·50	616
32	0·0	59·6	27·6	45·8	13·80	632

A disturbing factor arises from the fact that when one of the gases is present in excess and the system is in equilibrium, if the pressure be increased, equal volumes of hydrogen sulphide and ammonia recombine to form solid ammonium hydrosulphide. When equilibrium is again restored, the relative proportions of the ammonia and hydrogen sulphide remaining in the vessel will not be the same as before; conversely, if the pressure be diminished, some ammonium sulphide will be vaporized, and the relative proportions of the component gases will change.

CASE 2.—*A solid decomposes into one solid and one gas.* A much-quoted example occurs during the dissociation of calcium carbonate in the so-called process of "lime burning." A solid substance, calcium carbonate (A_1), furnishes upon dissociation a solid, calcium oxide (A_2), and a gas carbon dioxide (B_2). Hence—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The phenomenon was first studied by Debray, and later by Raoult.[1] According to the latter, the chemical view of the process is—

$$2CaCO_3 \rightleftharpoons (CaO)_2CO_3 + CO_2.$$

For equilibrium, using the former view of the process—

$$k_1(a_1 - \xi) = k_2(a_2 + \xi)(b_2 + \xi). \quad . \quad . \quad . \quad (3)$$

The active mass of the calcium carbonate, $a_1 - \xi$, and of the calcium monoxide, $a_2 + \xi$, are constant, say, c_1 and c_2 respectively; and the amount of carbon dioxide, $b_2 + \xi$, will be proportional to the pressure, p, of the gas; hence—

$$\frac{k_1c_1}{k_2c_3} = p\text{; or, } p = \text{constant,}$$

which is borne out by experiment. p remains constant at any definite temperature whatever amounts of calcium carbonate or of calcium monoxide may be present. Hence, p varies only with the temperature.

Similar results have been obtained for the dissociation of oxyhæmaglobin[2]—

$$\text{Oxyhæmaglobin} \rightleftharpoons \text{hæmaglobin} + \text{oxygen};$$

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[1] H. Debray, *Compt. Rend.*, **64**. 603, 1867; A. F. Wienhold, *Pogg. Ann.*, **149**. 221, 1879; L. Gmelin's *Handbuch der Chemie*, Heidelberg, **1**. 397, 1875; C. Birnbaum and M. Mahn, *Bull. Soc. Chim.* [2], **34**. 88, 1880; F. M. Raoult, *Compt. Rend.*, **92**. 189, 1110, 1457, 1881.

[2] G. Hüfner, *Zeit. physiol. Chem.*, **10**. 218, 1886; **13**. 285, 1889; V. Henri, *Compt. Rend.*, **138**. 572, 1904; A. Loewy and N. Zuntz, *Arch. f. Anat. Physiol.* (*Physiol. Abt.*), 166, 1904.

the dissociation of chloral hydrate;[1] of the ammonio-chlorides of silver, zinc, manganese, and mercury;[2] of ammonio-iodides and cyanides of silver; of manganese and silver carbonates;[3] of the oxides of mercury,[4] iridium,[5] lead,[6] and silver;[7] of barium peroxide;[8] of metallic hydrides;[9] of chlorine and bromine hydrate;[10] of ammonium chloride, cyanide, and sulphide;[11] of mercurous chloride;[12] of alkyl ammonium hydrosulphides;[13]

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[1] J. B. A. Dumas, *Ann. Chim. Phys.* [2], **56.** 132, 136, 1834; A. Naumann, *Ber.*, **9.** 822, 1876; **12.** 731, 1879; L. Troost, *Compt. Rend.*, **84.** 708, 1877; **85.** 32, 400, 1877; **86.** 1021, 1394, 1878; **89.** 229, 306, 1879; *Ann. Chim. Phys.* [5], **13.** 407, 1878; [5], **22.** 152, 1881; A. Wurtz, *Compt. Rend.*, **84.** 977, 1262, 1877; **85.** 49, 1877; **86.** 1170, 1878; **89.** 1062, 1879; A. Moitessier and R. Engel, *ib.*, **86.** 971, 1878; **88.** 285, 861, 1879; **90.** 97, 1880; H. St. Claire Deville, *ib.*, **89.** 803, 1879; E. Wiedemann and R. Schulze, *Wied. Ann.*, **6.** 293, 1879.

[2] A. Horstmann, *Ber.*, **9.** 749, 1876; F. Isambert, *Compt. Rend.*, **66.** 1259, 1868; **70.** 456, 1870; R. Jarry, *Compt. Rend.*, **124.** 288, 1897; **126.** 1138, 1898; *Ann. Chim. Phys.* [7], **17.** 327, 1899 (compounds of silver halides with ammonia, and with methylamine).

[3] L. Joulin, *Ann. Chim. Phys.* [4], **30.** 276, 1873.

[4] J. Myers, *Ber.*, **6.** 11, 1873; H. Debray, *Compt. Rend.*, **77.** 123, 1873; H. Pélabon, *ib.*, **128.** 825, 1899; *Mém. Soc. Sciences phys. Nat. Bordeaux* [5], **5.** 59, 1899.

[5] H. St. Claire Deville and H. Debray, *Compt. Rend.*, **87.** 441, 1878.

[6] H. le Chatelier, *Bull. Soc. Chim.* [3], **17.** 791, 1897.

[7] A. Guntz, *Compt. Rend.*, **128.** 997, 1899; M. Berthelot, *Ann. Chim. Phys.* [7], **22.** 289, 1901.

[8] J. Boussingault, *Ann. Chim. Phys.* [5], **19.** 464, 1880.

[9] L. Troost and P. Hautefeuille, *Compt. Rend.*, **78.** 686, 807, 968, 1874; **80.** 788, 1875.

[10] F. Isambert, *Compt. Rend.*, **86.** 481, 1878; H. W. B. Roozeboom, *Rec. Travs. Pays-Bas*, **3.** 59, 73, 1884; **4.** 69, 1886; H. le Chatelier, *Compt. Rend.*, **99.** 1074, 1884.

[11] H. St. Claire Deville, *Leçons faites à la Société chimique*, 360, 1864; L. Pebal, *Liebig's Ann.*, **123.** 199, 1862; *Ann. Chim. Phys.* [3], **67.** 93, 1863; O. Strauss, *Exner's Repert. d. Phys.*, **21.** 501, 1884; A. Wurtz, *Leçons faites à la Société chimique*, 77, 1863; *Association française*, Lyon, 288, 1873; C. Marignac, *Bull. Soc. Chim.* [2], **2.** 225, 1869; F. Isambert, *Compt. Rend.*, **93.** 731, 1881; **94.** 958, 1882; **95.** 1355, 1882; *Ann. Chim. Phys.* [5], **28.** 332, 1883.

[12] H. Debray, *Compt. Rend.*, **83.** 30, 1876.

[13] J. Walker and J. S. Lumsden, *Journ. Chem. Soc.*, **71.** 428, 1897.

of phosphonium chloride and bromide;[1] of cadmium hexammonium chloride; of mercury diammonium chloride;[2] of the ammonio-lithium halides;[3] of the ammonio-copper chlorides and sulphates;[4] of compounds of metallic hydrides with sulphur dioxide;[5] of salts containing water of crystallization,[6] etc.

In solution we have the dissociation of solid diphenylene picrate into diphenylene and picric acid,[7] and of urea picrate, oxalate, and nitrate into urea and the corresponding acid.

§ 52. Influence of an Excess of one of the Products of Dissociation.

For the sake of fixing our ideas, let us examine the result of adding chlorine to dissociating phosphorus pentachloride—

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

The condition of equilibrium is that—

$$K\frac{1-\xi}{v} = \frac{\xi}{v}\cdot\frac{\xi}{v}, \quad \ldots \ldots \quad (1)$$

where x denotes the number of gram-molecules of chlorine present in v volumes. Now add nv volumes of chlorine, or of PCl_3. The total volume becomes $(n+1)v$, and the total mass of the chlorine $(n+1)\xi$. The condition of equilibrium under the new conditions is—

$$K\frac{1-\xi}{(n+1)v} = \frac{\xi}{(n+1)v}\cdot\frac{(n+1)\xi}{(n+1)v}, \quad \ldots \quad (2)$$

which reduces to the original equation (1) when the factors

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[1] F. Isambert, *Compt. Rend.*, **96**. 643, 1883.

[2] W. R. Lang and A. Rigaut, *Compt. Rend.*, **129**. 294, 1899; M. François, *ib.*, **129**. 296, 1899.

[3] J. Bonnefoi, *Ann. Chim. Phys.* [7], **23**. 317, 1901; *Compt. Rend.*, **127**. 367, 516, 1898; **130**. 1394, 1900.

[4] A. Bouzat, *Compt. Rend.*, **135**. 292, 534, 1902.

[5] E. Péchard, *Compt. Rend.*, **130**. 1188, 1900.

[6] A. Findlay's *The Phase Rule and its Applications*, London, 82, 1904.

[7] J. Walker and J. R. Appleyard, *Journ. Chem. Soc.*, **69**. 1341, 1896.

$n + 1$ are cancelled out. This means that the addition of chlorine does not affect the dissociation of PCl_5.

This conclusion does not contradict the familiar statement that "the presence of an excess of one of the products of the dissociation prevents the dissociation of phosphorus pentachloride." In the text we are dealing with a constant pressure and variable volume, the observation just quoted refers to a variable pressure and constant volume. The student will see this on setting up the corresponding equilibrium equations.

When hydrogen iodide dissociates, according to the equation—

$$2HI \rightleftharpoons H_2 + I_2$$

the condition of equilibrium of which is—

$$K\left(\frac{1 - 2\xi}{v}\right)^2 = \frac{\xi}{v} \cdot \frac{\xi}{v},$$

where ξ denotes the number of gram-molecules of hydrogen or of iodine present in the system. Now add nv volumes of hydrogen or of iodine, and we have the momentary relation—

$$K\left(\frac{1 - 2\xi}{(n + 1)v}\right)^2 = \frac{(n + 1)\xi}{(n + 1)v} \cdot \frac{\xi}{(n + 1)v}.$$

The factor $n + 1$ does not cancel out, and consequently the left side of the equation is less than is required by the condition of equilibrium. Hence the dissociation will be forced back, or the products of dissociation will recombine to form the original gas, HI.

Now consider the dissociation of ammonium carbamate—

$$NH_4.COONH_2 \rightleftharpoons 2NH_3 + CO_2.$$

For equilibrium—

$$K\frac{1 - \xi}{v} = \left(\frac{2\xi}{v}\right)^2 \frac{\xi}{v}.$$

Now add nv of carbon dioxide, and we have momentarily the relation—

$$K\frac{1 - \xi}{(n + 1)v} = \left(\frac{2\xi}{(n + 1)v}\right)^2 \frac{(n + 1)\xi}{(n + 1)v}.$$

The factor $n + 1$ does not cancel out, and the right-hand side is less than what it should be for equilibrium. Hence, dissociation of the carbamate sets in.

If nv volumes of ammonia had been added—

$$K\frac{1 - \xi}{(n + 1)v} = \left(\frac{2(n + 1)\xi}{(n + 1)v}\right)^2 \frac{\xi}{(n + 1)v},$$

We get the original equation when the factors $n + 1$ are cancelled out. Consequently, the dissociation will not be changed.

It is therefore evident that we may get an increase, decrease, or no change when one of the products of dissociation is added to a system in a state of equilibrium.

Similar reasoning may be applied to reactions like—

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O,$$

where the condition for equilibrium is—

$$K\frac{a - \xi}{v} \cdot \frac{b - \xi}{v} = \frac{c + \xi}{v} \cdot \frac{d + \xi}{v};$$

if nv volumes of water vapour are added, we shall find on setting up the corresponding equation that the amount of ester formed will be decreased.

Some interesting problems on the application of the mass law to technical operations might now be made. In 1875, for example, C. Winkler[1] said that the best condition for the oxidation of sulphur dioxide occurs when two volumes of sulphur dioxide are mixed with one volume of oxygen, so that—

$$2SO_2 + O_2 \rightleftharpoons 2SO_2.$$

But let us apply the law of mass action.

$$C^2_{SO_2}.C_{O_2} = KC^2_{SO_3}; \ \therefore \frac{C_{SO_3}}{C_{SO_2}} = \sqrt{\frac{C_{O_2}}{K}}$$

This means that the greater the concentration of the oxygen, the greater will be the amount of sulphur trioxide formed, and the less the amount of sulphur dioxide which escapes oxidation.

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[1] C. Winkler, *Dingler's Polyt. Journ.*, **218**. 128, 1875; *Journ. Chem. Soc.*, **29**. 783, 1876; O. Sackur, *Zeit. Elektrochem.*, **8**. 77, 1902.

§ 53. Multi-molecular Homogeneous Equilibria.

For the sake of illustration, let us consider the action of three acids—say, hydrochloric, oxalic, and sulphuric acids—in competition for the base sodium. From the principle of the mutual independence of different reactions, the velocity of each individual reaction will be independent of the presence of other reactions simultaneously taking place in the same system. We can then attack the problem by considering the separate reactions—

$$\text{(i.)}\ Na_2SO_4 + 2HCl \rightleftharpoons H_2SO_4 + 2NaCl;$$
$$\text{(ii.)}\ Na_2SO_4 + H_2C_2O_4 \rightleftharpoons H_2SO_4 + Na_2C_2O_4;$$
$$\text{(iii.)}\ Na_2C_2O_4 + 2HCl \rightleftharpoons H_2C_2O_4 + 2NaCl;$$

with the following equations of equilibrium—

$$\text{(i.)}\ k_1(b_3 + \xi)(a_1 - \xi) = k_3(a_3 - \xi)(b_1 + \xi);$$
$$\text{(ii.)}\ k_2(b_3 + \xi)(a_2 - \xi) = k_4(a_3 - \xi)(b_2 + \xi);$$
$$\text{(iii.)}\ k_5(b_2 + \xi)(a_1 - \xi) = k_6(a_2 - \xi)(b_1 + \xi),$$

respectively; and also, (14), § 50—

$$k_1\frac{a_1 - \xi}{b_1 + \xi} = k_2\frac{a_2 - \xi}{b_2 + \xi} = k_3\frac{a_3 - \xi}{b_3 + \xi} = k_4\frac{a_3 - \xi}{b_3 + \xi} = k_5\frac{a_1 - \xi}{b_1 + \xi} = k_6\frac{a_2 - \xi}{b_2 + \xi}.$$

From these identical equations, it follows that—

$$k_1 = k_2;\ k_2 = k_6;\ k_3 = k_4.$$

Hence the condition of equilibrium may be written—

$$k_1\frac{a_1 - \xi}{b_1 + \xi} = k_2\frac{a_2 - \xi}{b_2 + \xi} = k_3\frac{a_3 - \xi}{b_3 + \xi}. \quad . \quad . \quad . \quad (1)$$

The constants k_1, k_2, k_3, are to be evaluated in the usual way. For the above-mentioned acids Guldberg and Waage found that $k_1 = 1$, $k_2 = 0{\cdot}25$, $k_3 = 0{\cdot}0676$. Now write—

$$a_1 - \xi = z(b_1 + \xi). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence—

$$\frac{a_2 - \xi}{b_2 + \xi} = \frac{k_1}{k_2}z;\ \frac{a_3 - \xi}{b_3 + \xi} = \frac{k_1}{k_3}z. \quad . \quad . \quad . \quad . \quad (3)$$

It is also evident that—

$$(a_1 - \xi) + (b_1 + \xi) = (z + 1)(b_1 + \xi) = a_1 + b_1. \quad (4)$$

In this manner it can be shown that—

$$b_1 + \xi = \frac{a_1 + b_1}{1 + z};\ b_2 + \xi = \frac{a_2 + b_2}{1 + \frac{k_1}{k_2}z};\ b_3 + \xi = \frac{a_3 + b_3}{1 + \frac{k_1}{k_3}z}. \quad (5)$$

Since—

$$(a_1 - \xi) + (b_1 + \xi) = a_1 + b_1;\ (a_2 - \xi) + (b_2 + \xi) = a_2 + b_2;\ \ldots$$

we must have—

$$a_1 - \xi + a_2 - \xi + a_3 - \xi = a_1 + a_2 + a_3.$$
$$b_1 + \xi + b_2 + \xi + b_3 + \xi = b_1 + b_2 + b_3.$$

Substituting equation (5) in the last result—

$$\frac{a_1 + b_1}{1 + z} + \frac{a_2 + b_2}{1 + \frac{k_1}{k_2}z} + \frac{a_3 + b_3}{1 + \frac{k_1}{k_3}z} = b_1 + b_2 + b_3. \quad . \quad (6)$$

We can evaluate z by solving this equation of the third degree in the usual way. Given z, we can calculate the distribution of the three acids, $a_1 - \xi$, $a_2 - \xi$, $a_3 - \xi$, at equilibrium from equations (2) and (3); and from these results, by means of equation (3), we can calculate the distribution of the three salts, $b_1 + \xi$, $b_2 + \xi$, and $b_3 + \xi$, at equilibrium.

Suppose that we started an experiment with—

$$a_1 = 1;\ a_2 = 0;\ a_3 = 1;\ b_1 = 0;\ b_2 = 1;\ b_3 = 0,$$

from equation (6), and the above-mentioned values of k—

$$\frac{1}{1 + z} + \frac{1}{1 + 4z} + \frac{1}{1 + 14 \cdot 8z} = 1;\ \text{or, } z = 0 \cdot 62.$$

When equilibrium sets in, the system will therefore contain—

$$0 \cdot 62 NaCl + 0 \cdot 29 Na_2SO_4 + 0 \cdot 10 Na_2C_2O_4 + 0 \cdot 38 HCl$$
$$+ 0 \cdot 71 H_2SO_4 + 0 \cdot 90 H_2C_2O_4.$$

The application of the law to the dissociation of gases may be done in a simple manner. In illustration let us take Le Chatelier's[1] investigation upon the dissociation of carbon dioxide at high temperatures—

$$2CO_2 \rightleftharpoons 2CO + O_2.$$

Since we are dealing with gases, we can substitute the partial

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[1] H. le Chatelier, *Zeit. phys. Chem.*, **2**. 782, 1888.

pressure of each component in place of the usual expression for concentration. The reaction is bimolecular from left to right, and termolecular from right to left. The condition of equilibrium is that—

$$k_1p_1^2 = k_2p_2^2p_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where p_1, p_2, and p_3 respectively denote the partial pressures of carbon dioxide, carbon monoxide, and of oxygen.

The degree of dissociation can be determined at any temperature by the vapour density method, and it is possible to calculate the degree of dissociation for all pressures by means of formula (8). This may be left as an exercise for the student. The general expression is—

$$K = \frac{k_1}{k_2} = \frac{x^3}{2(1 + x)(1 - x)^2}P, \quad . \quad . \quad . \quad (8)$$

where P denotes the total pressure of the mixed gases, and x the amount of carbon dioxide decomposed.

Deville[1] found that at 3000° and a pressure of one atmosphere, about 40 per cent. of carbon dioxide is decomposed; *i.e.* $x = 0·4$. Hence, from (8), it follows that at this temperature and a pressure of 0·001 atmosphere, 94 per cent., and at a pressure of 100 atmospheres, 10 per cent. of carbon dioxide would dissociate. The following table, calculated from Le Chatelier's experiments, represents the percentage decomposition of carbon dioxide at different temperatures and pressures:—

Temp.	Pressures.					
	0·001	0·01	0·1	1·0	10·0	100·0
1000	0·7	0·3	0·13	0·06	0·03	0·015
1500	7·0	3·5	1·7	0·8	0·4	0·2
2000	40·0	12·5	8·0	4·0	3·0	3·5
2500	81·0	60·0	40·0	19·0	9·0	4·0
3000	94·0	80·0	60·0	40·0	21·0	10·0
3500	96·0	85·0	70·0	53·0	32·0	15·0
4000	97·0	90·0	80·0	63·0	45·0	25·0

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[1] H. St. Claire Deville, *Compt. Rend.*, **56**. 195, 322, 1863; **59**. 873, 1864; **60**. 317, 1865.

Some important deductions can be drawn from these figures. In the smelting furnace, the temperature of which is about 2000°, the partial pressure of the carbon dioxide present is about 0·2 atmosphere. Hence only about 5 per cent. of carbon dioxide is decomposed. The heat necessary for effecting the decomposition of the carbon dioxide is derived from the furnace, thus lowering the temperature to a slight extent. In flames, the partial pressure of the carbon dioxide is only about 0·1 atmosphere, the temperature about 2000°, hence about 8 per cent. of carbon dioxide will be decomposed. This lowers the temperature of the flame about 8 per cent. The temperature attained during the explosion of gases lies between 2500° and 3000°. But the pressure of the exploding gases is some thousand atmospheres, hence it follows that the dissociation of the carbon dioxide can have no influence on the temperature attained by the exploding gases.

§ 54. Multi-molecular Heterogeneous Equilibria.

For example, if we start with a_1 gram-equivalents of barium sulphate, b_1 of barium carbonate; a_2 of potassium sulphate, b_2 of potassium carbonate; and a_3 of sodium sulphate, b_3 of sodium carbonate,[1] for equilibrium—

$$\frac{a_1 - \xi}{b_1 + \xi} = \text{constant} = c_1; \quad c_1\frac{k_1}{k_2} = c_2; \quad c_1\frac{k_1}{k_2} = c_3.$$

Hence—

$$\frac{a_2 - \xi}{b_2 + \xi} = c_2; \quad \frac{a_3 - \xi}{b_3 + \xi} = c_3. \quad . \quad . \quad . \quad . \quad (9)$$

If x and y respectively denote the quantities of potassium and sodium sulphates transformed into potassium and sodium carbonates—

$$x = \frac{a_2 - c_2 b_2}{1 + c_2}; \; y = \frac{a_3 - c_3 b_3}{1 + c_3}. \quad . \quad . \quad . \quad (10)$$

The sum $x + y$ represents the amount of barium carbonate transformed into barium sulphate; and if $x + y$ be negative, we are

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[1] See M. Berthelot (*Compt. Rend.*, **80**. 1564, 1875), “On the partition of an acid with several bases.”

dealing with the transformation of barium sulphate into barium carbonate. Guldberg and Waage found for this reaction—

$$c_2 = \tfrac{1}{4};\ c_3 = \tfrac{1}{5}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Initial concentrations.				$BaCO_3$	
K_2SO_4 a_2	K_2CO_3 b_2	Na_2SO_4 a_3	Na_2CO_3 b_3	Obs.	Calc.
0	0·5	0·0	0·5	0·164	0·183
0	1·0	0·0	1·0	0·367	0·367
0	0·5	0·0	3·5	0·735	0·693
0	1·5	0·0	2·5	0·702	0·717
0	2·0	0·25	0·0	0·187	0·192

§ 55. More Complex Examples.

If a solid decomposes into three gases, the simplest way of dealing with the problem is to write the condition of equilibrium—

$$k_1(a_1 - \xi) = k_2(b_1 + \xi)(b_2 + \xi)(b_3 + \xi).$$

But $a_1 - \xi$ represents the concentration of the solid. At equilibrium, this is constant. $b_1 + \xi$, $b_2 + \xi$, and $b_3 + \xi$ represent the concentration of the gaseous products of the dissociation, and as these are respectively proportional to the partial pressures p_1, p_2, p_3 of these gases, we may write—

$$p_1 \cdot p_2 \cdot p_3 = \text{constant} = c, \text{ say.} \quad . \quad . \quad . \quad (12)$$

Horstmann[1] first applied the law of mass action to the dissociation of solid compounds in 1877, using the dissociation of solid ammonium carbamate into gaseous ammonia and carbon dioxide.

$$NH_4OCONH_2 \rightleftharpoons 2NH_3 + CO_2.$$

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[1] A. Horstmann, *Liebig's Ann.*, **170**. 192, 1873; **187**. 48, 1877; A. Naumann, *ib.* (*Suppl.*), **5**. 341, 1867; **159**. 334, 1871; A. Bineau, *Ann. Chim. Phys.* [2], **67**. 235, 1838; [1], **68**. 434, 1838; H. Rose, *Pogg. Ann.*, **46**. 353, 1839. For application of the thermodynamical laws: J. Moutier, *Compt. Rend.*, **72**. 759, 1871; M. Peslin, *Ann. Chim. Phys.* [4], **24**. 208, 1871.

This is obviously a special case of (12), in which $p_1 = p_3$, say; hence—

$$p_1^2 \cdot p_3 = \text{constant}.$$

The partial pressure of the ammonia is two-thirds of the total pressure, and the partial pressure of the carbon dioxide is one-third of the total pressure. Equilibrium sets in when the product of the partial pressure of the carbon dioxide with the square of the partial pressure of the ammonia has a constant value. The addition of ammonia will therefore depress the total pressure more than the addition of an equal volume of carbon dioxide would. See § 52. Horstmann's conclusions were verified by Isambert's[1] experiments in 1881.

Another interesting example is the reaction—

$$3\text{Fe (solid)} + 4\text{H}_2\text{O (gas)} \rightleftharpoons \text{Fe}_3\text{O}_4 \text{ (solid)} + 4\text{H}_2 \text{ (gas)},$$

studied by Deville.[2] The condition of equilibrium is obviously—

$$\frac{p_1^4}{p_2^4} = \text{constant} = c; \ \therefore \frac{p_1}{p_2} = \sqrt[4]{c} = \text{constant}. \quad . \quad (13)$$

Equilibrium is therefore determined by the ratio of the pressure of the water vapour to that of the hydrogen, as the numbers in the following table will show:—

Temp.	Pressure of steam. p_1	Pressure of hydrogen. p_2	Constant.
200°	4·6	95·9	0·048
200	9·7	195·3	0·049
440	4·6	25·8	0·178
440	10·1	57·9	0·174

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[1] F. Isambert, *Compt. Rend.*, **93.** 731, 1881; **97.** 1212, 1883. For the dissociation of lead nitrate into solid lead monoxide, oxygen, and nitrogen peroxide, see L. Baekeland, *Journ. Amer. Chem. Soc.*, **26.** 391, 1904; J. L. R. Morgan, *Journ. Phys. Chem.*, **8.** 416, 1904.

[2] H. St. Claire Deville, *Compt. Rend.*, **70.** 1105, 1201, 1870; **71.** 30, 1870; H. Debray, *ib.*, **88.** 1341, 1879; *Liebig's Ann.*, **157.** 76, 1870; and more recently by G. Preuner, *Zeit. phys. Chem.*, **47.** 385, 1904.

If water vapour be passed over iron, the ratio $p_1 : p_2$ is *greater* than the above constant, and chemical change will go on until all the iron is converted into oxide; when hydrogen is passed over the oxide, the ratio $p_1 : p_2$ is *less* than the above constant, and consequently the oxide will be reduced. At about 1500° this ratio is unity, and if a mixture of equal volumes of water vapour and hydrogen be passed over either the metal or its oxide at this temperature, no chemical change will take place.

I. Lowthian Bell[1] recognized clearly the working of the "mass law" in the reduction of iron by the furnace gases of the blast furnace as early as 1869. "Iron oxide," he says, "can only be completely reduced by carbon monoxide when an excess of the gas is present." He also pointed out the complex nature of the conditions of equilibrium which must subsist between metallic iron, carbon monoxide, free carbon, iron oxides of various kinds, and the carbon dioxide at different temperatures. Thus we have the following reactions taking place:—

$$3CO + Fe_2O_3 \rightleftharpoons 2Fe + 3CO_2;\ CO + Fe \rightleftharpoons FeO + C;$$
$$3C + Fe_2O_3 \rightleftharpoons 2Fe + 3CO;\ 2CO_2 \rightleftharpoons C + CO;\ \text{etc.}$$

A closer study of the complex changes which take place in the blast furnace in the light of modern physical chemistry is urgently required in the interests of the iron industry.[2]

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[1] I. Lowthian Bell, *Journ. Chem. Soc.*, **22**. 203, 1869; *Iron and Steel Institute*, **1**. 85, 1871; papers collected in *Chemical Phenomena of Iron and Steel Smelting*, London, 1872; *Principles of the Manufacture of Iron and Steel*, London, 1884.

[2] A number of investigators are at present working on this problem. Among the more recent publications we have O. Boudouard, *Ann. Chim. Phys.* [7], **24**. 5, 1901; *Bull. Soc. Chim.* [3], **21**. 269, 463, 465, 712, 1899; **23**. 137, 1900; **25**. 227, 282, 484, 833, 1901; A. Smits and L. K. Wolff, *Koninklije Akad. van Wetenschappen te Amsterdam*, 417, 1902; *Zeit. phys. Chem.*, **45**. 199, 1903; O. Hahn, *ib.*, **42**. 705, 1903; **44**. 513, 1903; E. Baur and A. Glaessner, *ib.*, **43**. 354, 1903; *Stahl und Eisen*, **23**. 536, 1903; R. Schenck and F. Zimmermann, *Ber.*, **36**. 445, 1903; G. Charpy, *Compt. Rend.*, **137**. 120, 1903.

§ 56. Evolution of the Law of Mass Action from 1777 to 1870.

It will be remembered, from § 1, how the old idea that the strength of chemical action depended upon the nature and not upon the quantity of reacting substance, culminated in the work of Bergmann. We have seen how Wenzel brought to light the important part played by quantity of matter on the result of a chemical change. In spite of this, Wenzel's discovery fell back into oblivion. Bergmann's theory still prevailed.

The next advance was embodied in some papers read by C. L. Berthollet to the Egyptian Institute[1] at Cairo in July, 1799.

Berthollet explained the presence of large quantities of "trona" (sodium carbonate), found on the shores of the natron lakes of Egypt, by assuming that the sodium chloride, brought in by the rivers, was decomposed by the calcium carbonate present on the banks of these lakes—

$$CaCO_3 + 2NaCl = CaCl_2 + Na_2CO_3.$$

Although it was recognized that this reaction is the reverse of what is usually obtained in the laboratory, Berthollet pointed out that the relatively large quantities of calcium carbonate on the banks of these lakes were apparently able to "strengthen" the weaker affinity of the carbon dioxide for sodium, and of chlorine for calcium. Wenzel's generalization is rediscovered.

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[1] This was an association at which papers were read by the savants who joined in the retinue of Napoleon Bonaparte for the purpose of studying the customs of the country during the Egyptian campaign of the youthful conqueror of the Mamelukes.

C. L. Berthollet, *Memoirs National Institut*, 3, 1799; published in a separate pamphlet, *Recherches sur les lois de l'affinite*, par le citoyen Berthollet, Paris, an IX. (1801); M. Farrell's trans., London, 1804; also *Annales de Chimie*, 36. 302, 1801; 37. 225, 1801; 38. 113, 1801; *Essai de Statique Chimie*, Paris, 1801–1802; B. Lambert's trans., *An Essay on Chemical Statics*, London, 1804; W. Ostwald's *Klassiker*, No. 74.

Berthollet opposes Bergmann's idea that "the result of chemical attraction or affinity between two bodies is to cause a change *wholly* in the direction of the stronger attraction unless this should be reversed by the more powerful attractive force of heat."

A number of experiments were also described illustrating the influence of mass upon the course of a chemical reaction. "I believe," said Berthollet, in his first communication, "that elective affinity does not in general act as a determinative force by means of which one body can be completely separated from another, but that in all decompositions there is a division of the . . . one substance, C, between two other substances, A and B, so that *an excess of quantity can compensate for a weakness of affinity*."

We are therefore indebted to Wenzel, and to Berthollet, for two important ideas, namely—

1. Chemical action is conditioned not only by the affinity, but also by the relative masses of the reacting bodies.
2. A chemical change may be more or less reversed by changing the masses of the reacting bodies. Chemical change does not always proceed in one direction.

In the light of the present day we readily recognize the importance of Berthollet's work, and we have done little more than set these inductions upon the irrefutable basis of experiment. From one point it might appear remarkable how little Berthollet was appreciated by his contemporaries, and what little influence his work had upon the subsequent development of chemistry. We can understand why this is so if we bear in mind that Berthollet laid very great stress upon the influence of mass. It was argued that if chemical action is so dependent upon mass, then the quantity of one substance, A, which will combine with a given quantity of another substance, B, depends upon the relative masses of A and B. Consequently it was inferred that two substances must be capable of combining in all proportions. This conclusion was thought to contradict the laws of constant composition and of multiple proportions set up by Proust and Dalton. Hence Berthollet's work was shelved.

Gay Lussac[1] seems to have seen the confusion in the ideas of Berthollet between the *composition* and the *relative amount* of the compound formed in a chemical reaction. Still many chemists hold that the "erroneous" conclusion of Berthollet is the only law of combination which can be justified by experiment.[2]

Berthollet's conception of "quantity of matter" was different from that which is usually read into the law. His measure of chemical action was "chemical mass," meaning the product of the mass of the substance with the strength of its affinity. In common with his contemporaries—Bergmann, Kirwan, etc.—Berthollet regarded "strength of affinity" as equivalent to "power of saturation." The smaller the amount of acid required to neutralize a certain quantity of the base, the greater the affinity. But this is nothing more than the "equivalent weight" of the acid. "Power of saturation," therefore, is inversely proportional to "equivalent weight." Hence Berthollet's measure of chemical action is obtained by dividing the mass of the substance by the equivalent weight. The quotient obviously represents the number of equivalents of the substance taking part in the reaction. Translating Berthollet's conception into modern language, therefore, it would read: when, say a base simultaneously reacts with two other substances, say two acids, the amount of base which combines with each acid will be proportional to the equivalent weight of the respective acid present in the system. For example, if one equivalent of sodium hydroxide is added to a mixture of equivalent amounts of sulphuric and nitric acids, half of the sodium will combine with the one acid and half with the other; if two equivalents of sulphuric acid and one equivalent of nitric acid are employed, two-thirds of the base

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[1] J. L. Gay Lussac, *Annales de Chimie*, **49.** 21, 1804; *Ann. Chim. Phys.* [2], **1.** 32, 1806; **30.** 291, 1825; **49.** 325, 1832; **70.** 407, 1839; V. Regnault, *ib.* [2], **62.** 337, 1836.

[2] C. R. A. Wright, *Phil. Mag.* [4], **43.** 241, 1872; E. J. Mills, *ib.* [5], **1.** 1, 1876; P. Duhem, *Le Mixte et la Combinaison Chimique*, Paris, 142, *seq.*, 1903; J. B. Biot, *Ann. Chim. Phys.* [3], **59.** 206, 1860.

will unite with the sulphuric acid and one-third with the nitric acid. The tacit assumption is made that the equivalents of all acids are equal to one another.

Berthollet early recognized the influence of the physical state of the reacting bodies upon the result of a chemical reaction. "The simple law of mass action," said Berthollet, "only holds for homogeneous mixtures. When substances appear in a different state of aggregation, the state of equilibrium is disturbed." The influence of "cohésion" (*i.e.* separation of a solid) and of "elasticité" (*i.e.* separation of a gas) on the results of a chemical action were clearly explained. He showed how equilibrium is first established in the usual way, but when one of the substances separates out in a different state of aggregation, a fresh quantity of substance is formed; this is again separated, and the process repeats itself until the solid or gas is completely removed from the changing system. According to Berthollet, a chemical reaction carried to completion is an abnormal condition induced by a difference in the state of aggregation of the reacting components.

Interest in the subject was aroused in 1835, when J. Persoz[1] reclaimed the merits of Bergmann's theory over that of Berthollet. The subject attracted the attention of Rose,[2] who recognized the important part played by mass action in the operations of analytical chemistry. For example, Rose showed that the alkaline sulphides are decomposed by water—

$$2H_2O + CaS = H_2S + Ca(OH)_2,$$

in spite of the fact that the affinity of hydrogen sulphide for the corresponding hydroxide can produce alkaline sulphide and water. Rose also pointed out a number of other examples illustrating how necessary it is to pay attention to the relative quantities of the substances taking part in the reactions. Although silicate rocks (granite and feldspar) will resist the

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[1] J. Persoz, *Ann. Chim. Phys.* [2], **58**. 180, 1835.

[2] H. Rose, *Pogg. Ann.*, **55**. 415, 1842; **82**. 545, 1851; **94**. 481, 1855; **95**. 92, 284, 426, 1885; O. Henry, *Journ. Chim. Med.*, **1**. 257, 317, 380, 1825.

action of the most powerful acids, yet the "weathering" of these rocks shows that they are undergoing continual decomposition by the action of the most feeble of chemical agents—water and carbon dioxide.

The next important contribution to the subject was made by Wilhelmy[1] in 1850. His was the first successful attempt to establish the law of mass action in a quantitative manner. Here we find the differential equation first employed to represent the course of a chemical reaction. Wilhelmy varied the temperature, the concentration of the sugar and of the acid. He also tried the effect of different acids, but he did not arrive at any general conclusion beyond the fact that the rate of chemical action, at any moment, is proportional to the amount of substance undergoing transformation. Löwenthal and Lenssen[2] extended Wilhelmy's work, and showed that the velocities with which the acids invert cane sugar is proportional to the strengths of the acids. Hence it was inferred that the rates at which different acids invert sugar might be used to measure the relative strengths of the acids.

Confirmatory facts were published by Biot[3] (1835) on the action of water and of boric acid upon tartaric acid; by Gerhardt[4] (1847) on the composition of the precipitates formed when potassium hydroxide is added to an excess of copper sulphate, and when copper sulphate is added to an excess of potassium hydroxide, etc.; by Malaguti (1853)[5] on the reversibility of different reactions; by Margueritte[6] (1854) on the mutual solubility of sodium chloride and potassium chlorate,

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[1] L. Wilhelmy, *Pogg. Ann.*, **81**. 413, 499, 1850; W. Ostwald's *Klassiker*, No. 29.

[2] J. Löwenthal and E. Lenssen, *Journ. prakt. Chem.* [1], **85**. 321, 401, 1862.

[3] J. B. Biot, *Compt. Rend.*, **1**. 66, 1835; *Ann. Chim. Phys.* [3], **59**. 206, 1860; *Ann. Chim. Phys.* [3], **10**. 5, 175, 307, 385, 1844; **11**. 82, 1844; or, *Taylor's Scientific Memoirs*, **4**. 292, 1846.

[4] C. Gerhardt, *Journ. de Pharmacie* [3], **12**. 57, 1847; *Amer. Journ. Science* [2], **6**. 337, 1848.

[5] J. Malaguti, *Ann. Chim. Phys.* [3], **37**. 198, 1853; **51**. 328, 1857.

[6] F. Margueritte, *Compt. Rend.*, **38**. 304, 1854.

etc.; by Reynoso[1] (1855) on the reduction of copper salts by glucose; by Tissier[2] (1855) on the action of aluminium upon copper salts; by Gladstone[3] (1855) on the action of ferric salts upon potassium thiocyanate, etc.; by Scheerer[4] (1860) on the decomposition of sodium carbonate by silicic acid; and by Rainey[5] (1865) on the formation of double chlorides and oxalates. Excepting Wilhelmy's work, the investigations so far mentioned were mainly of a qualitative nature.

The dissociation of calcium carbonate is of great historical interest. Geologists used to wonder why marble or calcspar could be associated with igneous rocks, whose temperature, at certain geological epochs, must have greatly exceeded that of a lime-kiln. Hutton[6] pointed out in 1798 that the calcium carbonate in the lime-kiln only bears the pressure of the atmosphere, which is not sufficient to delay very long the separation of the molecules of carbon dioxide from the molecules of calcium oxide; whereas, in the igneous rocks, an enormous pressure must have hindered this decomposition, and allowed the calcium carbonate to melt and subsequently to crystallize. Hutton's theory was verified experimentally by Hall[7] in 1804; and in 1837 G. Aimé showed that "when a body is decomposed by heat, it is not the pressure of any gas or vapour chosen at random which can stop its decomposition; it is the gas which arises from the decomposition which alone can act."[8]

The dissociation of compounds under the influence of heat

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[1] A. Reynoso, *Compt. Rend.*, **41**. 278, 1855.

[2] C. Tissier, *Compt. Rend.*, **41**. 362, 1855.

[3] J. H. Gladstone, *Phil. Trans.*, **145**. 179, 1855; *Phil. Mag.* [4], **9**. 535, 1855; *Journ. prakt. Chem.* [1], **67**. 1, 1856; **88**. 449, 1863; *Journ. Chem. Soc.*, **9**. 54, 1856; **15**. 303, 1862.

[4] T. Scheerer, *Liebig's Ann.*, **116**. 129, 1860.

[5] G. Rainey, *Quart. Journ. Science*, **2**. 114, 1865.

[6] J. Hutton, *Trans. Roy. Soc. Edin.*, **4**. 7, 1798.

[7] J. Hall, *Trans. Roy. Soc. Edin.*, **5**. 43, 1805; *Nicholson's Journ.*, **4**. 8, 56, 1801.

[8] G. Aimé, *Thèse sur l'influence de la pression sur les actions chimiques*, Paris, 1837 (reprint, 1899); *Journ. Phys. Chem.*, **3**. 364, 1899.

was further investigated by Grove[1] in 1846, by Deville in 1857–64, and by Debray in 1867. As a result, it was found that "(1) the dissociation pressure of a solid is constant at a given temperature; (2) the pressure increases with temperature; (3) it is independent of the state of decomposition of the solid."

It is a remarkable fact that Deville thought that his experiments proved that mass had little or no influence on chemical action,[2] when to-day we know that these experiments furnish most conclusive evidence of the truth of this law.

Following this came the important work of Berthelot and Gilles,[3] of Harcourt and Esson,[4] and of Guldberg and Waage,[5] on the subject of mass action; and of Thomsen[6] on the thermal value of chemical reactions. These investigations have been so often quoted in various parts of this book that this brief mention will be sufficient.[7]

It may here be pointed out that J. W. Gibb's phase rule is the best system extant for the classification of equilibria—chemical and physical. All changes, both physical changes of

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[1] W. R. Grove, *Phil. Trans.*, **137.** 1, 1847; H. St. Claire Deville, *Compt. Rend.*, **45.** 857, 1857; **56.** 195, 729, 1864; **59.** 873, 1865; **60.** 317, 1865; *Leçons sur la Dissociation*, Paris, 1866; H. Debray, *Compt. Rend.*, **64.** 603, 1867.

[2] See influence of mass of solid in heterogeneous equilibria, p. 144.

[3] M. Berthelot and L. Péan de St. Gilles, *Ann. Chim. Phys.* [3], **65.** 385, 1862; **66.** 5, 1862; **68.** 225, 1863.

[4] A. V. Harcourt, *B.A. Reports*, 28, 1865; *Chem. News*, **10.** 171, 1864; **18.** 13, 1868; A. V. Harcourt and W. Esson, *Phil. Trans.*, **156.** 193, 1866; **157.** 117, 1867; **186.** 817, 1895; G. Lemoine's *Études sur les Équilibres Chimiques*, Paris, 1881.

[5] C. M. Guldberg and P. Waage, *Forhandlinger i Videnskabs-Selskabet i Christiania*, **35.** 92, 111, 1864; *Études sur les affinites chimiques*, Christiania, 1867; *Journ. prakt. Chem.* [2], **19.** 69, 1879; W. Ostwald's *Klassiker*, No. 104.

[6] J. Thomsen, *Pogg. Ann.*, **88.** 349, 1853; **90.** 261, 1853; **91.** 83, 1854; **92.** 34, 1854; **138.** 65, 1869.

[7] A study of this subject from the thermodynamical aspect will be found in F. G. Donnan's *Thermodynamics;* in J. S. Siegrist, *Ahrens' Sammlung*, **7.** 137, 1902; in P. Chroustchoff's *Introduction a l'étude des Équilibres chimiques*, Paris, 1894; etc.

state and changes of chemical composition, are found to depend upon the same general laws. For these the reader must consult a suitable text-book.[1]

§ 57. Alleged Deviation from the Law of Mass Action.

In 1853 R. Bunsen[2] thought that he had discovered a deviation from the simple law of mass action. Bunsen alleged that if a mixture of carbon dioxide and hydrogen gases be exploded with a quantity of oxygen not sufficient to oxidize the mixed gases completely, the oxygen will divide itself between the carbon monoxide and hydrogen, not in proportion to their quantities present, but so that the quantities of carbon dioxide and water formed will stand in some simple ratio. Thus on exploding a mixture of carbon monoxide, hydrogen, and oxygen, Bunsen found that—

$$CO_2 : H_2O = 1 : 1 ;$$

an increase in the quantity of hydrogen made no change in the value of the ratio $CO_2 : H_2O$ until, when sufficient hydrogen had been added, it *suddenly* jumped to—

$$CO_2 : H_2O = 1 : 2 ; \; .$$

on again increasing the amount of hydrogen, the value of this ratio remained at 1 : 2 until it suddenly jumped to—

$$CO_2 : H_2O = 1 : 3.$$

Similarly, by increasing the amount of carbon monoxide, the ratio suddenly jumped from—

$$CO_2 : H_2O = 1 : 1 \text{ up to } 2 : 1.$$

Some of Bunsen's experimental data are shown in the subjoined table. From this Bunsen inferred the existence of a peculiar

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[1] A. Findlay's *The Phase Rule and its Applications*, *l.c.* The facts discussed in this chapter should be reclassified by the student in the light of this work.

[2] R. Bunsen, *Liebig's Ann.*, 85. 131, 1853; *Gasometrische Methoden*, Braunschweig, 349, 1877.

force tending not only to produce definite whole bodies, but also to produce them in definite proportions.

Composition of the original mixture.			Relative amounts oxidized.		Ratio of $CO_2 : H_2O$ produced.
CO	H	O	CO	H	
72·57	18·24	9·14	12·18	6·10	2 : 1
59·93	26·71	13·36	13·06	13·66	1 : 1
59·00	40·00	20·00	6·80	13·20	1 : 2
36·70	42·17	21·13	10·79	31·47	1 : 3
40·12	47·15	12·73	4·97	20·49	1 : 4

E. von Meyer[1] followed up Bunsen's work and concluded, with Bunsen, that the proportions in which the oxygen is distributed between the carbon monoxide and hydrogen alters *per saltum*, and although the ratio $CO_2 : H_2O$ was not always so simple as Bunsen supposed, yet this proportion may always be expressed by whole numbers like—

17 : 18; 18 : 19; etc.

Bunsen's conclusions were apparently confirmed by the experiments of his pupil Debus[2] on the fractional precipitation of barium and calcium carbonates from a solution of barium and calcium hydrates. Debus appears to have thought that the ratio of the precipitates $BaCO_3 : CaCO_3$ varied *per saltum*, although he represented his experimental results by an algebraic expression which involved no discontinuity. Nor did Debus in his later paper regard his sudden changes as real discontinuities.[3]

It appears from the work of Horstmann[4] and of Dixon[5] that

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[1] E. von Meyer, *Journ. prakt. Chem.* [2], **10**. 273, 1874; see also p. 471.

[2] H. Debus, *Liebig's Ann.*, **85**. 103, 1853; **86**. 156, 1853; **87**. 238, 1853.

[3] E. J. Mills, *Phil. Mag.* [4], **48**. 241, 1874.

[4] A. Horstmann, *Liebig's Ann.*, **190**. 228, 1877; *Ber.*, **10**. 1626, 1877; **12**. 64, 1879.

[5] H. B. Dixon, *Phil. Trans.*, **175**. 617, 1884.

Bunsen's results are vitiated by numerous errors. There is, for example, a counter-reaction between the water produced during the reaction and the carbon monoxide of the original mixture—

$$H_2O + CO = CO_2 + H_2.$$

There is also an error due to the condensation of steam or water on the walls of the vessel when the experiment is performed below 60°. When these errors are eliminated, the reaction—

$$H_2O + CO_2 \rightleftharpoons H_2 + CO,$$

furnishes numbers in full accord with the law of mass action—

$$\frac{C_{H_2O}C_{CO}}{C_{H_2}C_{CO_2}} = K;$$

the condition of equilibrium[1] is satisfied, and the ratio $CO_2 : H_2O$ shows no sign of discontinuity. Thus—

CO = 78·1, 77·6, 77·4, 75·8, 75·5, 73·4, 72·6, . . .;
H_2 = 21·9, 22·4, 22·6, 24·2, 24·5, 26·6, 27·4, . . .;
$CO_2 : H_2O$ = 1·15, 1·12, 1·11, 1·01, 0·99, 0·89, 0·84, . . .

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[1] See also C. Hoitsema, *Zeit. phys. Chem.*, **25**. 695, 1898.

CHAPTER IX

ELECTROLYTIC DISSOCIATION

§ 58. Application of the Mass Law to Ionic Dissociation.

THE theory of electrolytic dissociation suggested by Arrhenius[1] in 1884 is primarily based upon the facts that the molecular conductivity of solutions increases with dilution; that solutions containing dissolved substances conduct electricity, and have abnormally low molecular weights, when tested by osmotic, freezing, or boiling-point methods, in harmony with the assumption that the "chemist's molecule" is broken up into two parts, called *ions*, the one part having a "+" charge of electricity, and the other a "−" charge; and finally, that the degree of "electrolytic dissociation" of salts in solution may be calculated from the electrical conductivity or from the results of the determination of the molecular weight of the substance in solution by the methods just mentioned.

It is maintained that the various physical properties of salt solutions support the dissociation hypothesis in an unmistakable manner. This is not the place to draw up a brief for or against the ionic hypothesis of solution. After reading the "evidence for" in the regular text-books, the reader should consult Kahlenberg's articles in *The Journal of Physical Chemistry*, commencing in the June number for 1901.[2]

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[1] S. Arrhenius, *Zeit. phys. Chem.*, **1**. 631, 1887; *Inaug. Dissert.*, Stockholm, 1884. See R. A. Lehfeldt's *Electrochemistry*.

[2] L. Kahlenberg, *Journ. Phys. Chem.*, **5**. 339, 1901; H. M. Dawson, *Nature*, **65**. 4143, 1902; L. Kahlenberg, *Chem. News*, **83**. 312, 1903; *Journ. Amer. Chem. Soc.*, **25**. 380, 1903; C. F. Roberts and L. Brown, *ib.*, **25**. 801, 1903; G. Fernekes, *Journ. Phys. Chem.*, **7**. 611, 1903; G. McP. Smith, *ib.*, **8**. 208, 1904; S. U. Pickering, *Nature*, **55**. 223,

In the case of weak electrolytes it is supposed that only part of the normal molecule AB is dissociated into ions. Both dissociated and undissociated molecules are present in the solution. It is supposed that electricity is conducted by the free ions present in the solution, and hence the conductivity of a given mass of dissolved salt is a measure of the degree of ionization. The conductivity is said to increase with dilution because of the increase of ionization with dilution. At the so-called "infinite dilution" the salt will be completely dissociated. Let μ_∞ denote the conductivity of the solution when the ionization of the salt is complete; μ the conductivity of the salt at any other dilution; and α that fraction of the substance which is split up into ions; then it is assumed that—

$$\text{Fraction ionized} = \frac{\text{number of molecules ionized}}{\text{total number of molecules}};$$

or—

$$\alpha = \frac{\mu}{\mu_\infty}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The ions are said to differ from the ordinary products of dissociation chiefly in being associated with positive or negative charges of electricity, and accordingly the law of mass action is supposed to be applicable to the ions as it is to the products of ordinary dissociation.[1]

If one gram of some weak acid is dissolved in water, we shall have a partial splitting up of the acid into ions. If the acid be CH_3COOH (acetic acid), the ions will be CH_3COO' and $H^\cdot$. (See § 20.) Hence we write—

$$CH_3COOH = (1 - \alpha)CH_3COOH + \alpha CH_3COO' + \alpha H^\cdot.$$

1896; **56.** 29, 1896, in M. M. P. Muir and H. F. Morley's *Watts' Dict. Chem.*, London, **4.** 492, 1894; S. Arrhenius, *ib.*, p. 484; J. H. Poynting, *Phil. Mag.* [5], **42.** 289, 1896; *Nature*, **55.** 33, 1896; W. C. D. Whetham, *ib.*, **54.** 571, 1896; **55.** 151, 606, 1896; **56.** 29, 1897; H. E. Armstrong, *ib.*, **55.** 78, 1896; O. J. Lodge, *ib.*, **55.** 150, 1896; E. F. Herroun, *ib.*, **55.** 152, 1896; W. D. Bancroft, *Trans. Amer. Electrochem. Soc.*, **4.** 175, 1903; J. W. Walker, *Journ. Chem. Soc.*, **85.** 1082, 1904.

[1] It is customary to use terms derived from "ionization" to distinguish this phenomenon from the "dissociation" discussed in the preceding chapter.

Let us now assume, as W. Ostwald[1] has done, that ionization follows the same law as that which describes the partial decomposition of ordinary reversible reactions. Then—

$$CH_3COOH \rightleftharpoons CH_3COO' + H^{\cdot},$$

and the condition of equilibrium is that—

$$k_1 C_{CH_3COOH} = k_2 C_{CH_3COO'} C_{H^{\cdot}};\ \text{or, } K = \frac{k_1}{k_2} = \frac{C_{CH_3COO'} C_{H^{\cdot}}}{C_{CH_3COOH}}. \quad (2)$$

$$\therefore \frac{\text{Product of the concentrations of the ions}}{\text{Concentration of the non-ionized part}} = \text{constant.}$$

But for every CH_3COO' ion there is one $H^{\cdot}$ ion, hence—

$$C_{CH_3COO'} = C_{H^{\cdot}}.$$

$$\therefore K = \frac{C^2_{H^{\cdot}}}{C_{CH_3COOH}}, \quad . \quad . \quad . \quad . \quad (3)$$

that is to say, there is a definite relation between the ionized and the non-ionized parts in a solution.

Remembering that α denotes that fraction of the dissolved substance which has dissociated into ions, $1 - \alpha$ will be that part which is not split up into ions. If the whole is dissolved in v litres of solvent—

$$\text{Fraction not ionized} = \frac{1 - \alpha}{v};\ \text{Fraction ionized} = \frac{\alpha}{v}.$$

Hence the condition of equilibrium will be—

$$k_1 \frac{1 - \alpha}{v} = k_2 \frac{\alpha^2}{v^2};\ \text{or, } K = \frac{\alpha^2}{(1 - \alpha)v}. \quad . \quad . \quad (4)$$

This is called Ostwald's dilution law. It follows directly that the greater the dilution of the solution the greater will be the amount of salt split up into ions.

If the concentration v, and the ionization constant K, are known, the degree of ionization α can be calculated. The ionization constant K is sometimes called the affinity constant.

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[1] W. Ostwald, *Zeit. phys. Chem.*, 2. 36, 1888.

From (1) and (4), it follows that—

$$K = \frac{\left(\frac{\mu}{\mu_\infty}\right)^2}{v\left(1 - \frac{\mu}{\mu_\infty}\right)}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and consequently by measuring the conductivity of a solution of an electrolyte at different concentrations (v), we can calculate K. This has been done for hundreds of acids[1] and bases.[2] Let us select two—aqueous solutions of acetic acid and ammonia.

Acetic acid, $\mu_\infty = 388$.			Ammonia, $\mu_\infty = 253$.		
$v = \frac{1}{C}$	μ	$10^4.K$	$v = \frac{1}{C}$	μ	$10^4.K$
16	6·5	1·79	8	3·4	2·3
32	9·2	1·82	16	4·8	2·3
64	12·9	1·79	32	6·7	2·3
128	18·1	1·79	64	9·5	2·3
256	25·4	1·80	128	13·5	2·3
512	34·3	1·80	256	18·2	2·4

The values of K agree remarkably well, and "in no other field has the law of mass action been applied with such good results."[3]

In spite of the fact that the application of the law of mass action has been so successful with electrolytes but partially ionized, it must be confessed that for some unknown reason Ostwald's dilution law cannot be used when dealing with strong acids or bases. The state of equilibrium appears to be modified by some disturbing action which has not yet been recognized. It is therefore necessary either to remodel the theory, or to adopt some auxiliary hypothesis. We might

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[1] W. Ostwald, *Zeit. phys. Chem.*, **3.** 170, 241, 369, 1889.

[2] G. Bredig, *Zeit. phys. Chem.*, **13.** 289, 1894.

[3] S. Arrhenius' *Text-book of Electrochemistry*, J. McCrae's trans. London, 163, 1902.

assume that the law of mass action does not hold for strongly ionized electrolytes; or else assume that a is not an exact measure of the degree of ionization of the salt. Arrhenius[1] and Ostwald incline to the former view, Jahn to the latter.[2]

Rothmund and Drucker[3] attribute the discrepancy to the use of inexact values for the degree of ionization. They show that the employment of methods of measurement more exact than those previously adopted, furnishes data for dilute and concentrated solutions of picric acid in close agreement with the requirements of the mass law.

Rudolphi[4] found it convenient to employ an empirical formula having no theoretical justification, viz.—

$$K = \frac{a^2}{(1 - a)\sqrt{v}}; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which was remodelled by van't Hoff[5] into—

$$K = \frac{a^3}{(1 - a)^2 v}; \text{ or, } K = \frac{a^{1\cdot 5}}{(1 - a)v}. \quad . \quad . \quad (7)$$

This means that the number of molecules ionized in unit time is proportional to the square of the total number of non-ionized molecules, while the number of ions recombining is proportional to the cube of the total number of ions.

Thus we have two sets of formulæ, one for weak electrolytes, and one for strong electrolytes. There can be no real line of demarcation between strong and weak electrolytes, and consequently the two formulæ just mentioned may be taken to represent two limiting cases—strong and weak electrolytes. To cover all intermediate forms, Storch[6] writes—

$$K = \frac{a^n}{(1 - a)v},$$

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[1] S. Arrhenius, *Zeit. phys. Chem.*, **36**. 28, 1901; **37**. 490, 1901; W. Nernst, *ib.*, **36**. 596, 1901; W. Ostwald's *Grundriss*, 406, 1899.

[2] H. Jahn, *Zeit. phys. Chem.*, **27**. 354, 1898. See R. A. Lehfeldt, *l.c.*

[3] V. Rothmund and K. Drucker, *Zeit. phys. Chem.*, **46**. 827, 1903.

[4] M. Rudolphi, *Zeit. phys. Chem.*, **17**. 385, 1895.

[5] J. H. van't Hoff, *Zeit. phys. Chem.*, **18**. 300, 1895.

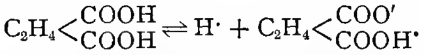
[6] L. Storch, *Zeit. phys. Chem.*, **19**. 13, 1896; **26**. 545, 1900; W. D. Bancroft, *ib.*, **31**. 188, 1899; F. Kohlrausch, *ib.*, **18**. 662, 1895.

where K and n are empirical constants to be evaluated from the experimental data for the particular substance under investigation.

Even then the results are not satisfactory, and it has been suggested that the addition of the ions of the "strong" electrolyte increases the dissociating power of the solvent, so that the ionization constant of the dissolved substance increases with the number of ions present in the solvent.[1]

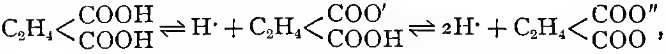
The theoretical deduction of Ostwald's law from the general laws of energy proceeds on the assumption that we are only dealing with very dilute solutions where the molecules are separated beyond each other's sphere of action. It is reasonable to assume that the sphere of action of the ionized molecules will, in virtue of their electric charges, extend far beyond that of non-ionized molecules. If many ions are present, we need not be surprised if the solution does not conform with the fundamental property of dilute solutions just mentioned.[2]

When an electrolyte breaks up into more than two ions, the ionization usually takes place in stages.[3] With weak polybasic acids, like succinic acid, the ionization constant for concentrated solutions can be obtained from the law for monobasic acids. This means that—



$$\mathrm{C_2H_4}{<}\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array} \rightleftharpoons \mathrm{H}^{\cdot} + \mathrm{C_2H_4}{<}\begin{array}{l}\mathrm{COO'}\\ \mathrm{COOH}\end{array}.$$

When about half the molecules are dissociated, the second group $\mathrm{COOH.C_2H_4.COO}$ begins to split up, producing in all three ions, so that, at great dilutions—



$$\mathrm{C_2H_4}{<}\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array} \rightleftharpoons \mathrm{H}^{\cdot} + \mathrm{C_2H_4}{<}\begin{array}{l}\mathrm{COO'}\\ \mathrm{COOH}\end{array} \rightleftharpoons 2\mathrm{H}^{\cdot} + \mathrm{C_2H_4}{<}\begin{array}{l}\mathrm{COO''}\\ \mathrm{COO}\end{array},$$

which gives an ionization constant in agreement with Ostwald's

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[1] S. Arrhenius, *Zeit. phys. Chem.*, **31.** 211, 1899.

[2] W. C. D. Whetham, *A Treatise on the Theory of Solution*, Cambridge, 344, 1902; *Phil. Mag.* [6], **5.** 279, 1903; *Electro-Chemist and Metallurgist*, **3.** 9, 1903. See J. Traube, *Phil. Mag.* [6], **8.** 158, 1904.

[3] W. Ostwald, *Zeit. phys. Chem.*, **9.** 553, 1892; J. E. Trevor, *ib.*, **10.** 321, 1892; A. A. Noyes, *ib.*, **9.** 603, 1892; **11.** 495, 1893; G. Bredig, *ib.*, **13.** 191, 1894; W. A. Smith, *ib.*, **25.** 144, 193, 1898.

dilution law for substances which dissociate into three ions namely—

$$\frac{a^3}{v^2(1-a)} = K.$$

For strongly ionized substances the three ions are formed at moderate dilutions, and Ostwald's law does not conform with the experimental data.

§ 59. Relation between the Ionization Constant and Chemical Activity.

We may now inquire what relation subsists between the ionization constant of acids and alkalies and their chemical activity. We are indebted to Ostwald for opening up this question in a most interesting manner. True enough Löwenthal and Lenssen[1] tried to "express in numbers the relative strengths of the different acids," and Berthelot also tried to get an idea of the strength of an acid by extending the old Bergmann idea, "that the stronger acid will displace the weaker from their salts," with not very satisfactory results. Berthelot, however, discovered the important fact that the stronger acids are better conductors of electricity. This idea was further developed by Arrhenius,[2] who, in 1884, showed that the strength of an acid is proportional to its conductivity.

I. Acids.—Ostwald[3] has arranged a number of the acids in—

1. The order of their power of conducting electricity.
2. According to their influence on the rate of hydrolysis of methyl ester.

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[1] J. Löwenthal and E. Lenssen, *Journ. prakt. Chem.* [1], **85**. 321, 1862.

[2] M. Berthelot and L. Péan St. Gilles, *Ann. Chim. Phys.* [3], **65**. 385, 1862; **66**. 5, 1862; **68**. 225, 1863; S. Arrhenius, *Inaug. Dissert.*, Stockholm, 1884; *Zeit. phys. Chem.*, **1**. 631, 1887.

[3] W. Ostwald, *Lehrbuch*, **2**. i., 650, 1903.

3. According to their influence on the rate of inversion of cane sugar.

Let us select a dozen typical acids from Ostwald's table, containing between thirty and forty members.

Acid.	Conductivity.	Hydrolysis of methyl acetate.	Inversion of cane sugar.
Hydrochloric acid	100·00	100·00	100·00
Hydrobromic acid	101·00	98·00	100·00
Nitric acid	99·60	92·00	100·00
Sulphuric acid	65·10	73·97	73·20
Trichloracetic acid	61·30	68·20	75·40
Dichloracetic acid	25·30	23·00	27·10
Oxalic acid	19·70	17·60	18·60
Monochloracetic acid	4·90	4·30	4·84
Formic acid	1·68	1·31	1·53
Lactic acid	1·04	0·90	1·07
Succinic acid	0·58	0·50	0·55
Acetic acid	0·42	0·35	0·40

Bearing in mind that neither the temperature nor the concentration of the acids is the same in each series, it will be evident that "in all these processes—electrical conductivity, hydrolysis of methyl acetate, and the inversion of cane sugar in the presence of acids—we are dealing with one definite property of the acids."

What is this definite property common to aqueous solutions of all the acids? The answer is hydrogen ions. The relative strengths of the different acids is usually explained on the assumption that they yield different amounts of ions in equivalent solutions. The acids which produce most hydrogen ions in solutions of a given concentration will be the most chemically active. Hence it is supposed that the degree of ionization of an acid furnishes a measure of its strength. The conductivity of an acid is also supposed to depend on the number of hydrogen ions it contains, and hence the conductivity is also proportional to the "strength" or "affinity" of the acid. The reason will now be obvious why the constant of ionization given by formula (4) is also called the affinity constant of the acids.

It will perhaps be remembered that the constant K for strong electrolytes is quite empirical, and has no theoretical *raison d'état.*

No acid can have more than a 100 per cent. degree of ionization. This is the limit to the strength of the acids, which is only reached by a few of the monobasic acids —HCl, HBr, HNO_3—at moderate dilutions. The dibasic acids—H_2SO_4, $H_2C_2O_4$—are not so strong as the monobasic acids.

Ionization increases with dilution. Experiment confirms this by showing that the difference in the strengths of the acids becomes less and less marked as the solution becomes more and more dilute. This will be evident from the subjoined diagram (Fig. 12), showing how the relative strengths of the three chloracetic acids gradually approach the limit, 100 per cent., as the concentration of the acid diminishes. Note the greater influence of water on the monochloracetic acid than on dichloracetic acid, and on the latter more than on the trichloracetic acid.

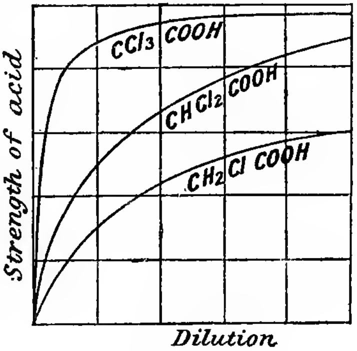

FIG. 12.

The effect of adding a salt containing an ion in common with the acid already in solution will be to lower the degree of ionization, and consequently the chemical activity of the acid. For example, the activity of acetic acid towards inverting cane sugar is diminished by the addition of sodium acetate containing the CH_3COO'-ion. A solution of cane sugar containing $\frac{1}{4}$N- acetic acid was mixed with sufficient sodium acetate to make the solution contain the amount of sodium acetate indicated in the first column of the following table. The succeeding columns show the results obtained.

Solution of cane sugar with $\frac{1}{4}$N-acetic acid and sodium acetate.	$\frac{\mu}{\mu_\infty}$	$k.10^3$	
		Obs.	Calc.
—	—	0·750	0·750
$\frac{1}{80}$-N	0·912	0·122	0·128
$\frac{1}{40}$-N	0·760	0·070	0·079
$\frac{1}{20}$-N	0·739	0·040	0·040
$\frac{1}{8}$-N	0·713	0·019	0·017
$\frac{1}{4}$-N	0·692	0·0105	0·0088

The calculation is not difficult. For $\frac{1}{4}$N- acetic acid it is found from the condition of equilibrium—

$$K = \frac{C_{\mathrm{H}}^2}{C_{\mathrm{CH_3COOH}}} = 0{\cdot}00001615. \quad . \quad . \quad . \qquad (1)$$

But, since the concentrations C are expressed in gram molecules per litre—

$$C_{\mathrm{CH_3COOH}} = \tfrac{1}{4} - C_{\mathrm{H}^{\cdot}}. \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Hence from (1) and (2)—

$$C_{\mathrm{H}^{\cdot}} = 0{\cdot}002.$$

But the velocity of inversion of cane sugar with an acid completely ionized, say, $\frac{1}{80}$N-HCl, is—

$$k' = 0{\cdot}00469,$$

or 4·69 parts of cane sugar, per thousand, are inverted in one minute by the hydrogen ions of $\frac{1}{80}$N-HCl. Assuming that the rate of inversion is proportional to the concentration of the hydrogen ions, the rate of inversion (k) by hydrogen ions of concentration 0·002 will be—

$$\tfrac{1}{80} : 0{\cdot}002 = k' : k\,;$$

$$\frac{\frac{1}{80}}{0{\cdot}002} = \frac{0{\cdot}00469}{k}\,; \text{ or, } k = 0{\cdot}0075.$$

If nN- sodium acetate now be added, there will be no CH_3COO' ions, and (1) must be written—

$$\frac{(na + C_{H\cdot})C_{H\cdot}}{\frac{1}{4} - C_{H\cdot}} = 1\cdot615.10^{-5}.$$

See (1), § 58. Solving for C_H, we get values which, when substituted in—

$$\frac{\frac{1}{80}}{C_{H\cdot}} = \frac{0\cdot00469}{k};\ \text{or, } k = 80 \times 0\cdot00469 C_{H\cdot},$$

furnish the values of k given in the above table.

II. Bases.—Let us now compare the ionization constants of the bases, as measured by their electrical conductivity, with the velocity constants obtained during the hydrolysis of ethyl acetate.

Base.	Conductivity.	Hydrolysis of ethyl acetate.
Potassium hydroxide	100·00	100·00
Sodium hydroxide	92·54	101·24
Lithium hydroxide	88·20	103·10
Tetraethylammonium hydroxide	79·60	81·36
Diethylamine	17·41	16·15
Dimethylamine	14·31	13·67
Ethylamine	12·46	11·80
Methylamine	12·42	11·80
Triethylamine	12·42	13·67
Trimethylamine	5·64	4·37
Amylamine	3·78	2·47
Ammonium hydroxide	2·53	1·87

Here, again, the agreement is as close as could be expected from the conditions of the experiment. Chemical activity is indeed proportional to the ionization of the base as measured by electrical conductivity.

The ionization constant might thus be employed as a measure of the chemical activity of an electrolyte, and, conversely, the chemical activity of a substance may be used as a measure of ionization.

Hydroxyl ions are responsible for the effects produced with the bases in the same sense that hydrogen ions "cause" the properties which characterize the acids.

III. Amphoteric Electrolytes.—There are a number of organic compounds which behave like acids towards bases, and like bases towards acids. It is supposed, on the ionic theory, that the ionization of these substances proceeds as indicated by the equations—

$$\mathrm{MOH} \rightleftharpoons \mathrm{M}^{\cdot} + \mathrm{OH}'\,;\ \mathrm{MOH} \rightleftharpoons \mathrm{MO}' + \mathrm{H}^{\cdot}.$$

The solution is therefore said to contain both OM'- and $\mathrm{M}^{\cdot}$-ions; in other words, to exhibit a kind of "electrolytic tautomerism." Typical examples are: amidoacetic acid, *o*-, *m*-, and *p*- amidobenzoic acid; the diazonium hydroxide of A. Hantzsch and W. B. Davidson; and the oximes: $\mathrm{R : N{\cdot}OH}$ of H. Goldschmidt. They are called **amphoteric electrolytes.**[1] Walker has shown that the concentrations of the various ions in aqueous solutions of the amidobenzoic acids, as measured by Winkelblech, are in agreement with those deduced from the law of mass action.

The ionic hypothesis is not yet invulnerable. The velocity of a chemical reaction is not always proportional to electrical conductivity. Ammonium cyanate, for example, is transformed into urea thirty times as fast in ethyl alcohol as it is in water, although the conductivity of the latter is much greater.[2] Kahlenberg, too, has shown us that chemical reactions may take place in a system which does not conduct electricity.

§ 60. Equilibrium between Electrolytes with a Common Ion. Isohydric Solutions.

Assuming that all electrolytes follow Ostwald's dilution law, Arrhenius[3] has proved that when solutions of two acids

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[1] G. Bredig, *Zeit. Elektrochem.* **6.** 34, 1899; K. Winkelblech, *Zeit. phys. Chem.*, **36.** 546, 1901; J. Walker, *Proc. Roy. Soc.*, **73.** 155, 1904; R. A. Lehfeldt's *Electro-chemistry*, London, i., 143, 1904.

[2] J. Walker and S. A. Kay, *Journ. Chem. Soc.*, **71.** 489, 1897.

[3] S. Arrhenius, *Wied. Ann.*, **30.** 51, 1887; *Zeit. phys. Chem.*, **2.** 284, 1888.

possess the same number of hydrogen ions, these solutions can be mixed without changing the degree of ionization of either acid. Such solutions were said to be **isohydric.** Arrhenius has still further shown that the two acids need not have the same basicity. The phenomenon is quite general. "What has just been said of isohydric solutions," adds Arrhenius, "can also be applied without change to other isohydric solutions having a common ion."[1] No proof of this statement has been given, but acetic acid and ammonium acetate were cited in illustration of this principle. The original definition must therefore be extended. Solutions are now called isohydric when the concentration of one of the products of ionization is the same in the two solutions.

Arrhenius's proof is easy to follow. Take two acids, HA_1 and HA_2. According to Ostwald's dilution law, for equilibrium—

$$\frac{a_1^2}{(1 - a_1)v_1} = K_1 ; \frac{a_2^2}{(1 - a_2)v_2} = K_2, \quad . \quad . \quad (1)$$

where all the symbols have their former significations. If the isohydric solutions be mixed together, the volume of the mixture will be $v_1 + v_2$, and the number of hydrogen ions in the mixture will be $a_1 + a_2$. Hence for the mixed acids—

$$\frac{(a_1 + a_2)a_1}{(1 - a_1)(v_1 + v_2)} = K_1, \quad . \quad . \quad . \quad . \quad (2)$$

because in the mixed solution we have $a_1 + a_2$ hydrogen ions and a_1 of A_1 ions. The a_2 ions have no influence on K_1. Divide (2) by the first of equations (1), rearrange terms, and we get finally—

$$\frac{a_1}{v_1} = \frac{a_2}{v_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or, in words, in a mixture of isohydric solutions of HA_1 and HA_2 the—

Concentration of H-ions in HA_1 = conc. of H-ions in HA_2.

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[1] S. Arrhenius, *B.A. Reports*, 315, 1886 ; W. D. Bancroft, *Journ. Phys. Chem.*, **4**. 274, 1900.

In the following table will be found the observed values[1] of the specific conductivity of a mixture of different volumes of isohydric solutions of acetic acid (specific conductivity $= 4·837 \times 10^{-8}$), and of oxalic acid (specific conductivity $= 4·947 \times 10^{-8}$) placed in juxtaposition with values calculated from the above formula. The results are in close agreement with theory.

Acetic acid.	Oxalic acid.	Specific conductivity × 10^{-8}.	
		Obs.	Calc.
10	3	4·863	4·863
10	10	4·896	4·892
3	10	4·922	4·921

Bancroft has questioned the accuracy of Arrhenius's generalization, and shown that it is only accurate under certain definite limitations. Let us consider what takes place when potassium acetate is mixed with acetic acid. For each substance we have—

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO'} + \mathrm{H^{\cdot}};\ \mathrm{CH_3COOK} \rightleftharpoons \mathrm{CH_3COO'} + \mathrm{K}.$$

The condition of equilibrium of the acid, deduced in the usual way, is—

$$K_1\frac{1 - x}{v} = \frac{x}{v} \cdot \frac{x}{v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Potassium acetate has not the same ionization constant as acetic acid, and we cannot, in consequence, take equivalent quantities of the two substances in equal volumes if we want to have the same number of $\mathrm{CH_3COO'}$ ions in equal volumes of the two solutions. Let a be the number of gram-molecules of potassium acetate which must be dissolved in v volumes of solvent in order to furnish a solution having the same number of $\mathrm{CH_3COO'}$ ions as v volumes of the acetic acid solution. Then—

$$K_2\frac{a - x}{v} = \frac{x}{v} \cdot \frac{x}{v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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[1] W. Ostwald's *Lehrbuch*, 2. i., 704, 1903.

Now add *nv* volumes of potassium acetate to the acetic acid solution, and we have the relations—

$$\text{Acetic acid: } K_1\frac{1 - x}{(n + 1)v} = \frac{(n + 1)x}{(n + 1)v} \cdot \frac{x}{(n + 1)v}; \quad (6)$$

$$\text{Potassium acetate: } K_2\frac{n(a - x)}{(n + 1)v} = \frac{(n + 1)x}{(n + 1)v} \cdot \frac{nx}{(n + 1)v}. \quad (7)$$

Now cancel out the common factors in each of these equations, and both equations resume their original form. This shows that the degree of ionization of each electrolyte is not altered when the isohydric solutions are mixed together. This is in harmony with equation (1). A similar result is obtained when solutions of isohydric zinc acetate and acetic acid, or isohydric sodium sulphate and sodium oxalate, are mixed together.

With isohydric solutions of zinc acetate and zinc sulphate, although the degree of ionization of the zinc sulphate remains unaltered, there will be an increase in the ionization of the zinc acetate, and, as a secondary effect, a decrease in the ionization of the zinc sulphate. A similar result is obtained with a mixture of zinc and potassium sulphates.

If we treat a mixture of sodium and potassium sulphates, or of zinc chloride and zinc acetate, in this way, we shall find that both salts tend towards an increased ionization.

We have assumed that Ostwald's dilution law holds good. If we are dealing with strong electrolytes, say KCl or HCl, obeying van't Hoff's dilution law—

$$KC_1^2 = C_2^3; \text{ or, } KC_1 = C_2^{\frac{3}{2}}, \quad . \quad . \quad . \quad (8)$$

where C_1 denotes the concentration of the undissociated salt, C_2 the concentration of the ions. Assume that the concentration of the common ion is the same in both solutions, we shall have—

$$K_1\frac{1 - x}{v} = \left(\frac{x}{v}\right)^{\frac{3}{4}}\left(\frac{x}{v}\right)^{\frac{3}{4}}; \ K_2\frac{a - x}{v} = \left(\frac{x}{v}\right)^{\frac{3}{4}}\left(\frac{x}{v}\right)^{\frac{3}{4}},$$

for hydrochloric acid and potassium chloride respectively. On adding *nv* volumes of potassium chloride to the hydrochloric acid, we finally get equations which show that the degree of ionization of each salt is diminished. This is not in agreement with the experiments of Arrhenius,[1] nor of Lincoln.[1] On the contrary, Lincoln finds that there is an increase in the ionization when *dilute* solutions of strong electrolytes, and a decrease of ionization when *concentrated* solutions are mixed together. This shows that there is some factor, not yet recognized, which causes a greater conductivity with such solutions than theory would lead us to expect.

It is, however, interesting to note that if a solution is saturated with respect to a given salt, the concentration of the non-ionized salt is decreased by the addition of a salt with a common ion. This means that the presence of a third ion increases the degree of ionization of the salt beyond what theory requires. This naturally increases the conductivity, because the latter depends upon the number of ions in solution. This is in harmony with Lincoln's experiments.

§ 61. Equilibrium of Electrolytes with no Common Ion. Double Decomposition.

If we now apply the ionization hypothesis to a mixture of two salts containing no common ion, the results obtained will depend upon whether we are dealing with strong or weak electrolytes.

With strongly ionized electrolytes like sodium chloride and potassium nitrate, there will be practically no interchange of ions, or rather the solution will contain the same ions previously present in the unmixed solutions.

$$(K^{\cdot} + NO'_3) + (Na^{\cdot} + Cl') = K^{\cdot} + NO'_3 + Na^{\cdot} + Cl'.$$

With feebly dissociated electrolytes the phenomenon is more complex. The subject has not yet been fully worked out. Let us assume that the two electrolytes M_1A_1 and M_2A_2

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[1] S. Arrhenius, *Zeit. phys. Chem.*, **31**. 204, 1899; A. T. Lincoln, *Journ. Phys. Chem.*, **4**. 285, 1900; H. C. Jones and N. Knight, *Amer. Chem. Journ.*, **22**. 110, 1899.

obey Ostwald's dilution law, and that the hydrolytic action of the water on the salt is negligibly small. We shall therefore be dealing with the non-ionized salts M_1A_1, M_1A_2, M_2A_1, M_2A_2; and with the ions M_1, M_2, A_1, A_2, in the mixed solution. It is required to determine the conditions which must subsist in order that the system may be in a state of equilibrium.

In the first place, it is easy to see that the four salt solutions, M_1A_1, M_1A_2, M_2A_1, M_2A_2, can be made isohydric, for M_1A_1 can be made isohydric with respect to both M_1A_2 and M_2A_1, and the latter in turn can be made isohydric with M_2A_2. Then let v_1, v_2, v_3, v_4, respectively denote the volumes of the isohydric solutions of M_1A_1, M_1A_2, M_2A_1, M_2A_2, which, when mixed, will produce no change of equilibrium. Before mixing, the condition of equilibrium for, say, M_1A_1 is—

$$\frac{\left(\frac{\alpha}{v}\right)^2}{\left(\frac{1-\alpha}{v}\right)v_1} = K; \text{ or, } \frac{\alpha^2}{(1-\alpha)v_1} = K. \quad . \quad . \quad (1)$$

After mixing these four salts together, the quantity of the M_1 ion will be increased in the ratio $(v_1 + v_2) : v_1$ because v_2 volumes of M_1A_2 have added to v_1 volumes of M_1A_1, and the concentration of the M_1 ions is the same in both solutions. But these M_1 ions are also contained in $v_1 + v_2 + v_3 + v_4$ volumes of solution. Consequently, the concentration of the M_1 ions will be—

$$\alpha \times \frac{v_1 + v_2}{v_1} \times \frac{1}{v_1 + v_2 + v_3 + v_4} = \frac{\alpha(v_1 + v_2)}{v_1(v_1 + v_2 + v_3 + v_4)}. \quad (2)$$

Again, the A_1 ion increases in the ratio $(v_1 + v_2) : v_1$, and its concentration will therefore be—

$$\frac{\alpha(v_1 + v_3)}{v_1(v_1 + v_2 + v_3 + v_4)}. \quad . \quad . \quad . \quad . \quad (3)$$

The non-ionized portion of the salt M_1A_1 remains the same as before, *i.e.* $1 - \alpha$. For equilibrium, therefore—

$$C_{M_1\text{-ion}}C_{A_1\text{-ion}} = KC_{M_1A_1}. \quad . \quad . \quad . \quad . \quad (4)$$

On introducing the values just determined for the concentrations of the ions M_1 and A_1, and for the non-ionized molecules M_1A_1 into equation (4), equating the result to the right side of (1) in virtue of the two identical K's, cancelling out the common factors, and finally reducing the expression to its simplest terms, we get—

$$v_1v_4 = v_2v_3, \quad \ldots \ldots \quad (5)$$

which expresses the condition which must hold between the four isohydric solutions in order that the equilibrium may not be displaced when the four solutions are mixed. Equation (5) in words, tell us that for equilibrium the products of the volumes of pairs of solutions containing no common ion must be equal.

The volumes v_1, v_2, v_3, v_4 are proportional to the ionized portions of the respective electrolytes M_1A_1, M_1A_2, M_2A_1, M_2A_2. If the *total* mass of the four salts in solution be respectively $C_{M_1A_1}$, $C_{M_1A_2}$, $C_{M_2A_1}$, $C_{M_2A_2}$, and the coefficients of ionization α_1, α_2, α_3, α_4, the concentration of the ionized portion in solution will be respectively $\alpha_1C_{M_1A_1}$, $\alpha_2C_{M_1A_2}$, $\alpha_3C_{M_2A_1}$, $\alpha_4C_{M_2A_2}$. For equilibrium, therefore—

$$\alpha_1C_{M_1A_1} \cdot \alpha_4C_{M_2A_2} = \alpha_2C_{M_1A_2} \cdot \alpha_3C_{M_2A_1}, \quad \ldots \quad (6)$$

which is obviously an expression of the mass law in which the active masses of the substances taking part in the reaction are not the total quantities of the substances derived from the equation—

$$M_1A_1 + M_2A_2 \rightleftharpoons M_1A_2 + M_2A_1,$$

in the usual way, but only the fractional parts of the several salts split up into ions.[1]

The above conclusions are true only when the fundamental assumptions are fulfilled. No difficulty need be experienced in extending the reasoning as outlined in the preceding section. If all four, or only two of the four, salts are highly dissociated, the law of mass action and the theory of isohydric solutions furnish the same equilibrium constant, but different

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[1] A. A. Noyes, *Zeit. phys. Chem.*, **27**. 267, 1898.

equilibrium constants when only one or three of the four salts are highly dissociated.

Let us now apply the theory developed in §§ 60 and 61 to observed facts.

§ 62. Ionization of Water.

Ordinary tap-water is a relatively good conductor of electricity. It is therefore inferred that it must contain dissolved impurities more or less ionized. The inference is further justified by the fact that the more care devoted to the purification of the water, the less does its conductivity become. Kohlrausch and Heydweiller[1] employed the most scrupulous care in the preparation of a specimen. Carefully purified water was distilled in platinum vessels *in vacuo*, and the conductivity determination was made as soon as the water was condensed. The result was—

$$0{\cdot}036 \times 10^{-10}.$$

Kohlrausch and Heydweiller add, "one millimetre of this water has at 0° a resistance equal to that of a copper wire of the same cross-section 40 million kilometres long, a wire that could therefore be wound a thousand times round the earth. This water is probably the purest that has ever existed, whether artificially prepared or occurring ready formed in nature, not even excepting the water precipitated in the form of clouds in the highest strata of the atmosphere. Simple contact with the air for a short time raised its conductivity ten-fold. The impurities still present in the water might be estimated at a few thousandths of a milligram per litre."

Some chemists argue that if absolutely pure water could be prepared, it would not conduct electricity at all. Be this as it may, it is remarkable that values calculated for the ionization constant of water by different observers using different methods

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[1] F. Kohlrausch and A. Heydweiller, *Wied. Ann.*, **53**. 209, 1894; *Zeit. Phys. Chem.*, **14**. 317, 1894.

give fairly concordant results. Thus it is found that the alleged ionization of water at 25° amounts to—

Ionization of water.	Authorities.	Method of measurement.
$1 \cdot 2 \times 10^{-7}$	Wijs	Hydrolysis of methyl acetate.
$1 \cdot 1 \times 10^{-7}$	Arrhenius, Shields	Hydrolysis of methyl acetate.
$1 \cdot 2 \times 10^{-7}$	Löwenharz	E.M.F. of acid-alkali cell.
$0 \cdot 6 \times 10^{-6}$	Kohlrausch	Electrical conductivity.

It is therefore assumed that in water, quite apart from the ionization of the impurities, there is a state of equilibrium between the undecomposed molecules and ions such that—

$$H_2O \rightleftharpoons H^{\cdot} + OH'.$$

It must be remembered that the amount of water so ionized is exceedingly small, too small indeed for accurate measurements, and the concordant results obtained are all the more surprising. The hydrogen ion will confer upon water the properties of a weak acid, and the hydroxyl ions the properties of a weak base.[1] Water is therefore an amphoteric electrolyte.

§ 63. Hydrolysis.

In his work upon the basic salts, H. Rose[2] recognized the fact that although many metallic salts might contain the strictly equivalent quantities of acid and base required for "neutrality," they may yet give, in aqueous solution, an acid or an alkaline reaction when tested with an indicator. For example, salts like potassium cyanide, potassium carbonate, and potassium chromate, have an alkaline reaction when dissolved in water; while others, like copper sulphate, mercuric nitrate, and ferric

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[1] For the alleged dissociation of water into two molecules of hydrogen and one molecule of oxygen in alcoholic solution, see R. Luther, *Zeit. phys. Chem.*, **26**. 317, 1898; R. A. Lehfeldt, *ib.*, **27**. 94, 1897.

[2] H. Rose, *Pogg. Ann.*, **83**. 132, 417, 1851.

chloride, have an acid reaction. Rose supposed that the salt is decomposed by the water into acid and base. The process of decomposition is called **hydrolysis.**[1]

It is interesting to examine more in detail the changes which take place when these salts are dissolved in water from the point of view of the ionization theory. Arrhenius[2] first developed the ionization theory of hydrolysis. For the sake of convenience, let us consider salts derived from strong acids and strong bases, from strong acids and weak bases, from weak acids and strong bases, and from weak acids and weak bases.

§ 64. Hydrolysis of Salts derived from Strong Acids and Strong Bases.

When potassium chloride, sodium chloride, potassium nitrate, and similar salts are dissolved in water, ionization takes place, and the solution, like water itself, is neutral. This means that acid ions—$H^{\cdot}$-ions—or alkaline ions—OH'-ions—are not present in any appreciable quantity.

In the process of the formation of a salt by the neutralization of a strong acid by a strong base, it must be remembered that acid, base, and salt are all split up into ions. The reaction represented by the ordinary chemical symbols—

$$HCl + NaOH = H_2O + NaCl,$$

must be written, according to the ionization theory—

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + H_2O.$$

Similarly, we have the reactions—

$$H^{\cdot} + NO'_3 + Na^{\cdot} + OH' = Na^{\cdot} + NO'_3 + H_2O;$$
$$H^{\cdot} + Br' + K^{\cdot} + OH' = K^{\cdot} + Br' + H_2O.$$

The process of neutralization in aqueous solution, therefore, is nothing more than the formation of water from hydrogen ions

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[1] See A. Ponsot, "Sur les phénoménes d'hydrolyse," *Les Actualities Chimiques*, **1**. 41, 1896; A. Werner, *Zeit. anorg. Chem.*, **9**. 408, 1895.

[2] S. Arrhenius, *Zeit. phys. Chem.*, **5**. 1, 1890.

and hydroxyl ions. Hence it is inferred that so long as the acid, base, and salt are completely ionized, the chemical action is quite independent of the acid and base used. This is in harmony with the fact discovered by J. Thomsen, that the heats of neutralization of a strong base by different acids, or of a strong acid by different bases, is always the same, being nothing more than the heat of formation of water. For example, take the heats of neutralization of sodium hydroxide with strong acids, and of hydrochloric acid by strong bases.

1 molecule of NaOH with		1 molecule of HCl with	
1 molecule of acid.	Heat of neutralization.	1 molecule of base.	Heat of neutralization.
HCl . . .	13750 cal.	NaOH . . .	13750 cal.
HBr . . .	13750 ,,	KOH . . .	13750 ,,
HIO_3 . . .	13800 ,,	$\frac{1}{2}Ba(OH)_2$ . .	13906 ,,
HNO_3 . . .	13700 ,,	$\frac{1}{2}Ca(OH)_2$ . .	13850 ,,

§ 65. Hydrolysis of Salts derived from Strong Acids and Weak Bases.

Examples are ammonium chloride, aluminium, copper, or zinc chlorides or nitrates; salts of aniline, pyridine, and urea with hydrochloric and other strong acids. In every case we have, on dissolution in water—

$$\text{Salt} + \text{water} \rightleftharpoons \text{acid} + \text{base}.$$

Walker[1] found that diphenylene salts are so unstable that they dissociate almost completely into free acid and base.

$$\text{Diphenylene picrate} = \text{diphenylene} + \text{picric acid}.$$

Why do aqueous solutions of these salts possess an acid reaction? We assume that the first action of water is to cause a more or less complete dissociation of the salt into free acid and free base, as indicated by the preceding equation. This is

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[1] J. Walker and J. R. Appleyard, *Journ. Chem. Soc.*, **69**. 134, 1896.

followed by the ionization of the acid and of the base. If the acid is strong and the base weak, the number of hydrogen ions produced by the former will greatly exceed the number of hydroxyl ions produced by the latter; any excess of hydrogen ions will cause an acid reaction. On the other hand, if the acid were weak and the base strong, the hydroxyl ions would predominate, and the solution would have an alkaline reaction. It is all a question of the relative "strength" or "degree of ionization" of acid and base produced by the dissociation of the salt.

As a matter of fact, the relative strength of a series of weak bases with respect to a given acid can be determined by measuring the extent of hydrolysis in equivalent solutions of the salt. The base and the water may both be regarded as competing for the acid. The weaker the base, the greater the hydrolysis, and the more free hydrogen ions will be present in the solution. The amount of acid cannot be determined by titration with standard alkali in the usual manner, because as soon as ever so little of the acid is withdrawn from the system by neutralization with alkali, more acid will be formed by hydrolysis of the unchanged salt. This explains why a solution of aniline hydrochloride consumes as much alkali on titration as an equivalent solution of hydrochloric acid.

Methods[1] must be employed which do not disturb the equilibrium between the salt and the products of dissociation. Advantage is taken of the fact that the hydrolysis of methyl acetate or the inversion of cane sugar is proportional to the amount of free acid present in the solution; or of the fact that the rate of hydrolysis of ethyl acetate is proportional to the amount of free base present in the solution. In this way J. Walker and G. Bredig[2] have measured the degree of hydrolysis of hydrochlorides of urea, and other feeble bases;

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[1] For the more useful methods, see H. Ley, *Zeit. phys. Chem.*, **30**. 193, 1899; R. C. Farmer, *B.A. Reports*, 240, 1901.

[2] J. Walker, *Proc. Roy. Soc. Edin.*, **18**. 255, 1894; *Journ. Chem. Soc.*, **77**. 5, 1900; *Zeit. phys. Chem.*, **4**. 319, 1889; **32**. 137, 1900; G. Bredig, *ib.*, **13**. 214, 1894; H. Euler, *ib.*, **32**. 348, 1900; L. Bruner, *ib.*, **32**. 133, 1900; T. Madsen, *ib.*, **36**. 290, 1901; H. Ley, *Ber.*, **32**. 2192, 1899.

sodium sulphide and hydrosulphide, etc.; Shields,[1] of the salts of feeble acids like carbonic acid, hydrocyanic acid, and boric acid with the strong bases; Foussereau, and Goodwin,[2] by measurements of the electrical conductivity and the freezing points of the solutions; Berthelot and Martin, and Farmer,[3] by finding how much of one salt dissolves when the solution is shaken out with another solvent; Moore,[4] by measuring the absorption spectrum; and Will and Bredig,[5] from the effect of the base on the rotatory power of hyoscyamine.

According to the law of mass action, we shall have for equilibrium

$$k_1 C_{\text{salt}} C_{\text{water}} = k_2 C_{\text{acid}} C_{\text{base}}. \quad . \quad . \quad . \quad (1)$$

But the active mass of the water may be regarded as a constant when we are dealing with dilute solutions, hence we may write—

$$\frac{C_{\text{acid}} C_{\text{base}}}{C_{\text{salt}}} = K, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K is a constant.

If a gram-molecules of salt have been dissolved in v litres of water, and ξ gram-molecules are hydrolyzed, $a - \xi$ of the salt will remain in solution when equilibrium has set in, and—

$$\frac{\left(\frac{\xi}{v}\right)^2}{\frac{a - \xi}{v}} = \frac{\xi^2}{(1 - \xi)v} = K. \quad . \quad . \quad . \quad . \quad (3)$$

The following table embodies the experimental data for the

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[1] J. Shields, *Zeit. phys. Chem.*, **12.** 167, 1893; *Phil. Mag.* [5], **35.** 365, 1893.

[2] G. Foussereau, *Compt. Rend.*, **103.** 42, 248, 1886; *Ann. Chim. Phys.* [6], **11.** 383, 1887; **12.** 553, 1887; H. M. Goodwin, *Zeit. phys. Chem.*, **21.** 1, 1896; J. H. Long, *Journ. Amer. Chem. Soc.*, **19.** 683, 1897.

[3] M. Berthelot and L. de St. Martin, *Ann. Phys. Chim.* [4], 26, 433, 1872; R. C. Farmer, *Journ. Chem. Soc.*, **79.** 863, 1901.

[4] B. E. Moore, *Phys. Review*, **12.** 151, 1901.

[5] W. Will and G. Bredig, *Ber.*, **21.** 2777, 1888; A. A. Noyes and W. J. Hall, *Zeit. phys. Chem.*, **18.** 240, 1895 (salicine).

hydrolysis of aniline hydrochloride,[1] and the calculated constant in the last column is in harmony with formula (3) :—

v	ξ	$K \times 10^4$
0·312500	0·0263	0·22
0·156250	0·0390	0·25
0·073125	0·0547	0·25
0·036562	0·0768	0·25
0·018280	0·1040	0·24
0·009140	0·1440	0·24

The amount of dissociated salt, ξ, shown in column 2, increases rapidly with dilution. The results are very satisfactory.

For a strong acid and a weak base, like ammonium chloride, the state of equilibrium will be—

$$NH^{\cdot}_4 + Cl' + H_2O = H^{\cdot} + Cl' + NH_4OH,$$

if we neglect the minute quantity of water and base ionized. The negative chlorine ion appears on both sides of the equation, and hence we may write more simply—

$$NH^{\cdot}_4 + H_2O = H^{\cdot} + NH_4OH,$$

and the condition of equilibrium according to the law of mass action is—

$$\frac{C_{H^{\cdot}} C_{NH_4OH}}{C_{NH^{\cdot}_4}} = \text{constant}, \quad . \quad . \quad . \quad . \quad (4)$$

since the water, being in very great excess, may be taken constant.

This result can be deduced another way without making the explicit assumption that water and base are not ionized at all. If we take the ionization constant, K_2, of water into consideration—

$$\frac{C_{H^{\cdot}} C_{OH'}}{C_{H_2O}} = K_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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[1] G. Bredig, *Zeit. phys. Chem.*, **13.** 289, 1894.

If the base ammonium hydroxide be also ionized—

$$\frac{C_{NH\cdot_4}C_{OH'}}{C_{NH_4OH}} = K_3. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Now divide (5) by (6), and we get

$$\frac{C_{H\cdot}C_{NH_4OH}}{C_{NH\cdot_4}C_{H_2O}} = \frac{K_2}{K_3}; \quad \frac{C_{H\cdot}C_{NH_4OH}}{C_{NH\cdot_4}} = \frac{K_2}{K_3} \times C_{H_2O} = \text{constant}, \quad (7)$$

which is the same result as (1). Notice that we have assumed that the concentration of the hydroxyl ions derived from the water and from the ammonium hydroxide is the same.

§ 66. Hydrolysis of Salts derived from Weak Acids and Strong Bases.

Among the many examples may be mentioned potassium cyanide, potassium sulphide, potassium hydrosulphide, sodium carbonate, potassium chromate, and sodium acetate. In order to fix our ideas, let us confine our attention to potassium cyanide in aqueous solution. According to the ionic hypothesis—

$$K\cdot + CN' + H_2O = K\cdot + OH' + HCN,$$

and for equilibrium, as usual—

$$\frac{C_{OH'}C_{HCN}}{C_{CN'}} = \frac{K_2}{K_4} \times C_{H_2O} = \text{constant}, \quad . \quad . \quad (8)$$

where K_4 denotes the ionization constant for the reaction—

$$H\cdot + CN' = HCN; \text{ and } \frac{C_{H\cdot}C_{CN'}}{C_{HCN}} = K_4.$$

Shields[1] has calculated the ionization constant of water from equation (8). Thus it was found that 0·008 per cent. of a 0·0952 N-solution of sodium acetate was hydrolyzed at 24°. Hence, from (8)—

$$\frac{K_2}{K_4} = \frac{C_{\text{acid}}C_{\text{base}}}{C_{\text{salt}}} = \frac{(0{\cdot}00008 \times 0{\cdot}0952)^2}{0{\cdot}0952} = 0{\cdot}61 \times 10^{-9} = \text{constant}. \quad (9)$$

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[1] J. Shields, *Zeit. phys. Chem.*, **12**, 167, 1893.

Given the value of the ionization constant K_4 for acetic acid, namely, $1{\cdot}81 \times 10^{-5}$, the value of K_2 for water, $1{\cdot}1 \times 10^{-7}$, follows directly; and from (2)—

$$C_{\mathrm{H}^{\cdot}} = C_{\mathrm{OH}'},$$

and $C_{\mathrm{H_2O}}$ is unity, the concentration of the hydrogen or the hydroxyl ion, in water, is

$$C_{\mathrm{H}^{\cdot}} = \sqrt{K_2} = 1{\cdot}05 \times 10^{-7}.$$

Given the ionization constants of water and of acetic acid, we can calculate the constant of hydrolysis of the given salt from (9).

The alkaline reaction of these salts will be readily understood from what has been said with respect to the strong acids and weak bases. It is obviously due to the presence of an excess of hydroxyl ions. The number of hydrogen ions derived from the weak acid is less than the number of hydroxyl ions derived from the strong alkali. The alkaline reaction of soaps, *i.e.* the alkali salts of the weak fatty acids, is readily explained by the hypothesis just outlined.

§ 67. Hydrolysis of Salts derived from Weak Acids and Weak Bases.

This phenomenon is a little more complex. By way of example, let us take a particular case, the hydrolysis of aniline acetate. Here the salt is completely dissociated, while the products of dissociation are scarcely ionized at all—

$$\text{Aniline acetate} + \text{water} \rightleftharpoons \text{aniline} + \text{acetic acid}.$$

For equilibrium, it follows from the preceding principles—

$$\frac{C_{\text{acid}} C_{\text{base}}}{C^2_{\text{salt}}} = \text{constant}.$$

Notice that we are here dealing with the second power of the concentration of the salt. If we revert to another system of symbols, and suppose that *a* gram-molecules of aniline acetate are dissolved in v litres of water, and let ξ denote the number of gram-molecules of salt hydrolyzed, we shall have

$$\frac{\left(\frac{\xi}{v}\right)^2}{\left(\frac{a-\xi}{v}\right)^2}; \text{ or, } \frac{\xi^2}{(a-\xi)^2} = \text{constant.}$$

In words, the degree of hydrolytic dissociation does not depend on the concentration of the solution. This has been proved for the hydrolysis of urea acetate,[1] aniline acetate, etc., where the value of ξ was determined from the conductivity of the solution For aniline acetate, when—

v = 0·08, 0·04, 0·02, 0·01, 0·005, 0·0025;
ξ = 0·0546, 0·0558, 0·0564, 0·0551, 0·0556, 0·0554.

The values of ξ are sensibly constant.

Some interesting examples will be found in the pages of analytical chemistry.[2] The sulphides and carbonates of aluminium are so completely hydrolyzed by water that aluminium is precipitated as hydroxide from solutions of its salts by hydrogen sulphide and by sodium carbonate. Magnesium salts, on the other hand, are but partially hydrolyzed, and in consequence they are precipitated as a mixture of hydroxide and carbonate ("basic carbonate") by a soluble carbonate.

The colour of a solution depends on the condition of the dissolved substance. If the solution is but slightly ionized, the coloration will be due to the non-ionized molecule; if the substance is ionized, the coloration will be that of a mixture of the colours of the two ions.[3] Any substance which shows a change of colour when the solution passes from an acid to a basic condition can be employed as an "indicator" for

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[1] S. Arrhenius and S. Walker, *Zeit. phys. Chem.*, **5**. 18, 1890.

[2] W. Ostwald's *Die wissenschaftlichen Grundlagen d. analyt. Chem.*, Leipzig. 1901; G. McGowan's trans., 1895.

[3] W. Ostwald, *Zeit. phys. Chem.*, **2**. 78, 1888; F. W. Küster, *ib.*, **13**. 127, 1897; R. Meyer and O. Spendler, *Ber.*, **36**. 2949, 1903; J. Herzig, *ib.*, **28**. 3258, 1895; **29**. 138, 1896; with H. Meyer, *Monatshefte Chem.*, **17**. 429, 1899; with J. Pollak, *ib.*, **23**. 709, 1902; O. Fischer, *Zeit. Farb. Text. Chem.*, **1**. 281, 1902.

volumetric analysis. Phenolphthaleïn, for example, is a weak acid with a colourless molecule and a red negative ion. In aqueous solution the dissociation is so slight that the solution appears almost colourless.

$$\text{Phenolphthaleïn (colourless)} \rightleftharpoons C_{20}H_{13}O_4' \text{ (red ion)} + H^{\cdot}. \quad (1)$$

If a strong base, say potassium hydrate, be added—

$$KOH = K^{\cdot} + OH', \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the OH′-ion of the base unites with the H·-ion of the indicator to form water. This destroys equilibrium (1); more phenolphthaleïn is dissociated until sufficient $C_{20}H_{13}O_4'$-ions have been formed to produce a red coloration. If a weak base like ammonium hydrate be employed, these changes are too slow for analytical requirements. The addition of an acid reverses these operations in an obvious manner.

Methyl orange is an acid of medium strength; the molecule itself is red, the negative ion yellow. The colour of an aqueous solution is a mixture of these two colours. The addition of a base brings out the yellow colour of the negative ion owing to the union of the OH′ of the base with the H· of the indicator. Owing to the relatively strong acid nature of the methyl orange, weak bases may be employed (see § 65). The H·-ions derived from strong acids lessen the ionization and bring out the red coloration of the molecule very quickly; with weak acids the number of H·-ions is too small to produce a visible change of coloration until a large excess of acid has been added. The indicator is therefore not suited for titration with weak acids.

In the selection of an indicator, or of a standard alkali for titration of an acid, or of a standard acid for titration of an alkali, the following considerations should be borne in mind:—

Solutions titrated.		Indicator.	Examples.
Acid.	Base.		
Strong.	Strong.	Any.	Any.
Strong.	Weak.	Strong acid.	Methyl orange; *p*-nitrophenol.
Weak.	Strong.	Weak acid.	Phenolphthaleïn; litmus.
Weak.	Weak.	None satisfactory.	Avoid the process.

I must remind the reader that there is another side to all this. Many believe that the "ionization theory" does not furnish a sufficient explanation of the behaviour of indicators, and substitute the so-called "chromophoric theory" in its place. According to the latter hypothesis, the alternations of colour of, say, phenolphthaleïn in acid and alkaline solutions are due to "hydration and dehydration changes, accompanied by a transition from the benzenoid to the quinonoid type, and *vice versâ*."[1]

§ 68. Chemical Activity, Affinity, or Avidity.

We can now consider what takes place when we mix together solutions of two weak acids, HA_1 and HA_2, with a base MOH not present in sufficient quantity to neutralize the acids completely. We have, in the first place, to deal with the changes—

$$HA_1 \rightleftharpoons H^{\cdot} + A'_1 ; \ \ HA_2 \rightleftharpoons H^{\cdot} + A'_2 .$$

The conditions of equilibrium are respectively—

$$\frac{C_{A'_1}C_{H^{\cdot}}}{C_{HA_1}} = K_1 ; \text{ and } \frac{C_{A'_2}C_{H^{\cdot}}}{C_{HA_2}} = K_2, \quad . \quad . \quad (1)$$

where K_1 and K_2 respectively denote the ionization constants of the two acids. Again, the salts formed on the addition of MOH to the two acids, namely, MA_1 and MA_2, are almost entirely ionized. We may neglect the concentration of the very small traces of non-ionized MA_1 and MA_2. Since the acids are weak, they will hardly be dissociated at all, the more so as they are in the presence of their ionized salts, MA_1 and MA_2. Hence the concentration of the ions of the acid will be negligibly small. $C_{A'_1}$ and $C_{A'_2}$ will then denote the concentrations of the salts MA_1 and MA_2. By division of equations (1), therefore—

$$\frac{K_1}{K_2} = \frac{C_{A'_1}C_{HA_2}}{C_{A'_2}C_{HA_1}} = \frac{\text{salt } MA_1 \times \text{acid } HA_2}{\text{salt } MA_2 \times \text{acid } HA_1} = \text{constant}, \quad (2)$$

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[1] A. G. Green and A. G. Perkin, *Journ. Chem. Soc.*, **85**. 398, 1904; P. Vaillant, *Compt. Rend.*, **137**. 849, 1903; J. Stieglitz, *Journ. Amer. Chem. Soc.*, **25**. 1112, 1903.

which is in agreement with the law of mass action, with the addition that the constant may be calculated from the ionization constant of the two acids. This conclusion has been established by some experiments by Arrhenius, which will be quoted further on.

Let one gram-molecule of each of the acids and of the base be taken; let ξ gram-molecules of the first acid be neutralized by the base; then $1-\xi$ will denote the amount of the second acid neutralized by the base; and, further, $1-\xi$ of the first acid, and ξ of the second acid, will remain uncombined. Consequently, from (2)—

$$\frac{K_1}{K_2} = \frac{\xi^2}{(1-\xi)^2}; \text{ or, } \frac{\xi}{1-\xi} = \sqrt{\frac{K_1}{K_2}}, \quad . \quad . \quad (3)$$

or the "ratio of distribution" of the base between the two acids is equal to the ratio of the square roots of the ionization constants of the two weak acids. If $\xi > (1-\xi)$, more of the base will combine with the acid HA_1 than with the acid HA_2. This we express by saying that the first acid will have a greater "strength," "affinity," "chemical activity," or "avidity," for the base than the second acid. From this point of view, "greater strength of the acid" means that, at the same concentration, the one acid is more ionized than the other.

The following table contains the fraction ξ of base which falls to the share of formic acid, HA_1, when this acid is competing with the acid named in the first column of the table. K_1 for formic acid = 0·0214.[1]

Formic acid with	K_2	ξ	
		Obs.	Calc.
Lactic acid . . .	0·0138	0·54	0·56
Acetic acid . . .	0·0180	0·76	0·75
Butyric acid . . .	0·00149	0·80	0·79
Isobutyric acid . .	0·00144	0·81	0·79

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[1] S. Arrhenius, *Zeit. phys. Chem.*, 5. 1, 1890.

We can use the numerical values of K_1 and K_2 for one pair of acids—HA_1 and HA_2—towards some base chosen as standard, and obtain a series of numerical ratios—

$$\frac{K_1}{K_2} : \frac{K_1}{K_3} : \frac{K_1}{K_4} : \ldots$$

for a series of acids, HA_2, HA_3, HA_4, . . . associated, in turn, with the acid HA_1.

In the following table the relative affinities of a few acids, referred to nitric acid as a standard, are arranged along with the heats of neutralization of the same acids with sodium hydroxide. These numbers show that there is no direct connection between the thermal value of a reaction and the affinity coefficients. The results in the second column were calculated by Thomsen from his measurements of the thermal value of the reaction, and he adds that "the numbers are only to be regarded as approximate." Thomsen's data are placed side by side with numbers obtained by Ostwald from measurements of the change of volume which takes place when the solutions are mixed together.

Acid.	Affinity.		Heat of neutralization.
	Thomsen.	Ostwald.	
Nitric acid . . .	100·0	100·0	13700
Hydrochloric acid .	100·0	98·0	13700
Sulphuric acid . .	49·0	—	13700
Trichloracetic acid .	36·0	80·0	13900
Formic acid . .	—	0·039	—
Acetic acid . . .	0·03	0·0123	13400

These numbers mean that if we are dealing with the distribution of, say, one equivalent of each of sulphuric and acetic acids with sodium hydroxide, the base will be divided between the two acids in the ratio 0·49 : 0·03. Hence—

$$\left(\frac{\xi}{1 - \xi}\right)^2 = \frac{0·49}{0·03}; \quad \therefore \xi = 0·80.$$

In other words, 80 per cent. of sodium hydroxide will form sodium sulphate, and 20 per cent. will form sodium acetate.

§ 69. Coefficients of Affinity.

Another interesting question might now be raised: What is the influence of the base upon the affinity of the acid? Take Ostwald's[1] measurements of the distribution of the bases, hydroxides of potassium, sodium, and ammonium, and the oxides of magnesium, zinc, and copper, between hydrochloric and nitric acids. The results were respectively 0·97, 0·96, 0·96, 0·99, 0·95, 0·97. Again, the following table contains the ratio of distribution of the given base between dichloracetic acid and the acid named in the first column:—

Acid.	KOH	NaOH	NH_4OH	Mean.
Nitric acid . .	77	77	75	76
Hydrochloric acid .	74	75	73	74
Trichloracetic acid .	71	71	70	71
Lactic acid . .	8	9	11	9

The conclusion is obvious: *The relative affinity of the acids is independent of the nature of the base.*

Dibasic acids, like sulphuric acid, deviate from this regularity, and the results obtained led Thomsen[2] to wrongly conclude that "the relative avidity of the acid is dependent upon the nature of the base." The disturbance arises from secondary reactions which were recognized by Berthelot in 1873.[3] The acid only acts upon *part* of the base to form an acid sulphate.

The above conclusions led Ostwald,[4] in 1877, to make the following deduction:—Let the absolute affinity of an acid for a

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[1] W. Ostwald, *Journ. prakt. Chem.* [2], **16**. 385, 1877; **18**. 328, 1878; E. Lellmann and A. Gross, *Liebig's Ann.*, **260**. 269, 1891; **263**. 286, 1891; E. Lellmann and J. Schliemann, *ib.*, **270**. 208, 1892; S. Arrhenius, *Zeit. phys. Chem.*, **5**. 1, 1890; E. J. Mills, *Proc. Roy. Soc.*, **18**. 348, 1870; *Phil. Mag.* [4], **40**. 134, 1870.

[2] J. Thomsen, *Pogg. Ann.*, **138**. 497, 1869.

[3] M. Berthelot, *Ann. Chim. Phys.* [4], **30**. 516, 1873.

[4] W. Ostwald, *Journ. prakt. Chem.* [2], **16**. 385, 1877.

base be represented by some function of both. Now, mathematicians usually represent a function of x by the symbol $f(x)$. Hence, we may write—

$$\text{Absolute affinity of A for B} = f(a, b), \quad . \quad . \quad . \quad (1)$$

meaning nothing more than that $f(a, b)$ is some mathematical expression which will enable the "absolute affinity" to be calculated when the numerical values of a and b are known. If, therefore, A_1 and A_2 are two acids, and B_1 and B_2 are two bases, we can write Ostwald's law that "the relative affinity of the acids is independent of the nature of the base" in the forms—

$$\frac{f(a_1, b_1)}{f(a_2, b_1)} = \frac{f(a_1, b_2)}{f(a_2, b_2)}; \text{ or, } \frac{f(a_1, b_1)}{f(a_1, b_2)} = \frac{f(a_2, b_1)}{f(a_2, b_2)}, \quad . \quad (2)$$

by a transposition of terms. In words, the latter relation means that *the relative affinity of the bases is independent of the nature of the acids.*

This "law" was noticed by Bergmann[1] as early as 1775 with over two dozen acids and as many bases, or "metallic calces." The fact comes out in a striking manner from his "Tables of Affinity." The relative order of the affinity of the bases was practically the same with all the acids. The uniformity of the order in which the different metals are precipitated in solutions of different acids was specially commented upon. "I was struck with great surprise," added Bergmann, "at the coincidence, . . . and I began to entertain the suspicion that the precipitation of the metals did not depend upon the affinities of the acids, but depended upon some other principle. . . ."

The tacit assumption has been made that each function $f(a, b)$ can be resolved into two factors, $\phi(a)$ and $\psi(b)$, the former depending upon the nature of the acid alone, and the latter upon the nature of the base alone.

$$\therefore f(a, b) = \phi(a) \cdot \psi(b). \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Otherwise expressed, the affinity between an acid and a base

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[1] T. Bergmann's *De Attractionibus Electivis*, Upsala, 1775; Anonymous trans., London, 83, 1785.

can be resolved into two factors—the one depending upon the nature of the acid and the other upon the nature of the base. When we know the relative affinities of the various bases B_1, B_2, B_3, . . . for one acid, arbitrarily chosen, and of the various acids A_1, A_2, A_3, . . . for one base, we can write these affinities in tabular form—

	$\phi(a_1)$	$\phi(a_2)$	$\phi(a_3)$
$\psi(b_1)$	—	—	—
$\psi(b_2)$	—	—	—
$\psi(b_3)$	—	—	—

The affinity of any base for any acid can then be determined by multiplying the first terms of the corresponding row and column.[1]

If we are dealing with the coefficient of distribution of two acids, A_1 and A_2, with one base, B, we get, for the ratio of distribution—

$$\frac{\phi(a_1)\psi(b)}{\phi(a_2)\psi(b)} = \frac{\phi(a_1)}{\phi(a_2)}.$$

From (6), § 48, the "ratio of distribution" is equal to the square root of the ratio of the velocity coefficients of the reaction; hence from (3), § 62—

$$\frac{K_1}{K_2} = \frac{k_1}{k_2} = \left(\frac{\phi(a_1)}{\phi(a_2)}\right)^2 = \left(\frac{\xi}{1 - \xi}\right)^2,$$

or the coefficients of the velocity of the action of two acids upon any base are proportional to the degrees of ionization of the acids when the latter are weak electrolytes.

Less work has been done on the affinity coefficients of the

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[1] To allow for the influence of temperature, it would be necessary to give this table a third dimension, containing the (yet unknown) influence of temperature on affinity.

bases than of the acids. Among the most important may be mentioned the work of Warder,[1] Goldschmidt,[2] and Reicher,[3] on the hydrolysis of ethyl acetate; of Bredig,[4] on the conductivity of various bases; of Schweinberger,[5] on the decomposition of the bromacetates; and of Goldschmidt and Salcher,[6] on the aminolytic constants.

The rate of conversion of diazoamide to amidoazo compounds—**aminolysis**—in aniline solution is proportional to the amount of acid added to the aniline. If pyridine hydrochloride be added, the aniline takes some of the hydrochloric acid from the pyridine, and the velocity of the above reaction is accelerated in a proportional manner. Assuming that the pyridine hydrochloride has no influence upon the reaction, a series of affinity (aminolytic) constants has been determined for a number of bases which agree with those determined in the usual way.

Since the nature of the base exerts no influence upon the relative affinity of the acids, all reactions which are accomplished by the agency of the acids themselves, may be utilized for finding the numerical values of the affinities of the acids. For example, Ostwald has determined the relative affinities of the acids from their action upon the salt of another acid which is insoluble in water. The salts employed were the oxalates of calcium and zinc, barium chromate, acid potassium tartrate, sulphates of barium, strontium, and calcium;[7] the accelerating influence of acids upon the decomposition of acetamide;[8] the hydrolysis of methyl acetate;[9] the inversion

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[1] R. B. Warder, *Amer. Chem. Journ.*, **3.** 55, 340, 1882; *Ber.*, **14.** 1361, 1881.

[2] H. Goldschmidt and L. Osian, *Ber.*, **32.** 3390, 1899; **33.** 1140, 1900.

[3] L. T. Reicher, *Liebig's Ann.*, **228.** 257, 1885.

[4] G. Bredig, *Dissertation*, Leipzig, 1892; *Zeit. phys. Chem.*, **13.** 289, 1894.

[5] A. Schweinberger, *Gazz. Chim. Ital.*, **31.** ii., 321, 1901.

[6] H. Goldschmidt and R. M. Salcher, *Zeit. phys. Chem.*, **29.** 89, 1899.

[7] W. Ostwald, *Journ. prakt. Chem.* [2], **28.** 493, 1883.

[8] W. Ostwald, *Journ. prakt. Chem.* [2], **27.** 1, 1883; see also E. J. Mills and T. U. Walton, *Proc. Roy. Soc.*, **28.** 268, 1879.

[9] W. Ostwald, *Journ. prakt. Chem.* [2], **28.** 449, 1883.

of cane sugar;[1] the action of bromic acid and chromic acid upon hydriodic acid;[2] and the retarding action of the acids upon the reaction between bromine and ammonia.[3]

The following table shows the results obtained with these six reactions and a few selected acids. For the purpose of comparison, the results obtained by measuring the distribution of base between the acids as indicated above, and also the conductivities of the acids, have been added.

Acid.	Distribution of acids.	Electrical conductivity.	Calcium oxalate.	Acetamide.
HCl	1·000	0·900	0·900	1·000
HNO_3	0·996	1·000	1·000	0·955
H_2SO_4	0·651	0·667	0·616	0·547
CCl_3COOH	0·623	0·800	0·580	0·670
$HCOOH$	0·017	0·039	0·023	0·005
CH_3COOH	0·004	0·012	0·009	0·001

Acid.	Methyl acetate.	Hydriodic acid.	Ammonia and bromine.	Cane sugar.
HCl	1·000	1·000	1·000	1·000
HNO_3	0·955	0·980	0·913	1·000
H_2SO_4	0·547	0·694	0·722	0·536
CCl_3COOH	0·682	—	—	0·754
$HCOOH$	0·015	0·003	—	0·013
CH_3COOH	0·003	0·001	0·025	0·004

The order of magnitude of these numbers obtained by such different methods is the same, and the agreement is all the more remarkable when we remember that the experiments were

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[1] J. Löwenthal and E. Lenssen, *Journ. prakt. Chem.* [1], **85**. 321, 401, 1862; W. Ostwald, *ib.* [2], **29**. 385, 1884; G. Fleury, *Ann. Chim. Phys.* [5], **7**. 381, 1876; F. Urech, *Ber.*, **13**. 1696, 1880; H. Goldschmidt and H. Buss, *Ber.*, **30**. 2075, 1897.

[2] W. Ostwald, *Zeit. phys. Chem.*, **2**. 127, 1888.

[3] W. Ostwald and S. Raich, *Zeit. phys. Chem.*, **2**. 124, 1888.

conducted at different temperatures, and with acids of different concentration, and that the presence of the products of the reaction often interfered with the results. It is also interesting to note that Levy's[1] experiments on the influence of acids upon the rate of multirotation of sugars furnished analogous results.

Cohnheim[2] also determined the "affinity" of the various albuminoses and antipeptone for hydrochloric acid by the "sugar inversion" method.

The numbers are not to be regarded as final. Some reactions furnish more trustworthy results than others owing to their freedom from side reactions, but the general order of magnitude of these affinity constants is to be regarded as a close approximation to the truth.

It follows, therefore, that—

1. The activity of an acid depends upon the nature and concentration of the acid alone; so also, *mutatis mutandis*, for a base.
2. The activity of the acids and bases is proportional to certain coefficients which are independent of the nature of the chemical process involved.
3. The ratio of distribution of a base between two acids is proportional to the square root of the velocity constants, and to the square roots of the ionization constants of the acids.

§ 70. The Measurement of Chemical Affinity.

The problem of finding the distribution of the components at different stages of the reaction is generally simple in the case of heterogeneous reactions, because it is usually sufficient to separate the heterogeneous constituents and determine their amounts in the ordinary way. With homogeneous systems the problem is a little more difficult. Chemical methods can be

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[1] A. Levy, *Zeit. phys. Chem.*, **17**. 301, 1895.

[2] O. Cohnheim, *Zeit. Biol.*, **33**. 489, 1896; S. Bugarszky and L. Liebermann, *Pflügers Arch.*, **72**. 51, 1898.

employed when the process takes place so slowly that the analytical operation can be performed before the system can sensibly alter. Thus, Berthelot and Gilles estimated the free acid produced in the hydrolysis of ethyl acetate by titration with standard baryta solution and litmus; and Löwenthal and Lenssen determined the rate of inversion of cane sugar by titration from time to time with Fehling's solution. Very often the state of the system cannot be so determined, because the relative distribution of the substances would be modified by the analytical process itself, as indicated on p. 209. In that case it is necessary to take advantage of the change in some physical property of the system which depends on the distribution of the reacting components at different stages of the reaction. Steinheil[1] and Hofmann[2] have developed the general theory of the methods of physical measurement for finding the constituents of a mixture.

As pointed out in § 10, there are two methods of measurement—dynamical and statical. The former methods have been so frequently referred to in the earlier parts of this work that it is not necessary to enter into further detail.

1. *By measurement of thermal changes.*—J. Thomsen[3] determined the distribution of a base, B, between two acids, A_1 and A_2, by measuring the thermal value of the reaction. Let q_1, q_2, and Q respectively denote the thermal values of the reactions between the base and the acid A_1 alone, the base and the acid A_2 alone, and of the base in contact with both acids A_1 and A_2. If $Q = q_1$, the base will have combined with all the

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[1] C. A. Steinheil, *Liebig's Ann.*, **48**. 153, 1843.

[2] K. Hofmann, *Pogg. Ann.*, **133**. 575, 1868. The following may be consulted: "Ueber physikalisch-chemische Messungen," K. Arndt, *Zeit. angew. Chem.*, **16**. 1245, 1903; "Ueber physiko-chemische Messmethoden," W. Ostwald, *Zeit. phys. Chem.*, **17**. 427, 1895; W. Ostwald and R. Luther's *Hand- und Hilfsbuch zur Ausführung physico-chemischer Messungen*, Leipzig, 1902; J. Walker's trans. of the earlier edition, *Manual of Physico-chemical Measurements*, London, 1894.

[3] J. Thomsen, *Pogg. Ann.*, **91**. 83, 1854; 138, 65, 1869; *Phil. Mag.* [4], **39**. 410, 1870; *Thermochemische Untersuchungen*, **1**. 98, 1882; F. A. Tarleton, *Trans. Irish Acad.*, **28**. 1, 1880.

acid A_1; and if $Q = q_2$, the base will have combined with all the acid A_2; while if Q lies between q_1 and q_2, the base will have divided itself between the two acids.

In practice equivalent quantities of dilute aqueous solutions of sodium hydroxide and sulphuric acid were mixed together in a calorimeter, and afterwards sodium hydroxide was mixed with nitric acid in the same manner. It was found that—

$$\mathrm{H_2SO_4aq} + \mathrm{(NaOH)_2aq} = 31{,}380 \text{ cal.};$$
$$\mathrm{(HNO_3)_2aq} + \mathrm{(NaOH)_2aq} = 27{,}230 \text{ cal.}$$

Equivalent quantities of nitric acid and sodium sulphate were then also mixed in dilute aqueous solution, when—

$$\mathrm{Na_2SO_4aq} + \mathrm{(HNO_3)_2aq} = -\ 3{,}500 \text{ cal.}$$

If the sole products of the reaction were sulphuric acid and sodium nitrate, the heat of the reaction would be $27{,}230 - 31{,}380 = -\ 4{,}500$ cal. Hence the whole of the sodium sulphate was not converted into sodium nitrate. If the only reactions concerned are those indicated in the equation—

$$\mathrm{Na_2SO_4} + 2\mathrm{HNO_3} \rightleftharpoons \mathrm{H_2SO_4} + 2\mathrm{NaNO_3},$$

and if x denote the number of equivalents of sodium sulphate which has changed, it follows that—

$$-\ 3{,}500 = (27{,}230 - 31{,}380)x; \quad \text{or, } x = 0{\cdot}84.$$

But the sulphuric acid produced reacts with the unchanged sodium sulphate to form sodium hydrogen sulphate.

If x equivalents of sodium sulphate are decomposed by nitric acid, x equivalents of sodium nitrate will be formed, x equivalents of sulphuric acid will also be formed, and $1 - x$ equivalents of sodium sulphate will remain. The total thermal change is the sum of three parts—

(1) Decomposition of $x\mathrm{Na_2SO_4}$ $= -\ 31{,}380$;
(2) Formation of $x2\mathrm{NaNO_3}$ $= +\ 27{,}230$;
(3) Reaction between $x\mathrm{H_2SO_4}$ and $(1 - x)\mathrm{Na_2SO_4}$ $= -\dfrac{x(1-x)}{0{\cdot}2x + 0{\cdot}8}3300.$

The thermal values of the secondary changes which take place between nitric acid and sodium nitrate, and between sulphuric and nitric acids, were negligibly small.

$$\therefore -3500 = (27230 - 31380)x - \frac{x(1-x)}{0{\cdot}2x + 0{\cdot}8}3300;$$

$$\therefore x = \tfrac{2}{3}.$$

This means that two-thirds of the sodium will be present as sodium nitrate, and one-third as sodium sulphate. Hence—

$$\frac{k_1}{k_2} = \left(\frac{\xi}{1-\xi}\right)^2 = \left(\frac{\frac{2}{3}}{1-\frac{2}{3}}\right)^2 = 4.$$

If a equivalents of nitric acid are mixed with one equivalent of sodium sulphate, the condition of equilibrium is—

$$4(a-\xi)(1-\xi) = \xi^2;$$

$$\therefore \xi = \tfrac{2}{3}\left(1 + a - \sqrt{(1+a)^2 - 3a}\right).$$

Thomsen found, for example—

a	ξ	Heat absorbed.	
		Calc.	Obs.
0·125	0·121	920	900
0·250	0·232	1660	1620
0·500	0·423	2660	2580
1·000	0·667	3550	3500

The differences are within the limits of experimental error.

2. *By measurement of the change in density.*—When the solution of an acid is brought into contact with a solution of a base, the resulting volume is different from the sum of the volumes of the two solutions. When the changes in volume which occur when a base is neutralized first by one acid, and then by another, as well as the change in volume when the base is mixed with both acids together, are known, simple proportion will serve to determine how much of the base has gone to each acid. Early attempts were made by Tissier,[1] in 1860,

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[1] C. Tissier, *Compt. Rend.*, **50.** 106, 1860; W. Ostwald, *Journ. prakt. Chem.* [2], **16.** 385, 1877; **18.** 328, 1878; *Pogg. Ann. Ergbd.*, **8.** 154,

to apply the method, but Ostwald's measurements were the first to come up to the required standard. The experimental results were as follows :—

	Volume occupied.
1 kilogrm. containing 1 grm.-mol. $NaOH$	956·632 c.c.
„ „ „ HCl	982·406
Calculated volume on mixing	1939·038
Observed volume on mixing	1958·275
Increase in volume on mixing	19·237

1 kilogrm. containing 1 grm.-mol. $NaOH$	956·632 c.c.
„ „ „ $CHCl_2COOH$	947·377
Calculated volume on mixing	1904·009
Observed volume on mixing	1916·714
Increase in volume on mixing	12·705

The increase in volume which accompanies the neutralization of sodium hydroxide by hydrochloric acid is greater by 6·532 c.c. than the increase which accompanies the neutralization by dichloracetic acid. If hydrochloric acid be added to sodium dichloracetate, and the latter is completely converted into sodium chloride and dichloracetic acid, the increase in volume will be 6·532 c.c. As a matter of fact, the observed increase is only 5·100 c.c. Thus—

	Volume occupied.
2 kilogrm. containing 1 grm.-mol. $CHCl_2COONa$	1916·714 c.c.
1 „ „ „ HCl	982·406
Calculated volume on mixing	2899·120
Observed volume on mixing	2904·220
Increase in volume on mixing	5·100

Consequently all the sodium dichloracetate will not be converted into sodium chloride and dichloracetic acid. Let x

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1878 ; Resume by M. M. P. Muir, *Phil. Mag.* [5], **8.** 181, 1879 ; W. Duane, *Amer. Journ. Science* [4], **11.** 19, 1901 ; M. Rogow, *Zeit. phys. Chem.*, **11.** 657, 1893 ; E. Ruppin, *ib.*, **14.** 467, 1894 ; G. Tammann, *ib.*, **11.** 689, 1893 ; E. Brunner, *Zeit. anorg. Chem.*, **38.** 350, 1904.

denote the fraction of the sodium dichloracetate which is decomposed—

$$\therefore 5·100 = 6·532x;\ \text{or, } x = 0·78.$$

Hence 2·2 times more sodium hydroxide goes to the HCl than to the $CHCl_2COOH$.

$$\frac{k_1}{k_2} = \left(\frac{0·22}{1 - 0·22}\right)^2 = 0·063.$$

When secondary actions occur, corrections must be introduced as in the preceding example studied by Thomsen. Other physical properties have been employed for finding the composition of a mixed solution. These are of more or less restricted application. For example, change of vapour density, § 50; change of the pressure of a gas or vapour, § 21; change of freezing or boiling point;[1] refraction of light;[2] coefficient of absorption of light;[3] absorption spectrum and change of colour;[4] rotation of the plane of polarized light;[5] specific heat, § 50; partition coefficient;[6]

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[1] L. Kahlenberg, D. J. Davis, and R. E. Fowler, *Journ. Amer. Chem. Soc.*, **21**. 1, 1899; T. W. Richards and F. Bonnett, *Proc. Amer. Acad.*, **39**. 1, 1903; *Zeit. phys. Chem.*, **47**. 29, 1904.

[2] C. A. Steinheil, *Liebig's Ann.*, **48**. 153, 1843; K. Hofmann, *Pogg. Ann.*, **133**. 575, 1868; W. Ostwald, *Journ. prakt. Chem.* [2], **18**. 342, 1878; W. Duane, *Amer. Journ. Science* [4], **11**. 19, 1901.

[3] E. Lellmann and J. Schliemann, *Liebig's Ann.*, **270**. 208, 1892; E. Lellmann and H. Gross, *ib.*, **260**. 269, 1890; **263**. 286, 1891; A. Görtz, *Dissertation*, Tübingen, 1892.

[4] J. H. Gladstone, *Phil. Trans.*, **145**. 179, 1855; *Journ. Chem. Soc.*, **9**. 144, 1856; *Phil. Mag.* [4], **9**. 535, 1855; G. Salet, *Compt. Rend.*, **67**. 488, 1868; G. Magnanini, *Zeit. phys. Chem.*, **8**. 1, 1891; J. T. Cundall, *Journ. Chem. Soc.*, **59**. 1076, 1891; **67**. 794, 1895; J. H. Kastle and B. C. Keiser, *Amer. Chem. Journ.*, **17**. 443, 1895.

[5] J. B. Biot, *Compt. Rend.*, **20**. 1747, 1845; L. Wilhelmy, *Pogg. Ann.*, **50**. 413, 499, 1850; J. H. Gladstone, *Journ. Chem. Soc.*, **15**. 303, 1862; *Journ. prakt. Chem.* [1], **83**. 449, 1863; J. H. Jellet, *Trans. Irish Acad.*, **25**. 371, 1875; A. Müller, *Pogg. Ann. Ergbd.*, **6**. 123, 1873; E. J. Mills and J. Hogarth, *Proc. Roy. Soc.*, **28**. 270, 1879; A. A. Noyes and W. J. Hall, *Zeit. phys. Chem.*, **18**. 240, 1895; J. Walker, *ib.*, **46**. 30, 1903.

[6] § 71. See H. M. Dawson and F. E. Grant, *Journ. Chem. Soc.*, **81**. 512, 521, 1902; **83**. 725, 1903; also *Journ. Phys. Chem.*, **7**. 46, 1903.

magnetic properties;[1] and the electrical conductivity of the solution.[2]

The reader must be careful not to wrongly interpret these results. We state that "if one acid be allowed to act upon the salt of another acid, the relative strengths of the acids can be determined from the division of the base between the two acids."

There is a notion amongst students of practical chemistry that sulphuric acid is a stronger acid than either hydrochloric or nitric acid, because the sulphuric acid is so frequently employed to displace hydrochloric acid from sodium chloride, and nitric acid from sodium nitrate. Again, when hydrosulphuric acid is allowed to act upon the soluble chloride or nitrate of a heavy metal, insoluble sulphide is precipitated. Does this mean that an aqueous solution of hydrogen sulphide is a stronger acid than nitric or hydrochloric acid? Again, if a current of carbon dioxide is passed through a saturated solution of sodium acetate, sodium hydrogen carbonate is precipitated; on the other hand, if acetic acid be added to sodium carbonate, the brisk effervescence shows that the carbonic acid is being displaced by the acetic acid.

A moment's reflection will show the disturbing factor. Either a *volatile* compound is formed which separates from the field of action, so that its active mass becomes zero; or else an *insoluble* compound is formed which also separates from the system. The relative affinity of the two acids can only be compared by allowing one acid to act upon the salt of another in such a way that both acids are under comparable conditions. We do not compare a liquid with a gas, nor a solid with a

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[1] G. Wiedemann (*Wied. Ann.*, **5**. 45, 1878) measured the change in the magnetic properties of ferric salts to determine the amount decomposed into free acid and colloidal ferric hydroxide when these salts are mixed with water.

[2] See R. A. Lehfeldt's *Electro-chemistry*; also § 59; G. Carrara and U. Rossi, *Rend. Accad. Lincei* [5], **6**. i., 152, ii., 208, 219, 1897; M. Schümann and A. Hantzsch, *Ber.*, **32**. 1691, 1899; M. Schümann, *ib.*, **33**. 527, 1900; D. Negreanu, *Compt. Rend.*, **106**. 1665, 1888; **107**. 176, 1888.

liquid, but when we are working with everything in solution throughout the whole course of the reaction, then the relative division of the base between the two acids may be taken as a measure of the affinities in question.

§ 71. Solubility. The Partition Law.

It is now interesting to compare the effect of adding one of the products of the ionization to a saturated solution of sodium chloride containing as it does the ions $Na^\cdot$ and Cl'. For equilibrium—

$$NaCl \rightleftharpoons Na^\cdot + Cl',$$

and the effect of adding one of the products of ionization to the system is perfectly analogous to the effect of adding one of the products of the reaction to a dissociating system, say, of ammonia to the system—

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

We may note in passing that ionization is not identical with dissociation, for the ionization of ammonium chloride would be—

$$NH_4Cl \rightleftharpoons NH_4^{\cdot} + Cl'.$$

In the illustration chosen, the condition of equilibrium will be—

$$K_1 = \frac{k_1}{k_2} = \frac{C_{Na^\cdot}.C_{Cl'}}{C_{NaCl}}.$$

But the NaCl is in saturated solution, hence the concentration of the sodium chloride, C_{NaCl}, is constant, and we may write—

$$K = C_{Na^\cdot}.C_{Cl'},$$

where $K = K_1 C_{NaCl}$. This means that the product of the concentration of the ions in a saturated solution is constant. If we increase the value of $C_{Na^\cdot}$ by adding $Na^\cdot$ ions, or of $C_{Cl'}$ by adding Cl' ions, $C_{Na^\cdot}$ or $C_{Cl'}$ must diminish in order that K may retain its constant value. This can only take place if the ions recombine to form molecules of NaCl. But the solution already contains as many molecules as it can hold under the conditions of the experiment. Hence, NaCl will separate out from the solution.

It is not possible to introduce $Na^{\cdot}$ or Cl' ions alone into the solution, but the addition of a solution containing the same ions associated with something else will do quite well. *E.g.*, $NaNO_3$, $NaClO_3$, $NaClO_4$, etc.; KCl, HCl, LiCl, etc. The apparent diminution of the solubility of a salt by the addition of another salt containing a common ion is a familiar phenomenon. The precipitation of sodium chloride by passing hydrogen chloride into a saturated solution of the salt is a well-known method of purification of sodium chloride; the solubility of silver bromate is diminished by the presence of silver nitrate and of potassium bromate; of thallium chloride by the presence of potassium chloride; of α-bromisocinnamic acid by the presence of oxanilic acid, etc.[1]

We can thus distinguish between the *total* amount of salt present in unit volume of a solution (*apparent solubility*), and the amount of non-ionized salt which exists in the same solution (*real solubility*). The apparent solubility of α-bromisocinnamic acid is $17{\cdot}6 \times 10^{-6}$ gram-molecules per litre. Let ξ denote that fraction of the $17{\cdot}6 \times 10^{-6}$ gram-molecules which is ionized, and $17{\cdot}6 \times 10^{-6}(1 - \xi)$ will denote the fraction non-ionized. From conductivity measurements, the ionization constant $K = 14{\cdot}4 \times 10^{-6}$.

$$C_9H_7BrO_2 \text{ (α-bromisocinnamic acid)} = C_9H_6BrO'_2 + H^{\cdot}.$$

$$\therefore (1 - \xi)17{\cdot}6 \times 10^{-6} \times 14{\cdot}4 \times 10^{-6} = (17{\cdot}6 \times 10^{-6}\xi)^2;$$

$$\therefore \xi = 0{\cdot}584,$$

and the fraction non-ionized will be $1 - 0{\cdot}584 = 0{\cdot}416$. But $17{\cdot}6 \times 10^{-6}$ gram-molecules of α-bromisocinnamic acid are present in a litre of saturated solution; of this, $0{\cdot}416 \times 17{\cdot}6 \times 10^{-6} = 7{\cdot}32 \times 10^{-6}$ gram-molecules will remain non-ionized, and there will be $C - 7{\cdot}32 \times 10^{-6}$ gram-molecules of negative

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[1] A. A. Noyes, *Zeit. phys. Chem.*, **6**. 241, 1890; **9**. 603, 1892; **16**. 125, 1895; **26**. 152, 1898.

ions of α-bromisocinnamic acid, where C denotes the total concentration of the α-bromisocinnamic acid. Now let C' gram-molecules of oxanilic acid be added. The concentration of the non-ionized α-bromisocinnamic acid will remain the same as before. Let u denote the fraction of the oxanilic acid which is dissociated, then $C'-u$ will denote the number of negative ions of oxanilic acid; the total number of hydrogen ions present will be $u + C - 7{\cdot}32 \times 10^{-6}$. Hence from the law of mass action—

$$(C-7{\cdot}32\times 10^{-6})(C+u-7{\cdot}32\times 10^{-6})=14{\cdot}4\times 10^{-6}\times 7{\cdot}32\times 10^{-6}$$

Again, since the ionization constant of oxanilic acid is $K = 11{\cdot}8 \times 10^{-6}$,

$$u(C+u-7{\cdot}32\times 10^{-6}) = 11{\cdot}8\times 10^{-6}(C'-u),$$

where $C'-u$ denotes the concentration of the non-ionized oxanilic acid. The value of C can readily be calculated from these two equations when the value of C' is given. This has been done in the following table containing the observed and calculated values of C for different values of C' :—

Oxanilic acid. $C_2 \times 10^{-6}$	Solubility of α-bromisocinnamic acid. $C_1 \times 10^{-6}$	
	Obs.	Calc.
0·0	17·6	—
27·2	14·0	13·6
52·4	12·9	12·0

This table furnishes a quantitative illustration of the fact that the solubility of a salt is diminished in presence of another salt having a common ion.[1]

Conversely, the solubility of a salt is increased in the presence of a salt containing no common ion. If potassium nitrate be

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[1] Complications arise when part of the salt forms polymerized molecules, as indicated later on.

added to a saturated solution of silver bromate, a number of molecules of silver nitrate and of potassium bromate will be formed by double decomposition. This obviously lessens the number of molecules of silver bromate in the solution, and these will be replaced by the dissolution of more salt.[1]

If nitric acid be added to a saturated solution of silver acetate, a large quantity of acetic acid will be produced. A solution of acetic acid is largely made up of non-ionized molecules of the acid. But the product of the silver and CH_3COO'-ions must regain its former value. This can only take place by the passage of more silver acetate into the solution. This explains how it is that calcium oxalate is more soluble in the presence of acids, and the increase in the solubility is proportional to the degree of ionization of the acid.[2]

By reversing the above reasoning, it is possible to calculate the degree of ionization of an electrolyte from the change in the solubility of one salt in the presence of another salt. The results obtained are in harmony with numbers obtained from other methods of measurement.

According to Henry's well-known law, the solubility of a gas in a liquid is regulated by the condition that at any given temperature the concentration of the gas in the solution is proportional to its concentration in the gaseous state. In the same way it is found that if a gas be exposed to the action of two solvents, the amount dissolved by each solvent will be proportional to the concentration of the supernatant gas. Hence, the amount of gas dissolved by one solvent is proportional to the amount dissolved by the other. This is the law of partition independently discovered by Aulich and by Nernst.[3] Extending the "law" to the distribution of a substance between two solvents, it is found that the ratio of the amount of substance present in each solvent is a constant. For example, take Nernst's experiments on the distribution of succinic acid

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[1] F. Margueritte, *Compt. Rend.*, **38.** 304, 1854.

[2] W. Ostwald, *Journ. prakt. Chem.* [2], **22.** 251, 1880.

[3] P. Aulich, *Zeit. phys. Chem.*, **8.** 105, 1891; W. Nernst, *ib.*, **8.** 110, 1891; W. S. Hendrixson, *Zeit. anorg. Chem.*, **13.** 73, 1896.

between ether and water, and of benzoic acid between water and benzene. In the table C_1 denotes the concentration of the acid in aqueous solution, and C_2 the concentration of the acid in the second solvent.

Succinic acid (water and ether).			Benzoic acid (water and benzene).			
C_1	C_2	C_1/C_2	C_1	C_2	C_1/C_2	$C_1/\sqrt{C_2}$
0·24	0·046	5·2	0·150	2·42	0·062	0·0305
0·70	0·130	5·2	0·195	4·12	0·048	0·0304
1·21	0·22	5·4	0·289	9·70	0·030	0·0293

While the proportionality obtains with succinic acid in water and ether, the ratio does not hold with benzoic acid in benzene and water. It appears, however, that while the molecules of benzoic acid are normal in aqueous solution, the molecule is polymerized in the benzene, so that—

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2.$$

Let C denote the concentration of the unassociated benzoic acid, and C_2 the total concentration of the benzoic acid, both in benzene solution, then from the law of mass action—

$$C^2 = K_0(C_2 - C_1).$$

Assuming that nearly all the benzoic acid in the benzene solution is polymerized, we may write—

$$C^2 = K_1C_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The more concentrated the solution, the greater the ratio of the concentration of the associated to the unassociated molecules of benzoic acid in benzene; but the partition law only refers to the distribution of the unassociated molecules in the two solvents. The ratio of the total benzoic acid in aqueous solution to the total benzoic acid in the benzene will be less the greater the concentration. This explains the decreasing values of the constant in the last but one column of the preceding table as the solutions become more concentrated.

The partition of the benzoic acid between the water and the benzene is—

$$C = K_2C_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

K_1 and K_2 are constants of proportion. Square (2), and we get by division of (1)—

$$C_1 = K\sqrt{C_2}; \text{ or, } C_1 \div \sqrt{C_2} = \text{constant}, \quad . \quad . \quad (3)$$

which is in harmony with the experimental results as shown in the last column of the above table.

The experiments of Berthelot and Jungfleisch[1] on the partition of iodine and bromine between water and carbon disulphide; of Jakowkin on the partition of iodine and bromine between water and each of the solvents, carbon disulphide, bromoform, chloroform, and carbon tetrachloride; and of Nernst (*l.c.*) on the distribution of acetic, benzoic, and salicylic acids, and of phenol between water and benzene, confirm the above deductions.

§ 72. Influence of Partial Ionization on Chemical Equilibria.

Calcium carbonate is practically insoluble in pure water, but if carbon dioxide be present, it readily passes into solution as calcium bicarbonate. Were the calcium bicarbonate completely ionized, we should have—

$$Ca(HCO_3)_2 = Ca^{\cdot} + 2HCO'_3,$$

and equilibrium would subsist between—

$$Ca^{\cdot} + 2HCO'_3 \rightleftharpoons CaCO_3 + H_2CO_3.$$

In the presence of insoluble calcium carbonate, we may suppose the active mass of calcium carbonate to be constant. The concentration of the HCO'_3-ions is obviously double that of the $Ca^{\cdot}$-ions; hence, if C_1 denotes the concentration of these

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[1] M. Berthelot and E. Jungfleisch, *Ann. Chim. Phys.* [4], **26**. 396, 1872; A. A. Jakowkin, *Zeit. phys. Chem.*, **18**. 585, 1895.

ions, and C_2 the concentration of the H_2CO_3, the condition of equilibrium will be—

$$C_1^3 = K'C_2; \therefore C_1 = K'C_2^{0\cdot33\cdots}.$$

According to the solubility law the amount of H_2CO_3 in solution is proportional to the partial pressure p of the super-incumbent gas—carbon dioxide—and consequently—

$$C_1 = Kp^{0\cdot33}\cdots.$$

Schlœsing[1] found experimentally that the exponent of p was 0·37866, not 0·33333. This agrees with the value 2·64, not 3, for the "total number of molecules" on the left side of the above equation; in other words, the ionization of calcium bicarbonate is not complete. One gram-molecule of calcium bicarbonate is resolved, on ionization, into 2·64, not 3, gram-molecules. In our usual notation, $1-\alpha$ of the molecules are non-ionized, and α are ionized; let each ionized molecule form n ions, then the total number of molecules will be—

$$i = 1 - \alpha + n\alpha.$$

There are several methods for finding the value of i (*vide* R. A. Lehfeldt's *Electro-chemistry*). The freezing-point method furnishes $i = 2\cdot56$ for calcium bicarbonate—a value very nearly identical with that obtained by Schlœsing. Similar results have been found for the solubility of magnesium and barium carbonates; of ammonium and copper sulphates;[2] for the action of sulphuric acid upon basic mercury sulphate.[3] Ostwald[4] investigated the reaction—

$$ZnS + 2HCl \rightleftharpoons H_2S + ZnCl_2,$$

and found for HCl, $i = 1\cdot98$; for $ZnCl_2$, $i = 2\cdot53$; and for H_2S, $i = 1\cdot04$. The active mass of solid zinc sulphide is constant, and—

$$C_{H_2S}^{1\cdot04} C_{ZnCl_2}^{2\cdot53} = KC_{HCl}^{2\times1\cdot98}.$$

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[1] T. Schlœsing, *Compt. Rend.*, **74**. 1552, 1872; **75**. 70, 1872.

[2] R. Engel, *Compt. Rend.*, **100**. 352, 444, 1885; **102**. 113, 1886; W. Herz and G. Muhs, *Zeit. anorg. Chem.*, **38**. 138, 1904 (magnesium hydroxide and ammonium chloride).

[3] H. le Chatelier, *Compt. Rend.*, **98**. 675, 1884.

[4] W. Ostwald, *Journ. prakt. Chem.* [2], **19**. 468, 1879.

In Guldberg and Waage's experiments on the reaction—

$$BaCO_3 + K_2SO_4 = BaSO_4 + K_2CO_3,$$

for K_2SO_4, $i = 2{\cdot}11$; and for K_2CO_3, $i = 2{\cdot}26$;

$$\therefore C^{2\cdot11}_{K_2SO_4} = KC^{2\cdot26}_{K_2CO_3}; \text{ i.e., } C_{K_2SO_4} = KC^{1\cdot07}_{K_2CO_3};$$

or—

$$C_{K_2SO_4} = KC_{K_2CO_3},$$

very nearly. Here, then, the ionic theory, and Guldberg and Waage's method of treatment, lead to the same results.

The condition of equilibrium for two opposing reactions now assumes the more general form—

$$k_1 C^{i_1}_{A_1} C^{i_2}_{A_2} \ldots = k_2 C^{i'_1}_{B_1} C^{i'_2}_{B_2} \ldots,$$

where the values $i_1, i_2, \ldots, i'_1, i'_2, \ldots$ denote how many times the number of molecules is increased, in each case, by ionization. The values of i are to be determined separately for each component of the system;[1] i may be integral or fractional.

Measurements of the concentrations of the different reacting substances when the system is in a state of equilibrium will therefore furnish us with information as to the degree of ionization, or polymerization (p. 235), of the substances concerned.

§ 73. Fractional Precipitation.

When an acid is allowed to act upon a mixture of two bases, or a base upon a mixture of two acids, the ratio in which the acid divides itself between the two bases, or the base between two acids, depends not only upon the relative masses of the substances taking part in the reaction, but also upon their "specific affinities" acting between the different substances. It is assumed that the amount of single base, or single acid, is not sufficient to precipitate the two acids, or two bases, present in

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[1] J. H. van't Hoff, *Zeit. phys. Chem.*, **1**. 481, 1887; *Phil. Mag.* [5], **26**. 81, 1888; W. Ostwald's *Klassiker*, No. 110; *Harper's Scientific Memoirs*, No. 4.

the system. In the same way, when a substance is added to a mixture of two or more salts of different metals, the relative amounts of salts decomposed depends upon the relative masses and specific affinities acting between the components of the system.

Let only sufficient C be added to partially precipitate A and B, and let the solution originally contain a gram-molecules of A, and b of B; let x and y denote the amounts of A and of B precipitated at the end of a certain time t, then, $a-x$ of A, and $b-y$ of B, will remain in solution; further, let z denote the amount of C required for the precipitation of x of A, and y of B, and let c denote the amount of C added to the solution at first. The velocity of precipitation of A and B will be—

$$\frac{dx}{dt} = k_1(a-x)(c-z);\ \frac{dy}{dt} = k_2(b-y)(c-z), \quad . \quad (1)$$

respectively. These simultaneous equations can be integrated by remembering that—

$$z = \alpha x + \beta y.$$

By division of equations (1), and integration in the usual way—

$$\frac{k_1}{k_2} = \frac{\log a - \log(a-x)}{\log b - \log(b-y)}, \quad . \quad . \quad . \quad . \quad (2)$$

which gives the relative amounts of precipitates formed in terms of their affinity coefficients.

Mills[1] has studied the fractional precipitation of a mixture of sulphates of different metals by means of sodium hydroxide and sodium carbonate. The following table shows the results obtained by Mills and Bicket, when a mixture of one gram of mixed sulphates was made up to 100 c.c.; 10 c.c. of sodium

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[1] E. J. Mills and J. H. Bicket, *Phil. Mag.* [5], **13.** 169, 1882; E. J. Mills and B. Hunt, *ib.* [5], **13.** 177, 1882; E. J. Mills and J. J. Smith, *Proc. Roy. Soc.* [5], **29.** 181, 1879; *Chem. News*, **40.** 15, 1879; E. J. Mills and D. Wilson, *Journ. Chem. Soc.*, **33.** 360, 1878; E. J. Mills and J. W. Pratt, *ib.*, **35.** 336, 1879; E. J. Mills and C. W. Meanwell, *ib.*, **39.** 533, 1881; E. J. Mills and G. Donald, *ib.*, **41.** 18, 1882; E. J. Mills and R. L. Barr, *ib.*, **41.** 341, 1882; J. J. Hood, *Phil. Mag.* [5], **21.** 119, 1886.

carbonate solution containing 0·5715 gram were added to each solution :—

A = $MnSO_4$; B = $NiSO_4$.

Temp. °C.	Composition of solution (gram).		Composition of precipitate (gram).		$\frac{k_1}{k_2}$
	$MnSO_4$	$NiSO_4$	$MnSO_4$	$NiSO_4$	
12·9	0·9	0·1	0·5850	0·0953	0·34
13·6	0·8	0·2	0·4616	0·1852	0·33
12·5	0·7	0·3	0·3766	0·2799	0·29
13·0	0·6	0·4	0·2976	0·3588	0·30
13·6	0·5	0·5	0·2450	0·4305	0·34
12·8	0·4	0·6	0·1536	0·4788	0·30
17·0	0·3	0·7	0·1089	0·4991	0·36
17·0	0·2	0·8	0·0722	0·5584	0·37
15·2	0·1	0·9	0·0363	0·5841	0·43

Mean: $k_1/k_2 = 0{\cdot}34$; $\therefore k_2 = 2{\cdot}94k_1$

The small deviations from the mean, 0·34, can be reasonably attributed to the variations of temperature and errors of experiment. The ratio 2·94 means that manganese sulphate "resists the decomposing action of sodium carbonate with a force 2·94 times greater than nickel sulphate, when both salts are simultaneously subjected to the action of the same agent." Otherwise expressed—

$$\frac{k_1}{k_2} = \frac{\text{Rate of precipitation of } MnSO_4}{\text{Rate of precipitation of } NiSO_4},$$

provided the solution be kept at unit concentration. If the original solution contains—

$$MnSO_4 : NiSO_4 = 2{\cdot}94 : 1,$$

and a very small fraction be precipitated, the precipitate will contain equal weights of the two sulphates; or, if the solution contain equal weights of the two salts, the precipitate will contain—

$$MnSO_4 : NiSO_4 = 1 : 2{\cdot}94.$$

We therefore conclude that the more k_2 exceeds k_1, the *less* will A tend to accumulate in the precipitate; and the more

k_1 exceeds k_2, the *more* will A tend to accumulate in the precipitate. In the fractional precipitation of salts, a process commonly employed in the separation of the rare earths, the mixed metallic salts may be precipitated as nitrates, oxalates, etc. The mixed precipitate is redissolved, and again partially precipitated. By many repetitions of the process, it will be obvious that the element with the greater value of k will tend to accumulate in the precipitate, and the other element in the filtrate. In this way Mosander[1] separated the constituents of the gadolinite earths; Welsbach[2] praseodidymium and neodidymium from the cerite earths; Crookes[3] the constituents of the "yttria" earths; and Curie separated the mixture of radium and barium chlorides derived from pitchblende.[4]

When k_1 is nearly equal to k_2, the ratio of the quantities of A and B in the precipitate will be nearly the same as in the solution, and the process of fractionation will be a prolonged operation. This would be the case with the precipitation of a mixture of nickel and cobalt sulphates by means of sodium hydroxide, for Mills and Smith find that—

$$k_2 : k_1 = 0{\cdot}97 : 1.$$

Hence, the precipitate from a solution containing equal weights would contain—

$$CoSO_4 : NiSO_4 = 1 : 0{\cdot}97.$$

In the limiting case, when $k_1 = k_2$, the ratio of A to B in the precipitate will be the same as in solution, and the constituents of the solution could no more be separated by fractional precipitation than two liquids boiling at the same temperature could be separated by fractional distillation.

Marignac[5] tried to prove that some common substances

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[1] A. Mosander, *Compt. Rend.*, **8**. 356, 1839; *Journ. prakt. Chem.* [1], **16**. 513, 1839; *Phil. Mag.* [3], **23**. 241, 1843.

[2] A. von Welsbach, *Monatshefte f. Chem.*, **5**. 508, 1884.

[3] W. Crookes, *Phil. Trans.*, **174**. 891, 1883; **176**. 691, 1885; *Chem. News*, **54**. 131, 155, 1886; *B. A. Reports*, 583, 586, 1886.

[4] S. Curie, *Recherches sur les substances radioactives*, Paris, 1903; *Chem. News*, **88**. 146, 1903.

[5] C. Marignac, *Ann. Chim. Phys.* [6], **1**. 289, 1884.

were homogeneous compounds by showing that fractional precipitation gave no indication of heterogeneity. The fact that no separation occurred might be ascribed to the fact that the substances really did contain two components for which $k_1 = k_2$, very nearly.

A little work has been done upon the subject by Debus[1] on the fractional precipitation of mixtures of barium and calcium hydroxide by a soluble carbonate; by Chiżyński,[2] upon the precipitation of mixtures of magnesium and calcium chlorides by ammonium phosphate; by Chroustchoff,[3] upon the composition of the precipitate from a mixture of strontium and barium chlorides after the addition of potassium sulphate, of mixtures of soluble sulphates and chromates, and soluble iodates and sulphates, by means of barium chloride; and by Küster and Thiel, of the precipitate from a mixture of potassium bromide and potassium thiocyanate by the addition of silver nitrate.[4]

§ 74. Ionization Phenomena in Fractional Precipitation.

We have seen that in the system—

$$BaSO_4 \text{ (solid)} + K_2CO_3 \rightleftharpoons BaCO_3 \text{ (solid)} + K_2SO_4,$$

we may assume that the concentration of the solid components have a constant mass. The condition of equilibrium is, therefore—

$$\frac{C_1}{C_2} = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_1 and C_2 respectively denote the concentration of the carbonate and sulphate of potassium. If, however, we assume

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[1] H. Debus, *Liebig's Ann.*, **85.** 103, 1853; **86.** 156, 1853; **87.** 238, 1853.

[2] A. Chiżyński, *Liebig's Ann. Suppl.*, **4.** 226, 1866.

[3] P. Chroustchoff and A. Martinoff, *Compt. Rend.*, **104.** 571, 1887; P. Chroustchoff, *ib.*, **104.** 1711, 1887. The authors were led to some erroneous conclusions from overlooking the fact that the solid phase of mixed precipitates can exist in any proportion. Equilibrium exists between the substances in solution. W. Ostwald, *Zeit. phys. Chem.*, **1.** 419, 1887.

[4] F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, **33.** 129, 1902.

that the reaction only takes place between ions, and that the fraction α_1 of the potassium carbonate and α_2 of the potassium sulphate is ionized, equilibrium depends upon the concentration of the ions CO_3'' and SO_4''; the concentration of the undissociated salts remains constant. Hence, for equilibrium—

$$\frac{\alpha_1 C_1}{\alpha_2 C_2} = K; \text{ or, } \frac{\text{Concentration of } CO_3\text{-ions}}{\text{Concentration of } SO_4\text{-ions}} = K, \qquad (2)$$

where K has a constant value.

If the ratio of the concentrations of the CO_3'' and SO_4'' ions in the original solution be *greater* than the constant K, and a barium salt is added, there will be a precipitation of the CO_3'' ions (*i.e.* of $BaCO_3$) until this ratio has been attained. And, similarly, if the above ratio is *less* than that just indicated, pure barium sulphate will be precipitated. One salt is not precipitated in preference to another, because, as formerly supposed, it produces a more insoluble salt. As a matter of fact, the more soluble salt may be precipitated under certain conditions. This can be illustrated graphically. In Fig. 13 the ordinates denote the numerical values of K, the abscissæ the quantities of soluble barium salt added; let $K = a$, and b of a soluble barium salt be added, a mixed precipitate of barium sulphate and carbonate will come down in the ratio $k_1/k_2 = K$; if $K < a$,

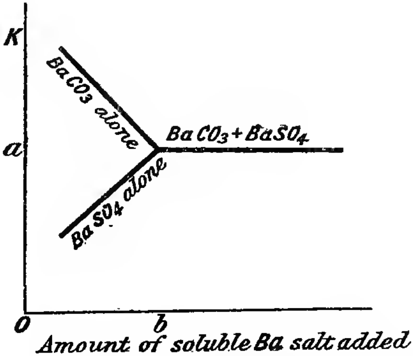

FIG. 13.—(Diagrammatic.)

the SO_4-ions will be removed from the solution as barium sulphate until the condition for equilibrium is restored; finally, if $K > a$, barium carbonate will be precipitated, and for a similar reason. These conclusions were verified by Findlay[1] for the reaction—

$$PbSO_4 \text{ (solid)} + 2NaI \rightleftharpoons PbI_2 \text{ (solid)} + Na_2SO_4,$$

where the condition of equilibrium, at 26°, is—

$$\frac{C^2_{\text{I-ions}}}{C_{SO_4\text{-ions}}} = K = 0{\cdot}3 \text{ (nearly).}$$

In Guldberg and Waage's experiments on the reaction between barium sulphate and potassium carbonate, the degree of ionization of the potassium carbonate and sulphate were very nearly equal, and consequently their experimental results agreed with the relation—

$$\alpha_1 = \alpha_2 \text{ (nearly)}; \ \frac{C_1}{C_2} = \text{constant.}$$

The experiments of Paul, Küster and Thiel, and of Heintz,[2] furnish studies of great technical interest in the separation of the non-volatile organic acids.

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[1] For fuller details than those here presented, see A. Findlay, *Zeit. phys. Chem.*, **34**. 409, 1900. For the addition of lead nitrate to a mixture of sodium sulphate and carbonate, see R. Salvadori, *Gazz. Chim. Ital.*, **34**. i., 87, 1904.

[2] T. Paul, *Zeit. phys. Chem.*, **14**. 105, 1894; A. Heintz, *Journ. prakt. Chem.* [2], **66**. 1, 1902; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, **19**. 81, 1899; **23**. 25, 1900; **24**. 1, 1900; **33**. 129, 1903.

CHAPTER X

CATALYSIS AND THE THEORY OF CHEMICAL CHANGE

§ 75. General Characteristics of Catalytic Reactions.

A GREAT number of chemical reactions commence immediately the different components are brought into contact, while other reactions only appear to take place when external energy of some kind is added from without. For example, chlorine and hydrogen gases combine with appreciable velocity when energy is supplied in the form of heat, light, or electricity. It has also been observed that these gases rapidly unite in the presence of platinum foil, platinum black,[1] or charcoal.[2] On the other hand, the rate of transformation is retarded in a remarkable manner when the reacting gases are mixed with a foreign gas like oxygen.[3] The velocity of the reaction is also greatly modified by the form and material of the vessel in which the reacting gases are enclosed.

These illustrations are types of a large class of reactions[4] in which the progress of the chemical transformation is modified by the mere presence of a substance which after the reaction

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[1] S. Cooke, *Chem. News*, **58**. 105, 1888.

[2] J. F. L. Meslens, *Compt. Rend.*, **83**. 145, 1876; M. Berthelot and A. Guntz, *ib.*, **99**. 7, 1884.

[3] R. Bunsen and H. E. Roscoe, *Pogg. Ann.*, **96**. 373, 1855; *Phil. Trans.*, **146**. 355, 1857.

[4] For a set of "lecture" experiments to illustrate the different types of catalytic reactions, see A. A. Noyes and G. V. Sammet, *Jour. Amer. Chem. Soc.*, **24**. 498, 1902; *Zeit. phys. Chem.*, **41**. 11, 1902. For the use of catalyzed reactions in technical operations, see G. Bodländer, *Zeit. Elektrochem.*, **9**. 732, 1903; and discussion, *ib.*, **9**. 733, 742, 1903.

has the same chemical composition as at the beginning. It was formerly thought that such reactions were entirely different in their nature from other chemical changes. Berzelius[1] postulated the existence of a new "innate force" to which he gave the name **catalytic force.** "A catalytic agent," said Berzelius, "is a substance which, merely by its presence and not through its affinity, has the power to render active affinities which are latent at ordinary temperatures." As with "affinity," so with "catalysis," the word explained the fact. Although the occult cause theory has been abandoned, it is still necessary to have some word to connote these chemical changes which are influenced by the presence of a "foreign" substance. Mitscherlich[2] proposed the term **contact actions,** Brodie,[3] **cyclic actions**; but Berzelius' designation, catalytic action, or **catalysis,** is now in pretty general use. The agent which effects the catalytic action may be called the catalyzer, or the catalyst.

What part the catalyst plays during the reaction is shrouded in mystery. The following, however, are generally recognized "articles of faith."

1. *The catalyst has the same chemical composition at the beginning as at the end of the reaction.* This fact was early recognized. Mrs. Fulhame[4] noticed, in 1794, that while water materially affected the oxidation of the metals and the reduction of their oxides, the water still retained its former

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[1] J. Berzelius, *Jahresberichte*, **13.** 237, 1836; **20.** 452, 1841; *Ann. Chim. Phys.* [3], **61.** 146, 1836. The word "catalysis" first occurs in the writings of A. Libavius, *Alchemia*, Lib. II., Tract I., caps. 39 and 40, Frankfurt, 1611. But the word seems to have been used with a different connotation from what it has to-day. H. Goldschmidt, *Zeit. Elektrochem.*, **9.** 736, 1903; W. Ostwald's *Aeltere Geschichte der Lehre von den Berührungwirkungen*, Leipzig, 1898; M. Bodenstein, "Katalyse und Katalysatoren," *Chem. Ztg.*, **26.** 1075, 1902; G. Hüfner, *Journ. prakt. Chem.* [2], **10.** 148, 385, 1874 (for historical details).

[2] E. Mitscherlich, *Pogg. Ann.*, **31.** 273, 1834; **55.** 209, 1842.

[3] See also J. J. Hood, in M. M. P. Muir and H. F. Morley's *Watts' Dict. of Chem.*, London, **1.** 750, 1888; B. C. Brodie, *Phil. Trans.*, **151.** 855, 1862.

[4] Mrs. Fulhame, *An Essay on Combustion*, London, 1794.

properties. In 1812, Kirchhof[1] showed that when starch is converted into dextrine and sugar by boiling with dilute acids, the acid which effects the change remains unaltered.

It must not be concluded that the catalyst is necessarily in the same *physical* state after the reaction is over. There is much evidence to show that the catalytic agent actually participates in the reaction. A spiral of platinum kept in a jet of hydrogen burning in air becomes corroded and covered with a grey or black powder of metallic platinum. This also occurs when a spiral of platinum is kept forty-eight hours in the vapour of alcohol.[2] In like manner De la Rive[3] found that if an electric current be passed alternately in opposite directions through water, both electrodes become covered with a fine dust of platinum, presumably produced by the repeated oxidation and reduction of the platinum. The crystalline variety of manganese dioxide is transformed into a fine powder when a mixture of this compound with potassium chlorate is heated. This is supposed to be due to the manganese dioxide taking an essential part in the decomposition of the chlorate.[4] The oxidation of ammonia by freshly prepared chromium sesquioxide is really an alternate series of oxidations to a bright green oxide by the oxygen of the air, and reductions to the ordinary oxide by the hydrogen of the ammonia.[5] The action of cobalt oxide on the hypochlorites appears to consist of a series of alternate oxidations and reductions.[6] Bielby and

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[1] J. Kirchhof, *Schweigger's Journ.*, **4**. 108, 1812; A. Nasse, *ib.*, **4**. 112, 1812; J. W. Döbereiner, *ib.*, **4**. 307, 1812; *ib.*, **5**. 281, 1812; H. A. Vogel, *ib.*, **5**. 89, 1812.

[2] A. Pleischl, *Schweigger's Journ.*, **39**. 142, 201, 351, 1823; *Gilbert's Ann.*, **76**. 98, 1824; *Repertorium für die Pharmacie*, **17**. 97, 1824; H. McLeod, *B.A. Reports*, 663, 1892.

[3] A. de la Rive, *Pogg. Ann.*, **46**. 489, 1839; R. Ruer, *Zeit. Elektrochem.*, **9**. 235, 1903; *Zeit. phys. Chem.*, **44**. 81, 1903.

[4] W. H. Sodeau, *Journ. Chem. Soc.*, **77**. 137, 717, 1900; **79**. 247, 939, 1901; **81**. 1066, 1902; *Proc. Durham Univ. Phil. Soc.*, **2**. 1, 1903.

[5] H. McLeod, *B.A. Reports*, 663, 1892; *Chem. News*, **66**. 75, 1892.

[6] G. Vortmann, *Monatshefte für Chem.*, **4**. 1, 1883; H. McLeod, *l.c.*; C. F. Schönbein, *Ann. Chim. Phys.* [4], **7**. 103, 1866.

Henderson[1] also observed that there is a complete alteration of the physical state of the catalyst when ammonia is decomposed by the agency of the metals. Titherley[2] also found that the decomposition of ammonia by sodamide at a dull red heat takes place in a series of stages. The sodamide at first splits up into nitrogen, hydrogen, and sodium; the latter combines with ammonia to reform sodamide. This in turn is again split up, and the cycle of reactions begins anew. The sodamide, after the action, has the same chemical composition as before. Many other actions might be cited to illustrate the fact that the catalytic agent actually takes part in the reaction.

When it is known that the catalytic agent is actually involved in the chemical change, Wagner proposes to call the phenomenon *pseudo-catalysis;* Ostwald, *catalysis by transvection* ("Uebertragungskatalyse"); but the above-mentioned term, *cyclic action*, is to be preferred.

2. *A small quantity of the catalytic agent is sufficient to effect the transformation of an indefinitely large quantity of the reacting substance.* This fact was recognized by Clément and Désormes in 1806.[3] A solution of cane sugar will contain the same amount of inverting acid before and after hydrolysis. Ernst[4] has also shown that a solution containing 0·0004 gram of colloidal platinum will bring about the combination of 10 litres of a mixture of hydrogen and oxygen, and that the activity of the colloidal metal is not affected by the process; and 0·000001 gram of potassium permanganate in 10 c.c. of solution accelerates the reduction of mercuric chloride by oxalic acid.[5] Titoff[6] states that the rate of oxidation of an aqueous solution of sodium sulphite is quite perceptibly accelerated in the presence of 0·000000 000000 1 N-$CuSO_4$, or

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[1] G. G. Henderson and G. T. Beilby, *Journ. Chem. Soc.*, **79**. 1245, 1901; W. Ramsay and S. Young, *Journ. Chem. Soc.*, **45**. 88, 1884.

[2] A. W. Titherley, *Journ. Chem. Soc.*, **65**. 504, 1894.

[3] C. B. Désormes and Clément, *Annales de Chemie*, **59**. 329, 1806; *Nicholson's Journ.*, **17**. 41, 1807.

[4] C. Ernst, *Zeit. phys. Chem.*, **37**. 448, 1901.

[5] J. H. Kastle and W. A. Beatty, *Amer. Chem. Journ.*, **24**. 182, 1900.

[6] A. Titoff, *Zeit. phys. Chem.*, **45**. 641, 1903.

even by merely dipping a strip of clean metallic copper in the water for less than a minute.

In some cases secondary actions modify the catalytic agent itself. For example, Phillips' process[1] for the manufacture of sulphuric acid by the oxidation of sulphur dioxide with spongy platinum was abandoned because the platinum gradually lost its power. Knietsch[2] has, however, traced the "sickening" of the platinum to the action of arsenical and other impurities in the sulphurous gases employed in the process. When these impurities are removed from the gases, the activity of the platinum remains unimpaired, and the process is a commercial success, promising to supplant the cumbrous "lead chamber process." A similar explanation will no doubt account for the gradual diminution of the activity of a platinum plate when placed in a mixture of hydrogen and oxygen. Certain enzymes also appear to lose their catalytic power after having been in use for some time.

Some catalyzers disappear during the reaction, owing to independent side reactions. This was found to be the case with ferrous salts in the reaction between potassium permanganate and hydrochloric acid;[3] and with aluminium chloride in the Friedel-Crafts reaction.[4] In the catalysis of methyl acetate by acetic acid the catalytic agent is a product of the reaction, and the amount of catalyzer in the system is continually increasing as the reaction goes on (see Autocatalysis).

3. *A catalytic agent is incapable of starting a reaction; it can only modify the velocity of the reaction.* Wijs[5] has shown that a mixture of pure methyl acetate and water, even in the absence of acids, slowly reacts; and Titoff has shown that the rate of oxidation of a solution of sodium sulphite is diminished by purification of the water. It is assumed that, however the

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[1] P. Phillips' *Eng. Patent*, No. 6096, 1831.

[2] R. Knietsch, *Ber.*, **34**. 4069, 1901.

[3] J. Wagner, *Zeit. phys. Chem.*, **28**. 33, 1899.

[4] B. D. Steele, *Journ. Chem. Soc.*, **83**. 1471, 1903.

[5] J. J. A. Wijs, *Zeit. phys. Chem.*, **11**. 492, 1893; **12**. 514, 1893; A. Titoff, *ib.*, **45**. 641, 1903.

reacting substances be purified, a slow reaction would always take place. Accordingly W. Ostwald[1] defines a catalytic agent to be "a substance which changes the velocity of a reaction without itself being changed by the process." This implies that a reaction must not only be possible, but actually taking place before the catalytic agent can produce any effect. In other words, a catalytic agent is not capable of starting a reaction; it can only modify the rate of change. Ostwald[2] compares the action of a catalyzer to the influence of the whip on a horse, or of oil on the wheels of a rusty machine. When oiled, the machine will go faster, in spite of the fact that the energy of the driving spring is not changed. The total energy of the driving spring is not altered by the catalyzer.

There is not yet any direct proof that a mixture of, say, pure hydrogen and oxygen will combine at ordinary temperatures. All we know is that if such a combination does take place at ordinary temperatures, the process is too slow to be detected by the analytical methods at our disposal.

On the other hand, some—C. F. Schönbein, J. J. Thomson, H. E. Armstrong, P. Duhem—believe that the catalyst can actually start the reaction; nor does there seem any particular objection to our extending Ostwald's analogy by assuming that the "friction," before oiling, is so great as to prevent the motion of the machine altogether.

4. *A catalytic agent cannot affect the final state of equilibrium of opposing reactions.* The amount of energy transformed during a chemical reaction depends only on the initial and final state of the system, and not on the actual course of the reaction. When chemical energy, for example, is transformed into thermal energy, the amount of heat generated is the same whether it takes place all at once or in steps.[3] Other things being equal, the velocity of chemical reactions would no doubt be proportional to the amount of energy transformed during

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[1] W. Ostwald, *Lehrbuch*, **2**. ii. 248, 262, 1896–1902.

[2] W. Ostwald, *Ueber Katalyse*, Leipzig, 1902; *Zeit. Elektrochem.*, **7**. 995, 1901; *Nature*, **65**. 522, 1902; *Die Schule der Chemie*, Leipzig, **1**. 88, 1903.

[3] H. Hess, *Pogg. Ann.*, **50**. 385, 1840.

the process, but the velocity, in reality, depends upon so many external factors—known and unknown—that no generalization has yet been formulated.

Although the velocity of a chemical reaction may be modified by the catalytic agent, yet the final state of equilibrium remains unaffected; if otherwise, we could allow the substances to react alternately with and without the catalyzer, and so utilize the process to perform work. This would lead to a perpetual motion, which is assumed to be impossible.

In illustration, Lemoine[1] found that equilibrium set in at 350° when 18·6 per cent. of hydrogen iodide had decomposed, while Hautefeuille[2] found that 19 per cent. decomposed in the presence of platinum black; Ditte,[3] too, found that about 46 per cent. of hydrogen selenide decomposed at 440° in the presence or absence of pumice stone; and Koelichen[4] found that the state of equilibrium in the reaction—

$$\text{Acetone} \rightleftharpoons \text{diacetone};$$
$$2CH_3.CO.CH_3 \rightleftharpoons CH_3.CO.CH_2.C(CH_3)_2.OH,$$

was not altered by the presence of the "hydroxyl" bases: ammonia, piperidine, triethylamine, tetraethylammonium, and sodium.[5]

The fact that the catalytic agent can have no influence on

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[1] G. Lemoine, *Ann. Chim. Phys.* [5], **12**. 145, 1877.

[2] P. Hautefeuille, *Compt. Rend.*, **64**. 608, 1867; *Bull. Soc. Chim.* [2], **7**. 203, 1867.

[3] A. Ditte, *Compt. Rend.*, **74**. 980, 1872.

[4] K. Koelichen, *Zeit. phys. Chem.*, **33**. 129, 1900.

[5] O. Ruff (*Ber.*, **34**. 3509, 1901) thought that the state of equilibrium—

$$2SO_2ClOH \rightleftharpoons H_2SO_4 + SO_2Cl_2,$$

was displaced by mercury sulphate in favour of the sulphuryl chloride. But since the amount of the latter was determined by distillation the explanation is that in the absence of the catalyzer the action takes place so slowly that there is practically no change during distillation, while the reaction proceeds much more rapidly in the presence of the catalyzer. R. Schiff (*Ber.*, **31**. 601, 1898) also thought that in the condensation of benzaldehyde with ethyl acetoacetate, while the presence of a trace of sodium ethoxide produced the enolic compound, a trace of pyridine produced the ketonic form. K. Schaum (*Ber.*, **31**. 1964, 1898) has disproved Schiff's conclusion experimentally. See also E. von Meyer, p. 270.

the numerical value of the equilibrium constant might be employed in doubtful cases as *a test for catalytic actions.* If a substance changes the velocity of the reaction, and at the same time has no influence on the equilibrium constant, we are dealing with catalysis pure and simple.

Many apparent exceptions to this "law" occur in the literature of chemistry, but these will be found, on closer examination, to be founded upon imperfect observations. In illustration, W. Michaelis[1] found that while picric acid accelerated the hydrolysis of ethyl acetate, it also raised the equilibrium constant K. Thus when the concentration of the picric
acid was = 0·0125, 0·025, 0·05, 0·1, 0·2, 0·32-N;
K = 2·406, 2·432, 2·482, 2·610, 2·765, 2·965;
$10^4 \times k$ = 0·023, 0·043, 0·086, 0·175, 0·325, 0·460.

This is supposed to be due to the fact that the presence of picric acid not only accelerates the velocity of the reaction, as shown by the augmented values of k with the more concentrated solutions, but it also induces a secondary reaction of some kind. A similar conclusion is to be drawn from the displacement of equilibrium observed by Tammann[2] when the catalyst emulsin is added to a solution of amygdaline.

5. *The velocity of two inverse reactions is affected by the catalyst to the same extent.* The condition of equilibrium of the reversible reaction—

$$2SO_2 + O_2 \rightleftharpoons 2SO_3,$$

may be written—

$$k_1 C^2_{SO_2} C_{O_2} = k_2 C^2_{SO_3}; \text{ or, } K = \frac{k_2}{k_1} = \frac{C^2_{SO_2} C_{O_2}}{C^2_{SO_3}}, \quad . \quad (1)$$

where C_{SO_2}, C_{O_2}, C_{SO_3} respectively denote the concentrations of the molecules SO_2, O_2, and SO_3 which take part in the reaction. The rate of decrease of SO_2 and the rate of decomposition of SO_3 are respectively—

$$-\frac{dC_{SO_2}}{dt} = k_1 C^2_{SO_2} C_{O_2}; \quad -\frac{dC_{SO_3}}{dt} = k_2 C^2_{SO_3}.$$

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[1] W. Michaelis, *Inaug. Dissert.*, Heidelberg, 1889.

[2] G. Tammann, *Zeit. phys. Chem.*, **18.** 426, 1895.

When equilibrium is attained we have equation (1). Since the state of equilibrium is independent of the catalytic agent, the relation between k_1 and k_2 must remain constant, and the velocity of one reaction in the presence of the catalyzer must increase in the same proportion as the other.

W. Michaelis[1] found that the velocities of esterification and hydrolysis of an ester at different concentrations were influenced by the catalytic agent in the same way. Slight deviations were observed at the higher concentrations. Bodenstein[2] observed a similar thing in the reaction—

$$H_2 + Se \rightleftharpoons H_2Se,$$

in which the catalytic agent was molten selenium; and R. Knietsch[3] found that the rate of formation of sulphur trioxide from sulphur dioxide and air was slower in the presence of fragments of porcelain than in the presence of platinum; and this result is in harmony with the fact that the trioxide decomposes more slowly in the presence of porcelain than in the presence of platinum. Similarly, Baker[4] has shown that dry ammonia and hydrogen chloride may be brought in contact without the formation of ammonium chloride, and also that dry ammonium chloride may be volatilized without dissociation into ammonia and hydrogen chloride. The presence of moisture in the former case favours combination, and in the latter favours dissociation.

6. *The state of equilibrium is independent of the nature and quantity of the catalytic agent.* This follows directly from the fact that the state of equilibrium is independent of the presence or absence of a catalytic agent. Turbaba[5] proved that the equilibrium between aldehyde and paraldehyde was the same whether sulphur dioxide, zinc sulphate, hydrogen chloride, oxalic acid, or phosphoric acid were employed as catalytic agents.

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[1] W. Michaelis, *Inaug. Dissert.*, Heidelberg, 1899.

[2] M. Bodenstein, *Zeit. phys. Chem.*, **29**. 429, 1899.

[3] R. Knietsch, *Ber.*, **34**. 4069, 1901.

[4] H. B. Baker, *Journ. Chem. Soc.*, **65**. 612, 1894.

[5] D. Turbaba, *Zeit. phys. Chem.*, **38**. 505, 1901; *Zeit. Elektrochem.*, **8**. 70, 1902.

It is easy to see that if side reactions occur, the catalyzer may exercise a specific influence on each, so that the products of the reaction may differ in the presence and in the absence of the catalyzer. For example, an aqueous solution of hydroxylamine[1] decomposes according to the equation—

$$3NH_2OH = NH_3 + N_2 + 3H_2O,$$

with the formation of traces of nitrous oxide, thus—

$$4NH_2OH = 2NH_3 + N_2O + 3H_2O.$$

In the presence of oxidizing media or platinum black, the chief product of the action is nitrous oxide. Tanater has shown that a like phenomenon occurs during the catalysis of hydrazine (N_2H_4).

7. *The phenomenon of catalysis is universal.* To enumerate all the different reactions susceptible to catalytic influences would require a "Beilstein" or a "Richter." Thénard[2] concluded that all substances exert some catalytic influence on hydrogen peroxide—some increasing and some decreasing its stability. "There is probably no kind of chemical reaction," says Ostwald, "which cannot be influenced catalytically, and there is no substance, element, or compound which cannot act as a catalyzer."[3]

§ 76. Classification of Catalytic Reactions.

No satisfactory method of classifying the great group of catalytic agents has hitherto been proposed. Those which have been published depend upon what particular view is taken of the mechanism of the change in question. It is, however, very common to divide catalytic reactions into homogeneous and heterogeneous catalyses according as the components of the

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[1] S. Tanater, *Zeit. phys. Chem.*, **40**. 475, 1902; **41**. 37, 1902; M. Berthelot, *Ann. Chim. Phys.* [5], **10**. 433, 1877; [6], **21**. 384, 1890.

[2] J. Thénard, *Ann. Chim. Phys.*, **9**. 314, 1818.

[3] W. Ostwald, *Zeit. Elektrochem.*, **7**. 995, 1901; *Nature*, **65**. 522, 1902.

system are in the same or in different states of aggregation. An homogeneous reaction might be accelerated by a catalyst in the same or in a different state of aggregation from the normal reacting system. Thus, the inversion of cane sugar is not only accelerated by dilute acids, but also by the presence of metals like platinum or gold.

The following systems of classification present points of interest:—

Ostwald's Classification.[1]

- *I. Crystallization from supersaturated solutions. E.g.* the crystallization of sodium sulphate from a supersaturated solution in the presence of a flake of dust or the fragment of a crystal.
- *II. Catalyses in homogeneous systems. E.g.* the action of acids upon aqueous solutions of cane sugar.
- *III. Catalyses in heterogeneous systems. E.g.* the action of platinum upon a mixture of air and sulphur dioxide gases.
- *IV. Action of the enzymes. E.g.* the action of emulsin upon amygdaline.

Henri and Larguier des Bancels' Classification.[2]

- *I. Reactions induced by one catalytic agent.*
    - (i.) Simple contact action. *E.g.* the action of acids upon an aqueous solution of cane sugar.
    - (ii.) Formation of intermediate compounds. *E.g.* the action of nitric oxide in the manufacture of sulphuric acid.
- *II. Reactions which take place in the presence of two catalytic agents.*
    - 1. The two catalysts produce the same final products.
        - (i.) Simple contact action.
            - (*a*) Catalysts have no action upon one another *E.g.* the decomposition of hydrogen peroxide by colloidal gold and platinum.

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[1] W. Ostwald, *l.c.*; L. P. Simon, *Bull. Soc. Chim.*, **29**. appendix, 1904.

[2] V. Henri and Larguier des Bancels, *Compt. Rend. Soc. Biol.*, **55**. 864, 1903.

        (*b*) Catalysts mutually influence each other's action. *E.g.* the action of a mixture of salts of iron and copper upon hydrogen persulphate and potassium iodide.
    (ii.) Formation of intermediate compounds. *E.g.* the action of acids and of invertin upon cane sugar.

2. The two catalytic agents produce different reactions. *E.g.* the action of pancreatic juice and of kinase upon a mixture of gelatine and starch.
3. Two consecutive reactions are produced by the two catalytic agents. *E.g.* the hydrolysis of gentianose by a mixture of emulsin and invertase.

The former system is purely empirical, while the latter, unfortunately, requires more knowledge of the mechanism of each reaction than we possess. Dare we assert that there is absolutely *no* intermediate compound formed in the inversion of cane sugar by dilute acids? Velocity measurements, at any rate, give no answer to the question.

§ 77. Catalysis of Gaseous Reactions in Presence of Solids or Liquids.

In 1817 Humphrey Davy[1] noticed that when oxygen or air is mixed with hydrogen, carbon monoxide, ethene, or cyanogen gases, or with the vapours of hydrogen cyanide, alcohol, ether, naphtha, or turpentine, and the mixture is placed in contact with platinum foil or wire heated to a temperature "short of redness," combination takes place. Erman[2] then showed that the platinum need only be heated to 50°–51° in order to effect the union of hydrogen and oxygen gases. E. Davy,[3] in 1820, found that finely divided platinum when,

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[1] H. Davy, *Annals of Philosophy*, **9.** 152, 1817; *Phil. Trans.*, **97.** 45, 1817.

[2] P. Erman, *Abhandlungen der Akad. der Wissenschaften der Berlin*, 368, 1818–9.

[3] E. Davy, *Phil. Trans.*, **100.** 108, 1820.

damped with "spirit of wine," became incandescent in air, owing to the heat developed during the oxidation of the alcohol. In 1822, Döbereiner[1] discovered that spongy platinum will, in the cold, spontaneously induce the rapid combustion of hydrogen and oxygen. Dulong and Thénard[2] then proved that the power of "exciting" the combination is possessed in a less degree by other solid substances. For example, by palladium, rhodium, iridium, osmium, gold, silver, cobalt, nickel, charcoal, pumice-stone, porcelain, glass, and rock crystal. The action must, in many cases, be assisted by raising the temperature, but not so high as to reach the ignition point of the gases. Fluorspar, marble, and mercury did not exhibit any perceptible action even when heated up to the boiling-point of the mercury.

Hempel's method[3] of analyzing certain mixtures of gases by **fractional combustion** is based on an observation of W. Henry that if oxygen gas is added to a mixture of hydrogen, carbon monoxide, methane, and nitrogen gases, and the mixture is led over spongy platinum at 177°, the hydrogen and carbon monoxide are alone oxidized. The methane is not *perceptibly* affected. Palladium sponge or platinum asbestos is now used in place of platinum sponge.

Shortly after Döbereiner's discovery Turner[4] noticed that

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[1] J. W. Döbereiner, *Schweigger's Journ.*, **34**. 91, 1822; **38**. 321, 1823; **39**. 4, 142, 1823; **42**. 60, 1824; **47**. 133, 1826; **63**. 465, 1833; *Gilbert's Ann.*, **74**. 269, 1823; *Journ. prakt. Chem.* [1], **1**. 114, 1834; *Liebig's Ann.*, **14**. 10, 1835; *Ueber neuentdeckte und hochst merkwürdige Eigenschaften des Platins*, Jena, 1823.

[2] P. L. Dulong and J. Thénard, *Ann. Chim. Phys.* [2], **23**. 440, 1823; **24**. 380, 1823; *Gilbert's Ann.*, **76**. 81, 89, 1824; *Schweigger's Journ.*, **40**. 229, 1824; *Kastner's Archiv.*, **1**. 81, 1830.

[3] W. Hempel, *Ber.*, **2**. 1006, 1879; W. Henry, *Annals of Philosophy*, **25**. 422, 1825; E. Jaeger, *Journ. f. Gasbeleuchtung*, **41**. 764, 1898; E. Harbeck and G. Lunge, *Zeit. anorg. Chem.*, **16**. 26, 1898; F. Richardt, *ib.*, **38**. 65, 1904.

[4] E. Turner, *Edin. Phil. Journ.*, **11**. 99, 311, 1824; *Pogg. Ann.*, **2**. 210, 1824; W. Henry, *Phil. Trans.*, **104**. 266, 1824; *Annals of Phil.*, **9**. 416, 1825; R. Böttger, *Schweigger's Journ.*, **63**. 372, 1831; see also M. Faraday, *Experimental Researches in Electricity*, London, **1**. 165,

certain impurities like hydrogen sulphide, ammonia, carbon disulphide, ethylene, ammonium sulphide, retard the activity of the platinum. The interesting feature is that these gases may be regarded as catalytic agents, which inhibit the action of another catalytic agent. This phenomenon will be called **negative catalysis.** In 1831, P. Phillips[1] patented the use of platinum wire and sponge for the rapid oxidation of sulphur dioxide in the manufacture of sulphuric acid. Kullman employed Phillips' method at the sulphuric acid works at Lille in 1883, but the process was abandoned because the platinum gradually lost its catalytic power.

Saussure[2] observed that various organic substances (peas, corn, humus) in the act of decomposition may excite the combination of hydrogen and oxygen, and that mixtures of these gases "behave with fermenting substances the same as with platinum."

§ 78. Faraday's "Condensation" Theory.

Many powdered substances like silica, alumina, barium, sulphate, and glass, as well as graphite, platinum, and different metals, act catalytically upon the vapours of various organic substances, inducing polymerization and decomposition.[3] This

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1849 (6th Ser., Nos. 564–659); *Phil. Trans.*, **114**. 55, 1834; *Pogg. Ann.*, **33**. 149, 1834; W. Ostwald's *Klassiker No.* 87; W. C. Henry, *Phil. Mag.* [3], **6**. 354, 1835; **9**. 324, 1836; *Journ. prakt. Chem.* [1], **5**. 109, 1835; **9**. 347, 1836; *Pogg. Ann.*, **36**. 150, 1835; **39**. 385, 1836; *B. A. Reports*, 54, 1836; T. Graham, *New Quart. of Science*, **6**. 354, 1829.

[1] P. Phillips, *Eng. Pat.*, No. 6069, 1831; see also G. Magnus, *Pogg. Ann.*, **24**. 610, 1832; J. W. Döbereiner, *ib.*, **24**. 603, 1832; J. T. Jullion, *Eng. Pat.*, No. 11425, 1846; R. Knietsch, *Ber.*, **34**. 4069, 1901. For oxidation of sulphur dioxide in presence of copper sulphate, see H. Roessler, *Ding. Polyt. Journ.*, **242**. 278, 1881; in presence of ferric oxide, J. Krutwig, *Rec. Trav. Pays-Bas*, **16**. 173, 1897; G. Lunge and G. P. Pollitt, *Zeit. angew. Chem.*, **15**. 1105, 1902; J. Brode, *ib.*, **15**. 1081, 1902.

[2] T. de Saussure, *Mem. Soc. phys. et d'hist. nat. de Genève*, **8**. 163, 1839; *Journ. prakt. Chem.* [1], **14**. 152, 1838; C. F. Schönbein, *Journ. prakt. Chem.* [1], **89**. 344, 1863.

[3] D. Konowalow, *Ber.*, **18**. 2808, 1885; with N. Menschutkin, *ib.*

may or may not be associated with the power possessed by all finely divided substances of condensing gases on their surface.

The superficial film of "condensed" gas adheres very tenaciously to the surface of the solid. This is shown by the fact that the film of moisture or air which covers the surface of glass vessels is very difficult to remove—a temperature just short of redness *in vacuo* is necessary for this purpose.[1] It seems as if glass is able to absorb many of the gases and vapours which are usually supposed to be merely condensed upon its surface.

Platinum, palladium, and carbon all possess, in a marked degree, the power of absorbing or adsorbing large quantities of gas. Faraday [2] (1833) supposed that the layers of gases in the immediate neighbourhood of the surface of the metal are more concentrated than the rest of the gas, and the molecules of the reacting gases are in closer contact. Consequently the reaction takes place with a greater velocity in the vicinity of the catalyzer. This might explain the fact that hydrogen, carbon monoxide,

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18. 3328, 1885; W. Alexejeff, *Ber.*, **18**. 2898, 1885; J. A. Trillat, *Oxydation des alcools*, Paris, 1903; *Bull. Soc. Chim.* [3], **27**. 797, 1902; **29**. 35, 1903; *Compt. Rend.*, **136**. 53, 1903; **137**. 189, 1903; W. Ipatieff, *Ber.*, **34**. 595, 1901; **35**. 79, 1048, 1058, 1902; **36**. 1990, 2003, 1903; *Journ. prakt. Chem.* [2], **67**. 420, 1903; W. Ipatieff and W. Huhn, *Ber.*, **36**. 2014, 1903; O. Šulc, *Zeit. phys. Chem.*, **28**. 719, 1899; **33**. 47, 1900; W. P. Jorissen and L. T. Reicher, *ib.*, **31**. 142, 1899; V. Henri, *Journal de physiol. et de pathol. générale*, 933, 1900.

[1] A. Houzeau, *Compt. Rend.*, **70**. 519, 1870; G. Quincke, *Pogg. Ann.*, **108**. 326, 1859; *Wied. Ann.*, **2**. 145, 1877; *Phil. Mag.* [5], **3**. 314, 1877; L. Joulin, *Compt. Rend.*, **90**. 741, 1880; *Ann. Chim. Phys.* [5], **22**. 398, 1881; P. A. Favre, *Compt. Rend.*, **68**. 1306, 1520, 1869; **77**. 649, 1873; *Ann. Chim. Phys.*, [5], **1**. 209, 1874; M. Berthelot, *ib.*, [4], **18**. 85, 1869; P. Villard, *Compt. Rend.*, **130**. 1752, 1900; A. Guoy, *ib.*, **122**. 775, 1896; A. F. Girvan, *Proc. Chem. Soc.*, **19**. 236, 1903; J. T. Bottomley, *Chem. News*, **51**. 85, 1885; R. Bunsen, *Wied. Ann.*, **20**. 545, 1883; *Ann. Chim. Phys.* [6], **3**. 407, 1884; P. Mülfarth, *Drude's Ann.*, **3**. 328, 1900; P. Chappuis' *Recherches sur la condensation des gaz à la surface du verre*, Genéve, 1880; G. Melander, *Boltzmann's Festschrift*, 789, 1904.

[2] M. Faraday, *l.c.*; see also M. Bodenstein, *Chem. Ztg.*, **26**. 1075, 1902; *Zeit. phys. Chem.*, **46**. 725, 1903; *Ber.*, **37**. 1361, 1904; A. Stock and O. Guttmann, *ib.*, **37**. 901, 1904.

ethene, propene, and isobutene are more readily oxidized by copper oxide if the latter is intimately mixed with finely divided palladium (palladinized copper oxide);[1] the assumption being made that the palladium, in virtue of its great condensing power, brings the reacting gases within the "sphere of activity" of the copper oxide.

The activity of the catalytic agent depends on its physical condition. As a general rule the finer its state of division the greater will be its chemical activity. Thus, platinum black is far more active than spongy platinum, and this, in turn, is more active than platinum foil.

In our museum of abandoned theories we have a suggestion by O. Loew[2] that when a molecule of the reacting substance abuts against the catalyst, the "sharp corners" of the latter break up the molecules into atoms, and so render the substance more chemically active. On this view, the more finely divided the state of the catalyst, the greater the number of "corners" exposed to the gas.

For a given weight of platinum the finer the state of division the greater will be the surface presented to the gases by the catalytic agent. In illustration, if a 10 c.c. sphere, surface area about 22 sq. cm., be replaced by a number of spherules, about 0·00000025 cm. diameter, occupying the same volume, the superficial area will be increased to about 20,000,600 sq. cm. Mitscherlich[3] estimates that "the layer of carbon dioxide which condenses on the walls of wood charcoal is about 0·00005 cm. thick;" and that at least "one-third of the carbon dioxide so condensed is in the liquid[4] state." We therefore inquire if chemical change takes place more readily when the reacting substances are in the *liquid* state.

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[1] E. D. Campbell, *Amer. Chem. Journ.*, **17**. 681, 1895.

[2] O. Loew, *Journ. prakt. Chem.* [2], **11**. 372, 1875.

[3] E. Mitscherlich, *Pogg. Ann.*, **59**. 94, 1843; *Taylor's Scientific Memoirs*, **4**. 1, 1846.

[4] A. Fusinieri (*Giornale di Fisica*, **8**. 259, 1825) seems to have thought that the layer of gas was condensed to the *solid* state of aggregation.

H. B. Dixon[1] has shown that oxygen does not combine with sulphur dioxide in the presence of water *vapour* at 100°, although in the presence of a particle of *liquid* water oxidation readily occurs. Berthelot and Gilles[2] have also shown that a reaction proceeds much more rapidly when the reacting substances are in the liquid than in the gaseous state of aggregation. Thus, at 200°, 65·2 per cent. of a liquid mixture of equivalent amounts of acetic acid and ethyl alcohol had etherified in ten hours, but only 10 per cent. of a gaseous mixture had etherified in the same time; with equivalent amounts of ethyl acetate and water, 11·5 per cent. was hydrolyzed in half an hour, but with a gaseous mixture no action was observed after 142 hours. Similarly, while gaseous tertiary amyl acetate suffers no perceptible decomposition at 180°, the liquid decomposes below this temperature.

There is, however, room to doubt whether the condensation theory furnishes a sufficient explanation. D. Konowalow[3] has shown that the catalytic decomposition of gaseous amyl acetate is less the more the gas is compressed; nor will a liquefied mixture of sulphur dioxide and chlorine react, although the gases readily combine in the presence of camphor.[4]

Russell and Smith have also shown that when a mixture of sulphur dioxide and oxygen is passed over many metallic oxides, the sulphur dioxide may be absorbed without oxidation taking place.[5]

Hooke,[6] in 1803, stated that if detonating gas be allowed

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[1] H. B. Dixon, *Journ. of Gas Lighting*, **37**. 704, 1881; see also G. Bodländer and K. Köppen, *Zeit. Elektrochem.*, **9**. 559, 1903.

[2] M. Berthelot and L. Péan de St. Gilles, *Ann. Chim. Phys.* [3], **66**. 1, 1862; N. Menschutkin, *Ber.*, **15**. 2512, 1882; D. Konowalow, *ib.*, **18**. 2808, 1885.

[3] D. Konowalow, *Ber.*, **18**. 2808, 1885; *Zeit. phys. Chem.*, **1**. 62, 1887; see also A. von Hemptinne, *ib.*, **27**. 429, 1898.

[4] H. Schulze, *Journ. prakt. Chem.* [2], **24**. 168, 1881.

[5] E. J. Russell and N. Smith, *Journ. Chem. Soc.*, **77**. 340, 1900.

[6] B. Hooke, *Nicholson's Journ.*, **5**. 228, 1803; "T. S. T." of Orkney, *ib.*, **8**. 301, 1804; A. von Humboldt and J. F. Gay Lussac, *Gilbert's Ann.*, **20**. 143, 1805; N. W. Fischer, *Scherer's Ann.*, **3**. 123, 1820; A. de

to stand in the presence of water for some months, the hydrogen and oxygen absorbed by the water enter into combination; Saussure contradicted this statement, but Marcacci seems to have rediscovered Hooke's observation.[1] If, however, the solution also contains colloidal platinum, combination takes place very rapidly. Ernst[2] has found that the rate of formation of water is proportional to the amount of colloidal platinum in the solution, and to the pressure or concentration of the gases. This is taken to mean that the velocity of formation of water is proportional to the rate of solution of the mixed gases, because the actual velocity of transformation of the dissolved hydrogen and oxygen into water is immeasurably great. The rate of absorption of the two gases in water is thus alone accessible to measurement. It is also supposed that the rate of solution of the two gases is nearly the same. Any excess of one of the gases acts as an inert gas would on the rate of solution, and not according to the law of mass action. The effect of temperature is twofold. First, the rate of occlusion of the dissolved gases by the colloidal platinum will be accelerated; second, the rate of absorption of gas by the solution will be diminished. As the temperature rises the one effect ultimately neutralizes the other; below 60° the former prevails; above 60° the latter reaction is more marked. This explains the fact that up to 60° the velocity of the reaction is slightly accelerated; above that temperature the velocity of the reaction diminishes with rise of temperature. The presence of traces of the following substances, hydrogen cyanide, iodine cyanide, sodium thiosulphate in alkaline solution, mercuric chloride, hydrogen sulphide, iodine, bromine, phosphine, carbon disulphide, hydroxylamine hydrochloride, mercuric cyanide, hydrazine sulphate, arsenic trioxide, phenol, retard the action, and the relative magnitude of the effect produced by each substance is in the order named. The inhibitory effect is due to some

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Marty, *Annales de Chim.*, **61.** 271, 1807; *Gilbert's Ann.*, **28.** 417, 1808; *Gehlen's Journ.*, **4.** 141, 1807.

[1] T. de Saussure, *Gilbert's Ann.*, **47.** 163, 1815; A. Marcacci, *Rend. Accad. Lincei* [5], **11.** 1, 324, 1902.

[2] C. Ernst, *Zeit. phys. Chem.*, **37.** 448, 1901.

unknown action which these substances exert upon the colloidal platinum. Formic acid accelerates the action to three times its normal value, and this in spite of the fact that a 10 per cent. solution of formic acid precipitates the platinum from its solution. A satisfactory explanation has not yet been worked out.

It must also be borne in mind that a considerable amount of heat may be developed during the occlusion of a gas. Thus, Mond, Ramsay, and Shields[1] found that 1100 cals. are evolved during the occlusion of one gram of oxygen by platinum black, and 6800 cals. by the occlusion of one gram of hydrogen. The heat of occlusion of hydrogen by palladium is 4640 cals. per gram of hydrogen. Now, the condensation of gases on the surface of the metal ought to diminish as the temperature rises, whereas the velocity of the chemical reaction increases. It is, however, possible that the heat of occlusion helps to "start" a chemical change by bringing the mixture up to the "temperature of reaction;" and in a great majority of cases where the reaction is exothermal, the temperature necessary for the rapid combustion may be maintained by the heat of the reaction. (See "Explosions.")

The spontaneous inflammation of wool saturated with oil, that is, "engine waste," is due to the heat developed by the absorption of oxygen from the atmosphere, raising the temperature to the ignition point of the oil.[2]

§ 79. Catalytic Influence of the Walls of the Vessel.

It has long been known that the course of a chemical reaction is modified by the catalytic action of the walls of the

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[1] L. Mond, W. Ramsay, and J. Shields, *Zeit. anorg. Chem.*, **10.** 178, 1895; *Zeit. phys. Chem.*, **19.** 25, 1896; **25.** 657, 1898; **26.** 109, 1898; **28.** 368, 1899; A. von Hemptinne, *ib.*, **27.** 429, 1898; A. Winkelmann, *Drude's Ann.*, **6.** 104, 1901; **8.** 338, 1902; G. N. St. Schmidt, *ib.*, **13.** 747, 1904.

[2] T. E. Thorpe's art. on "Flame" in H. F. Morley and M. M. P. Muir's *Watts' Dict. of Chem.*, London, **2.** 549, 1889.

vessel in which the action takes place,[1] and van't Hoff[2] has shown that the disturbing influences depend upon the superficial area and upon the nature of the walls of the vessel in which the reaction takes place. By heating the same volume of anhydrous cyanic acid in two vessels, one a simple bulb, and the other a spiral tube, it was found that the rate of polymerization is much faster in the vessel with the greater internal surface. The polymerization is also three times as fast in a glass vessel coated with cyamelide as in a plain glass vessel. Carbon dioxide also dissociates several hundred degrees lower in a porcelain vessel than in a platinum vessel.[3] The union of hydrogen and oxygen starts at 182° in a glass vessel coated with silver, and at 448° in an ordinary glass vessel.[4]

The velocity of decomposition is greatly dependent upon the previous history of the walls of the vessel in which the reaction takes place. Kooij,[5] for example, found a velocity coefficient of 0·0023 for the decomposition of phosphine in a vessel which had not been much used, while in an old vessel $k = 0{\cdot}0064$. Cohen[6] noticed that the rate of decomposition of arsine is constant in a vessel whose walls are covered with metallic arsenic, but the coefficient gradually rose from 0·0122 to 0·173 in a new vessel. Of seven bulbs containing the same mixture of electrolytic gas kept for a week at 350°, Bone and Wheeler[7] observed no combination with six of the bulbs, but water could be detected in the seventh. It was noticed,

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[1] J. L. Gay Lussac and J. Thénard, *Compt. Rend.*, **40**. 935, 1855 (decomposition of aqueous HOCl during distillation).

[2] J. H. van't Hoff, *Études*, 55, 1884.

[3] C. Langer and V. Meyer, *Pyrochemische Untersuchungen*, Braunschweig, 64, 1885.

[4] V. Meyer and F. Freyer, *Ber.*, **25**. 622, 1892.

[5] D. M. Kooij, *Zeit. phys. Chem.*, **12**. 155, 1893.

[6] E. Cohen, *Zeit. phys. Chem.*, **20**. 303, 1896.

[7] W. A. Bone and R. V. Wheeler, *Journ. Chem. Soc.*, **81**. 538, 1902. This is in agreement with the experiments of V. Meyer and G. Krause, *Liebig's Ann.*, **264**. 85, 1891; V. Meyer and P. Askenasy, *Liebig's Ann.*, **269**. 49, 1892; A. Gautier and H. Hélier, *Compt. Rend.*, **122**. 566, 1896. According to some old experiments of van't Hoff, devitrification retards the rate of union of detonating gas.

however, that the glass of the seventh bulb was slightly devitrified.

The effect of the walls of the containing vessel upon the course of a reaction may therefore be attributed to various secondary actions—catalytic action of the film of moisture, conduction of heat from the zone of the reaction, superficial tension between the surface of the glass walls and the reacting substance, greater concentration of the gases near the surface of the solid, etc.

In connection with his abortive attempts to eliminate the "irregular" disturbing effects of the walls of the containing vessel on the course of a gaseous reaction, by making the bulbs of as "smooth" glass as possible, by roughening the internal surface by an etching liquid, and by silvering the internal surface, van't Hoff found that "the surfaces of the glass bulb, cleaned in the most careful manner, may possess irregularities which may be sufficiently different, or become so during the reaction, to account for the discordant experimental results" obtained when the attempt is made to measure the rate of combination of hydrogen and oxygen.

Berthelot[1] found that the rate of combination of hydrogen and oxygen, at 250°–300°, was accelerated by the presence of barium hydrate, by alkalies, and by traces of manganese salts. Now, these substances may be regarded as decomposition products of glass, and are therefore always present on the surface of glass vessels, and Berthelot thinks that the discordant results obtained when the speed of the reaction is measured in different vessels might be due to the presence of varying amounts of the decomposition products of the glass.

Reactions in liquid menstrua are not so sensitive to the nature of the walls of the vessel as gaseous reactions. But still the nature of the vessel does exercise a measurable influence on the course of some reactions. For example, Raẏman and Šulc[2] find that metal vessels exert a specific influence on the inversion of cane sugar. Polished platinum vessels, however,

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[1] M. Berthelot, *Compt. Rend.*, **125**. 271, 1897.

[2] B. Raẏman and O. Šulc, *Zeit. phys. Chem.*, **21**. 481, 1896; **33**. 47, 1900; F. Plzák and B. Hušek, *ib.*, **47**. 733, 1904.

do not influence the decomposition of hydrogen peroxide.[1] The rate of reduction of Fehling's solution by invert sugar is augmented by the use of vessels with a large internal capacity.[2] The cuprous oxide formed during the reaction also seems to accelerate the velocity of the reduction.

§ 80. J. J. Thomson's "Surface Tension" Theory.

The molecules at the boundary surface of a liquid medium are not in the same condition as the molecules in the body of the medium. Particles in the body of a liquid are attracted in every direction, while those at the surface are only attracted inwards. This "inward tension" of the surface molecules gives rise to the phenomena of "surface tension" and of "capillarity." J. J. Thomson thinks[3] that the catalytic effects produced by the walls of a vessel might be attributed, in part, to the change in the physical condition of the molecules[4] of the reacting substance in contact with the surface of the catalytic agent or the walls of the vessel.

If one system, say electrolytic gas, in a state of "apparent" (false) equilibrium,[5] be brought into contact with some other substance, the conditions of equilibrium at the surface of contact may be so altered by surface tension that the "passive resistance" is overcome, and chemical action is possible. If a solution be spread out in thin films, the influence of capillarity

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[1] W. Spring, *Bull. de l'Acad. roy. de Belgique* [3], **30.** 37, 1895; *Zeit. anorg. Chem.*, **8.** 424, 1895.

[2] F. Urech, *Ber.*, **15.** 2687, 1882.

[3] J. J. Thomson's *Applications of Dynamics to Physics and Chemistry*, London, 206, 236, 1888.

[4] J. Babinet, *Ann. Chim. Phys.* [2], **37.** 183, 1828; L. Meyer, *Pogg. Ann.*, **104.** 189, 1858; G. H. Quincke, *Pogg. Ann.*, **150.** 118, 1877; *Phil. Mag.* [5], **3.** 314, 1877; L. Gmelin's *Handbuch der Chemie*, **1.** 126, 1843.

[5] We frequently assume that a mixture of, say, hydrogen and oxygen gases would react to form water were it not for the existence of something we call passive resistance, which prevents chemical change taking place. See § 119.

may be sufficient to change the conditions of equilibrium in a marked degree from what they are under the usual conditions when free from the action of capillary forces.

Since surface tension depends upon the nature and concentration of the system, the surface tension of a reacting system must change as chemical action goes on, because the composition of the reacting system also changes. J. J. Thomson (*l.c.*) has shown that "if the surface tension increases as chemical action goes on, capillarity will tend to stop the action; while if the surface tension diminishes as the action goes on, capillarity will tend to increase the action." Thomson uses the experiments of O. Liebreich[1] on "the dead space in chemical reactions" to illustrate this law.

When alkalies act upon chloral a white precipitate of chloroform separates out, and Monckman has shown that the surface tension of the solution increases to a very considerable extent during the reaction. In fine capillary tubes no formation of chloroform can be observed at all, and when the reaction takes place in a test tube, just at the upper surface of the liquid, a thin film of liquid can be seen, quite clear and free from chloroform. This is what Liebreich calls "the dead space" of the reaction.[2]

§ 81. Intermediate Compound Theory in Heterogeneous Systems.

Some think that the action of platinum and palladium on a mixture of hydrogen and oxygen is due to the formation of "intermediate oxides," and of "intermediate carbonyls" in

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[1] O. Liebreich, *Berliner Sitzungberichte*, 959, 1886; *Zeit. phys. Chem.*, **1.** 194, 1887; **5.** 529, 1890; *Phil. Mag.* [5], **23.** 468, 1887; **29.** 216, 1890.

[2] For other experiments on the influence of capillarity upon chemical reactions, see G. D. Liveing, *Proc. Camb. Phil. Soc.*, **14.** 370, 1883-9; E. Becquerel, *Compt. Rend.*, **65.** 51, 720, 1867; R. S. Dale, *Manchester Memoirs* [3], **10.** 1, 1885; W. Spring, *l.c.*; G. Bredig and R. Müller von Berneck, *Zeit. phys. Chem.*, **31.** 258, 1899; J. U. Lloyd, *Chem. News*, **51.** 51, 1885.

the case of a mixture of carbon monoxide and oxygen. Berliner[2] attributes the greater efficacy of palladium to the greater power that metal has for occluding hydrogen.

When platinum black charged with occluded oxygen is introduced into a vessel of hydrogen, the absorbed oxygen combines with hydrogen to form water. When the platinum is again exposed to air, it absorbs more oxygen, and the experiment may be repeated again and again. It is therefore evident that the platinum black, in Döbereiner's words, "carries oxygen over" to the hydrogen.[3] De la Rive[4] suspected that a layer of platinum oxide was formed on the surface of the platinum. This inference has been confirmed by the fact that the heat of occlusion of oxygen gas (17,600 cal.) is nearly the same as the heat of oxidation to platinum monoxide (PtO). The catalytic process, on this view, consists of a series of alternate oxidations and reductions in accord with the equations—

$$\text{Oxidation: } 2\text{Pt} + n\text{O}_2 = 2\text{PtO}_n;$$
$$\text{Reduction: } \text{PtO}_n + n\text{H}_2 = \text{Pt} + n\text{H}_2\text{O}.$$

The formation of an oxide of platinum is therefore an intermediate stage in the reaction. Several investigators[5] have shown that platinum saturated with oxygen exerts a more active catalytic action upon hydrogen peroxide than platinum alone.

It has been suggested that measurements of the "order" of the reaction would indicate how many molecules take part in the reaction. But the information furnished by these measurements is not always conclusive. For example, it is often stated that because the decomposition of hydrogen peroxide by

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[1] E. Harbeck and G. Lunge, *Zeit. anorg. Chem.*, **16**. 26, 1898; G. Lunge and J. Akunoff, *ib.*, **24**. 191, 1900.

[2] A. Berliner, *Wied. Ann.*, **35**. 791, 1888.

[3] J. W. Döbereiner, *Journ. prakt. Chem.* [1], **1**. 114, 1834; *Liebig's Ann.*, **14**. 10, 1835; A. de la Rive and F. Marcet, *Ann. Chim. Phys.* [2], **39**. 328, 1828; W. Henry, *Phil. Mag.* [3], **6**. 364, 1835.

[4] A. de la Rive, *Pogg. Ann.*, **46**. 489, 1839; **54**. 386, 397, 1841; M. Berthelot, *Compt. Rend.*, **119**. 834, 1894.

[5] H. Euler, *Ofvers. of Svensk. Vetensk. Akad. Forhandl.*, 57, 267, 1900; K. Bornemann, *Zeit. anorg. Chem.*, **34**. 1, 1903.

coloidal platinum is a reaction of the first order, that "therefore the platinum does not play an essential part in the decomposition." But it is quite possible for the platinum to take part in the reaction in such a way that the experimental data would agree with the equation for a unimolecular reaction. All depends on the relative velocities of the two dependent reactions. Thus the data for—

$$Pt + H_2O_2 = PtO_2H_2 \text{ (fast)}; \quad 2PtO_2H_2 = 2Pt + O_2 + 2H_2O \text{ (slow)},$$

would agree with that for a unimolecular reaction.

If, as seems very likely, gaseous reactions take place on the walls of the containing vessel, or on the surface of the catalytic agent, all a reaction of the "first order" proves is, that the gases unite at a rate proportional to the pressure of the gas.

Engler and Wöhler[1] find that platinum black with occluded oxygen turns neutral potassium iodide and starch solution blue, a property which is not destroyed by heating to 260° in an atmosphere of carbon dioxide, or by washing with hot water; it is also soluble in dilute hydrochloric acid; the amount dissolved by the acid corresponds with the amount of iodine liberated from potassium iodide, and with its catalytic activity. The relation between the amount of platinum dissolved and the amount of occluded oxygen agrees with the formation of a compound having the formula, PtO. Organic compounds like alcohol and ether can reduce warm platinum black charged with oxygen, the platinum black loses its activity when so treated, and will no longer liberate iodine from potassium iodide.

On account of the greater activity of platinum black than platinum monoxide, Engler and Wöhler think that platinum peroxide—PtO_2 (or PtO_3H_2, or $Pt_2O_3H_2$)—is formed. E. von Meyer[2] raises the objection that the behaviour of platinous or platinic oxide, or of platinic hydroxide towards a mixture of carbon monoxide and oxygen is not the same as it is towards a mixture of platinum black and oxygen, for in the former

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[1] C. Engler and L. Wöhler, *Zeit. anorg. Chem.*, **29**. 1, 1901; R. Vondráček, *ib.*, **39**. 24, 1904; L. Wöhler, *Ber.*, **36**. 3475, 1903; A. Purgotti, *Gazz. Chim. Ital.*, **26**. ii., 559, 1896; with L. Zanichelli, *ib.*, **34**. i., 57, 1904 (catalytic decomposition of hydrazine by platinum black).

[2] E. von Meyer, *Journ. prakt. Chem.* [2], **14**. 124, 1876.

case more hydrogen is oxidized than carbon monoxide, and in the latter case more carbon monoxide than hydrogen, and he is inclined to the view of Hüfner[1] that platinum acts by loosening the affinities of the atoms within the oxygen molecules, thus rendering it more active. Engler and Wöhler, however, have pointed out that Meyer's results are probably due to the oxidation of carbon present as an impurity in Meyer's platinum black. But, after all, there is no necessity for assuming that the above-mentioned oxides are the same as those alternately formed and reduced during the oxidation of the platinum black. This view of the process is in harmony with an old suggestion made by Brodie,[2] that the catalytic process is a series of alternate oxidations and reductions.

Berthelot[3] suggests that compounds having the formulæ $Pt_{30}H_2$ or $Pt_{30}H_3$ are produced with the evolution of heat when platinum black is placed in a mixture of hydrogen and oxygen. The hydride is supposed to decompose in the presence of oxygen with the formation of water and the regeneration of the platinum, and an evolution of a still greater amount of heat. More hydrogen then attacks the platinum, and more hydride is formed; this in turn is oxidized as before. This alternation of reactions—formation and decomposition of the hydride—is supposed finally to bring the temperature up to the point of ignition of the mixture. Mond, Ramsay, and Shields (*l.c.*) doubt the existence of Berthelot's hydrides, and seem to think that the occluded hydrogen is in a monatomic or "nascent" condition. This agrees with the view of Gladstone and Tribe,[4] that the reducing action of the copper-zinc couple is due to the

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[1] G. Hüfner, *Journ. prakt. Chem.* [2], **10.** 148, 385, 1874.

[2] B. C. Brodie, *Phil. Trans.*, **151.** 855, 1862; T. Bayley, *Phil. Mag.* [5], **7.** 126, 1879.

[3] M. Berthelot, *Compt. Rend.*, **94.** 1377, 1882; *Ann. Chim. Phys.* [5], **30.** 519, 1883; L. P. Cailletet and E. Colardeau, *Compt. Rend.*, **119.** 830, 1894.

[4] J. H. Gladstone and A. Tribe, *Journ. Chem. Soc.*, **35.** 567, 1879. For the monatomic condition of occluded gases, see A. Winkelmann, *Drude's Ann.*, **6.** 104, 1901; **8.** 388, 1902; G. N. St. Schmidt, *ib.*, **13.** 747, 1904; O. W. Richardson, *Phil. Mag.* [6], 7, 266, 1904; with J. Nicol and T. Parnell, *ib.*, **8.** 1, 1904.

fact that the hydrogen first produced is occluded by the metal and then given off as nascent hydrogen.

P. Sabatier and J. B. Senderens[1] also believe that the formation of ethene and of ethane from acetylene and hydrogen in the presence of finely powdered metals (nickel, cobalt, iron, platinum, and copper) depends on the preliminary formation of a metallic hydride.

§ 82. Influence of Catalytic Agents upon the Rate of Dissolution of Solids.

"Insoluble" (violet) chromic chloride only dissolves very slowly in water,[2] but it is very quickly dissolved if a minute trace of chromous chloride be present. According to Peligot,[3] 0·000025 gram of chromous chloride per gram of insoluble chromic chloride is necessary for the purpose. Here, then, we have a most interesting process of catalysis. Peligot and Löwel[4] explain the reaction by a very plausible theory of intermediate reactions. It is assumed that the chromous chloride first reduces the insoluble chromic chloride to chromous chloride, and the original chromous chloride is transformed into soluble chromic chloride. Thus—

$$CrCl_3 \text{ (insol.)} + CrCl_2 = CrCl_2 + CrCl_3 \text{ (sol.)};$$

the newly formed chromous chloride then acts on the insoluble chromic chloride as before. A great number of reducing

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[1] P. Sabatier with J. B. Senderens, *Compt. Rend.*, **130**. 250, 1539, 1628, 1761, 1900; **131**. 40, 187, 267, 1766, 1900; **132**. 210, 566, 1254, 1901; **133**. 321, 1901; **134**. 514, 689, 1127, 1185, 1902; **135**. 225, 278, 871, 1902; **136**. 738, 921, 936, 983, 1903; **137**. 301, 1025, 1903; **138**. 457, 1904; *Bull. Soc. Chim.* [3], **25**. 671, 678, 1901; with A. Mailhe, *Compt. Rend.*, **138**. 245, 407, 1904.

[2] At 180°–200°, H. Moissan, *Compt. Rend.*, **92**. 1051, 1881.

[3] E. Peligot, *Ann. Chim. Phys.* [3], **12**. 533, 1844; **14**. 240, 1845; P. Rohland, *Zeit. anorg. Chem.*, **21**. 37, 1899; **29**. 159, 1901; gives the number 0·000005 gram per gram of $CrCl_3$.

[4] E. Peligot, *l.c.*; H. Löwel, *Journ. de Pharm.*, **7**. 424, 1843; *Journ. prakt. Chem.* [1], **37**. 38, 1846; see also A. Recoura, *Compt. Rend.*, **102**. 421, 1886; C. A. Barreswill, *Journ. de Pharm.*, **7**. 433, 1845.

agents invoke this catalytic action in common with chromous chloride. Rohland has investigated the action of a great number of metals on the process. It is supposed that the reducing agent first reduces insoluble chromic chloride to chromous chloride, and that the latter then acts as indicated above. A direct proof of this pretty theory has not been made out. K. Drucker[1] has recently investigated the process, but he does not seem to be able to suggest a more satisfactory substitute for Löwel's hypothesis. Ostwald[2] still thinks that "a sufficient explanation of the action is wanting."

The influence of hydrogen ions and hydroxyl ions on the rates of solution of marble, metals, arsenious oxide, etc., has been investigated. Acids and alkalies accelerate the rate of dissolution of arsenious oxide. The acceleration is proportional to the square root of the concentration of the H or OH ions. The influence of the hydroxyl ions is more marked than H ions.[3]

While the velocity of dissolution of marble in hydrochloric, hydrobromic, hydriodic, and other acids is equally great, this is not the case with zinc. Hydrobromic acid acts upon this metal more rapidly than the other acids, and hydrochloric acid dissolves the metal twenty-seven times as fast as sulphuric acid. This great difference points to the fact that the dissolution of zinc in sulphuric acid is of a different nature from the solution in the haloid acids. The cause of the phenomenon is not yet known. There is no doubt that the electrolytic conductivity of the acids, the heat of dissolution, and the solubility of the salts produced, play an important part in the reaction.[4]

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[1] K. Drucker, *Zeit. phys. Chem.*, **36**. 173, 1901.

[2] W. Ostwald, *Grundlinien der anorganischen Chemie*, Leipzig, 1900; A. Findlay's trans., 603, 1902.

[3] K. Drucker, *Zeit. phys. Chem.*, **36**. 693, 1901.

[4] W. Spring and E. van Aubel, *Zeit. phys. Chem.*, **1**. 465, 1887; J. G. Boguski, *Ber.*, **9**. 1442, 1599, 1646, 1876; *Zeit. phys. Chem.*, **1**. 558, 1886; with N. Kajander, *Ber.*, **10**. 34, 1877; T. Ericson von Aurén, *Zeit. anorg. Chem.*, **27**. 209, 1901; T. Ericson-Aurén and W. Palmaer, *Zeit. phys. Chem.*, **39**. 1, 1902; **45**. 182, 1903; J. Ball, *Journ. Amer. Chem. Soc.*, **17**. 641, 1897 (effect of soluble sulphates on dissolution of zinc in sulphuric acid, and of soluble chlorides upon dissolution of zinc in hydrochloric acid)

De la Rive[1] has shown that the dissolution of zinc in dilute sulphuric acid depends upon the amount of "impurity" present in the zinc and on the conductivity of the acid. The less the impurity the less the chemical action; and it is inferred that absolutely pure zinc would be insoluble in pure dilute acid. If a salt of platinum be added to the dilute sulphuric acid (1 acid : 12 water), Millon[2] has shown that dissolution takes place about 150 times as fast again. The addition of any salt which can be reduced to the metallic state by contact with the zinc also serves to promote the action. If a piece of pure (insoluble) zinc be placed in contact with a piece of platinum wire, chemical action commences at once, and an electric current flows from the zinc to the platinum *in* the solution, and from the platinum to the zinc *outside* the solution. It is therefore assumed that the chemical action does not depend on the relative affinity of zinc for the acid, but that the process of dissolution is an electrical phenomenon evoked by the contact of the zinc with the impurity always associated with ordinary zinc, the acid serving as conductor. But since the rate of dissolution of zinc (lead impurity) in dilute acids is not exactly proportional to the electrical conductivity of the solution, T. Ericson-Aurén and Palmaer[3] suggest that a "local element" is formed, consisting of the dissolving metal, the metallic salt formed, acid and impurity, say—

$$\mathrm{Zn} \mid \mathrm{ZnCl_2} \mid \mathrm{HCl} \mid \mathrm{Pb}.$$

It is claimed that anything which increases the electromotive force of this combination—addition of zinc salts, or of depolarizers,[4] replacement of lead with other metals, etc.—increases the rate of dissolution, and *vice versâ.* But the experiments of Kahlenberg and of his co-workers on the dissolution of the metals in various solvents do not fit in with this theory.

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[1] A. de la Rive, *Pogg. Ann.*, **19**. 221, 1830; *Ann. Chim. Phys.* [2], **43**. 425, 1830.

[2] C. Millon, *Annales de Chim.*, **6**. 73, 1842.

[3] T. Ericson-Aurén, *l.c.*; H. E. Patten, *Journ. Phys. Chem.*, **7**. 153, 1903; L. Kahlenberg, *ib.*, **6**. 1, 1902; *Journ. Amer. Chem. Soc.*, **25**. 380, 1903; C. F. Roberts and L. Brown, *ib.*, **25**. 801, 1903.

[4] J. M. Weeren, *Ber.*, **24**. 1785, 1891.

§ 83. Armstrong's Theory of Catalysis and of Chemical Action.

Armstrong[1] has amplified De la Rive's suggestion, and put forward the hypothesis that two substances will only react in presence of certain impurities (catalytic agents). Interaction does not take place between pure substances. He assumes that "when the complex formed by the association of the interacting substances meets with the necessary third component, a conducting system is established, and that as soon as this is formed a change sets in. . . ." According to this hypothesis, "a circuit of change must comprise three distinct terms or components." One of these must be a conductor of electricity which is capable of forming with the reacting substance a system analogous with a closed voltaic circuit. Thus, in the oxidation of carbon monoxide the change occurs with the system—

Carbon monoxide | conducting water | oxygen;

so that, in chemical symbols—

$$\begin{array}{c|c|c} CO & OH_2 & O \\ CO & OH_2 & O \end{array} = \begin{array}{c|c} CO_2 & H_2O \\ CO_2 & H_2O \end{array}.$$

The reaction between hydrogen and oxygen may be represented by the symbols—

$$H_2 \mid OH_2 \mid O_2 = H_2O \mid H_2O_2,$$

so as to agree with Traube's view that hydrogen peroxide invariably accompanies the formation of water. The hydrogen peroxide may be subsequently decomposed by heat, or it is possible that—

$$H_2 \mid OH_2 \mid H_2O_2 = H_2O \mid H_2O \mid H_2O.$$

If water be not present, a conducting system cannot be produced. In the case of

Hydrogen | conducting water | oxygen,

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[1] H. E. Armstrong, *B. A. Reports*, 962, 1885; *Proc. Roy. Soc.*, **40.** 287, 1886; **70.** 99, 1902; **74.** 86, 1904; *Journ. Chem. Soc.*, **49.** 112, 1886; **67.** 1122, 1895; **83.** 1088, 1903; *Proc. Chem. Soc.*, **1.** 39, 1885; **8.** 22, 1892; *Nature*, **49.** 100, 1893; *Encyc. Brit.*, **26.** 740, 1902.

for example, the withdrawal of moisture renders the combination of hydrogen and oxygen exceedingly difficult. "The gases do not explode on heating to redness." Baker[1] has published a still more remarkable result. When the partially dried gases are heated, "water is slowly formed, and although it is then present in enormously larger quantity than is necessary to bring about the action, no explosion takes place." Armstrong assumes that pure water is a non-conductor; that the water formed by the union of Baker's gases is so pure that it will not allow the necessary "conducting system" to be formed with the reacting gases.

With the majority of chemical reactions which take place when apparently pure water is the only impurity present, it is merely "necessary to bear in mind that as we invariably operate in glass vessels which are to some extent soiled, it is impossible to avoid the presence of traces of acids or of salts which render the water an electrolyte, and therefore the introduction of water means the introduction of an electrolyte."

In the case of chemical actions which appear to take place between *two* components, as in Shenstone's experiment on the union of pure chlorine with pure mercury,[2] it is urged that the process of purification has not been sufficiently exhaustive. The occurrence of chemical change is said to be a sufficient proof that "dirty water" was really present. The argument is, of course, invulnerable.

According to this theory, the function of the catalytic agent is to collect in one system the various elements necessary for a particular chemical change. Thus, when benzene and methyl chloride are brought into contact there is no chemical action. If, however, aluminium chloride be present, Armstrong assumes that a more or less stable "molecular complex" is formed by the union of the methyl chloride, benzene, and aluminium chloride. "In like manner ferric chloride probably conditions the interaction of bromine and benzene by combining with both and so bringing them within each other's range in an unstable

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[1] H. B. Baker, *Journ. Chem. Soc.*, **81**. 400, 1902.

[2] W. A. Shenstone, *Journ. Chem. Soc.*, **71**. 471, 1897.

system." This, too, is the function of the impurity in the solution of zinc in dilute sulphuric acid.

Electrolysis, as we all know, is the breaking up of a compound into simpler constituents by means of an electric current. Armstrong's theory is that chemical combination is an inversion of this process. Chemical combination takes place when the reacting substances are brought within the sphere of one another's influence in an hypothetical voltaic circuit. Hence, Armstrong calls chemical combination "reversed electrolysis."

§ 84. Ionic Theory of Heterogeneous Catalyses.

Just as a liquid continues to evaporate at its surface until the pressure of the vapour is equal to the vapour pressure of the liquid, so Nernst[1] suggests that every metal, when placed in contact with water or any other solution, tends to send positively charged ions into the solution, and the metal itself assumes a negative charge. This process continues until the concentration of the metal has attained a certain value, when a state of equilibrium ensues. The force driving the ions into solution is called the "electrolytic solution pressure." This force varies with the nature of the metal. For example—

Metal.	Solution pressure.
Zinc . .	10^{18} atmospheres
Iron . . .	10^{3} ,,
Hydrogen .	10^{-4} ,,
Copper . .	10^{-12} ,,
Mercury .	10^{-15} ,,

In particular, if zinc be placed in a solution of sulphuric acid, it is assumed, in the first place, that the acid is already more or less dissociated into positive hydrogen ions and negative SO_4 ions, say—

$$H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4''.$$

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[1] See R. A. Lehfeldt's *Electro-chemistry*.

When the positive hydrogen ions come into contact with the negative zinc plate, they lose their positive charge, and the above table shows that the force driving positive hydrogen ions into the solution is very much less than that driving positive zinc ions into the solution. Consequently, the $H^{\cdot}$ ions are gradually replaced by the zinc ions. The reaction is—

$$Zn^{\cdot} + 2H^{\cdot} = Zn^{\cdot} + H_2.$$

Whether or not sufficient hydrogen ions are neutralized to cause a liberation of hydrogen gas depends, for one thing, on the number of ions of the metal sent into the solution. But further, we have seen that when pure zinc is used no hydrogen is liberated. Under this circumstance, if a piece of platinum wire be brought in contact with the zinc, as shown in Fig. 14, hydrogen is at once liberated, *not* from the surface of the zinc, but from the surface of the platinum, and zinc passes into the solution. The negative charge left on the zinc as positive zinc ions pass into the solution travels through the wire to the platinum plate, and there neutralizes the positive charge of the hydrogen ions which come into contact with the plate. The formation of a similar "voltaic couple" is said to explain why the presence of impurities appears to acclerate the solution of zinc in acids. In the absence of foreign metals the neutral hydrogen forms a film, or varnish, over the surface of the metal, protecting it from the acid. The impurity is supposed to prevent the accumulation of hydrogen on the surface of the zinc in the manner indicated in the preceding figure.

Now, let a syphon be filled with a solution of potassium sulphate and placed in two beakers (Fig. 15) also containing a solution of the same salt. An amalgamated zinc rod is placed in one beaker, and a platinum wire in metallic communication with the zinc is placed in the other beaker. A block of unglazed porcelain, or a piece of parchment paper, may be used to block up the syphon tube, or the tube may be left as it is. If sulphuric acid be poured around the zinc plate there will be no chemical action, but if sulphuric acid be poured in the beaker containing the platinum wire, zinc dissolves in the one cup, and hydrogen is liberated from the platinum wire.

The explanation, according to Nernst's theory, is obvious. The passage of zinc ions into the solution of potassium sulphate causes the platinum wire to assume a negative charge, and the positive ions derived from the sulphuric acid in the vicinity of the platinum wire are neutralized, and escape as gaseous hydrogen. Ostwald[1] has described this along with a number of similar experiments in a paper entitled "Chemical Action at a Distance," published in 1891.

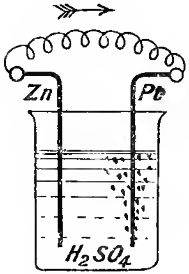

FIG. 14.[2]

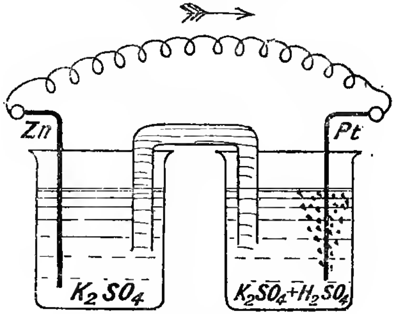

FIG. 15.

If, now, a metal (M) be placed in a solution containing oxygen, it is possible that the ions of the metal combine with oxygen to form a peroxide—

$$2M^{\cdot} + O_2 = M_2O_2 \text{ (peroxide)},$$

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[1] W. Ostwald, *Konig. Sächs. Akad. d. Wissen.*, 239, 1891; *Zeit. phys. Chem.*, **9**. 540, 1892; *Phil. Mag.* [5], **32**. 145, 1891; C. R. A. Wright and C. Thomson, *Journ. Chem. Soc.*, **51**. 672, 1887; P. Drude, *Wied. Ann.*, **62**. 693 and Suppl., 1897; W. D. Bancroft, *Zeit. phys. Chem.*, **10**. 387, 1892. For an explanation without the aid of the theory of ions, see S. U. Pickering, *Phil. Mag.* [5], **32**. 478, 1891.

[2] The arrow in the diagrams—Figs. 14 and 15—represents the direction of the "flow" of the negative charge. Positive electricity—the electric current itself—flows along the wire in the opposite direction, *i.e.* from the platinum to the zinc outside the solution.

which in contact with water or a dissolved acid forms a base or a salt and hydrogen peroxide—

$$M_2O_2 + 2H_2O = 2MOH + H_2O_2;\ M_2O_2 + 2HCl = 2MCl + H_2O_2.$$

In the extraction of gold from "poor" ores by the "cyanide process" advantage is taken of the fact that gold dissolves in a dilute solution of potassium cyanide in the presence of free oxygen.[1] In this case, the formation of an oxide of gold by the process just indicated is very unlikely, because gold oxide is a very unstable compound which decomposes, even at ordinary temperatures, into the metal and free oxygen. It is more likely that the oxygen does not react with the metal, but with the hydrogen, spread over its surface so as to form hydrogen peroxide directly. The hydrogen on the surface of the metal is obtained by the neutralization of the positive hydrogen ions normally present in an aqueous solution of potassium cyanide[2]—

$$KCN + H_2O = K^{\cdot} + OH' + H^{\cdot} + CN'.$$

The concentration of the hydrogen ions is thus diminished, more gold ions pass into the solution, and more hydrogen is deposited on the metal. This is in turn removed by the oxygen dissolved in the solution of potassium cyanide. The dissolved oxygen thus acts as a "depolarizer," cleansing the surface of the metal from the adhering film of hydrogen.

G. Bodländer[3] has indeed demonstrated the formation of hydrogen peroxide during the solution of gold in aqueous solutions of potassium cyanide, and that one molecule of hydrogen peroxide is formed for every two atoms of gold dissolved. Hence, he represents the first reaction by the equation—

$$2Au + 4KCN + 2H_2O + O_2 = 2KOH + 2AuK(CN)_2 + 2KOH;$$

the hydrogen peroxide then reacts with more potassium cyanide and gold according to the equation—

$$H_2O_2 + 2Au + 4KCN = 2KAu(CN)_2 + 2KOH.$$

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[1] J. S. Maclaurin, *Journ. Chem. Soc.*, **63**. 724, 1893; **67**. 199, 1895.

[2] J. Shields, *Phil. Mag.* [5], **35**. 365, 1893.

[3] G. Bodländer, *Zeit. angew. Chem.*, **10**. 583, 1896.

This is in harmony with the well-known fact that the presence of hydrogen peroxide accelerates the dissolution of gold by potassium cyanide.

§ 85. The Catalytic Action of Hydrogen and Hydroxyl Ions.

The velocity of inversion of cane sugar, or the speed of hydrolysis of the esters, in the presence of acids, is strictly proportional to the concentration of the hydrogen ions[1] when the solutions are dilute, but at higher concentrations, deviations occur. Thus, a 0·5 N-solution of nitric acid inverts a given solution of cane sugar 6·07 times as fast as a 0·1 N-solution, although the former only contains 4·64 times as many ions as the latter.[2]

Suppose a neutral salt is added to an acid which contains a common ion, the concentration of the hydrogen ions of the acid will be lowered, and we should expect that the inverting power of the acid would be lessened in a corresponding manner. As a matter of fact, the velocity is sometimes accelerated. For example, the velocity of inversion of a given solution of cane sugar by a 0·05 N-solution of nitric acid is 29·9; the addition of 0·4 N-potassium nitrate raises this coefficient to 33·9 instead of lowering it to 27·2, as we should expect from the decrease in the degree of ionization of the acid. The presence of a neutral salt, therefore, acts in two ways upon the inverting acid. First, it lowers the concentration of the hydrogen ions of the acid; and second, it stimulates, so to speak, the activity of the remaining hydrogen ions. Consequently, instead of writing the velocity coefficient k proportional to the number m of hydrogen ions present in the solution, we have—

$$k = am + bm^2,$$

where a and b are constants; a is the same for all acids, thus indicating that all the hydrogen ions exert the same influence,

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[1] S. Arrhenius, *Zeit. phys. Chem.*, **4.** 244, 1889; W. Palmaer, *ib.*, **22.** 92, 1897. For hydrolysis of sulphonic acids with *concentrated* acids, see J. M. Crafts, *Journ. Amer. Chem. Soc.*, **23.** 250, 1901.

[2] H. Ostwald, *Journ. prakt. Chem.* [2], **31**, 307, 1885.

no matter from what acid they may be derived; *b*, on the other hand, depends on the nature of the ion which is "paired" with the hydrogen ion.

Similar results have been obtained for the influence of hydroxyl ions derived from the hydroxides of the alkalies and alkaline earths upon the velocity of hydrolysis of esters.[1]

The etherification of trichloracetic acid and of formic acid in the presence of a large excess of alcohol is a bimolecular reaction. We should expect a unimolecular reaction (§ 14). Goldschmidt assumes that the "hydrogen ions of the acid exert a catalytic action upon its own etherification;" and Donnan, that "the reaction takes place between the alcohol and the ions of the acid." Both suggestions furnish practically the same velocity equations.[2]

Rohland thinks that the alleged "acceleration by hydrogen ions is possibly due to the formation of water from the OH' ions of water and the $H^{\cdot}$ ions of the acid, or from the $H^{\cdot}$ ions of the water and the OH' ions of the base. Although the water molecules *in statu nascendi* are not dissociated, they are very reactive."[3]

§ 86. Influence of the Concentration of the Reacting Substance upon the Velocity of a Reaction.

The velocity of a reaction does not always obey Wilhelmy's law of mass action: "the rate of transformation is proportional

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[1] L. T. Reicher, *Liebig's Ann.*, **228**. 257, 1885.

[2] H. Goldschmidt, *Ber.*, **28**. 321, 1895; **29**. 2209, 1896; F. G. Donnan, *ib.*, **29**. 2422, 1896; E. Petersen, *Zeit. phys. Chem.*, **16**. 385, 1895; **20**. 331, 1896; J. Tafel, *ib.*, **19**. 592, 1896; H. Goldschmidt, *ib.*, **31**. 235, 1899; J. C. Cain, *ib.*, **12**. 751, 1898; A. Villiers, *Ann. Phys. Chem.* [5], **21**. 72, 1880; T. S. Price, *Journ. Chem. Soc.*, **79**. 303, 1901. A most interesting investigation which should be read by the student is H. Goldschmidt with A. Merz, *Ber.*, **30**. 670, 1897; and with F. Buss, *ib.*, **30**. 2075, 1897.

[3] P. Rohland, *Chem. Ztg.*, **24**. 312, 1014, 1900; **25**. 1006, 1901; *Zeit. phys. Chem.*, **41**. 739, 1902; A. A. Noyes and G. V. Sammet, *ib.*, **41**. 11, 1902; *Journ. Amer. Chem. Soc.*, **24**. 498, 1902.

to the active mass of the substance taking part in the reaction," if we understand by the "active mass" the concentration, or number of gram-molecules of the reacting substance in a litre of solution. For example, Ostwald[1] has shown that the rate of inversion of a 40 per cent. solution of cane sugar is not double the rate of inversion of a 20 per cent. solution, nor quadruple the velocity of a 10 per cent. solution. Similar results have been obtained by Spohr,[2] as indicated in the following table:—

Spohr.		Freezing-point (osmotic pressure).	Ostwald.		Freezing-point (osmotic pressure).
Conc. of sugar.	k=velocity of inversion.		Conc. of sugar.	k=velocity of inversion.	
30%	8·76	(2·0)	40%	11·68	3·41
20%	4·84	1·37	20%	4·54	1·37
10%	2·10	0·61	10%	2·07	0·61
4%	0·41	(0·18)	4%	0·77	0·23

Cohen[3] has pointed out that the actual volume occupied by the sugar has been neglected. If the amount of acid is the same in the two solutions, the space in which the acid and sugar molecules move is less in the 40 per cent. than in the 20 per cent. solution. Hence the rate of inversion will be greater in the former case than in the latter. If a gram-molecules of cane sugar are made up to v c.c., and if b denotes the volume actually occupied by the sugar, the initial concentration must be written $a/(v-b)$ in place of the usual a/v.

$$\therefore k_{40} : k_{20} = \frac{a_{40}}{100 - b_{40}} : \frac{a_{20}}{100 - b_{20}},$$

where k_{40} and k_{20} respectively denote the velocity constants in the 40 per cent. and 20 per cent. solutions; b_{40} and b_{20} the

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[1] W. Ostwald, *Journ. prakt. Chem.* [2], **31**. 307, 1885.

[2] J. Spohr, *Journ. prakt. Chem.* [2], **33**. 272, 1886; *Zeit. phys. Chem.*, **2**. 216, 1888. See also A. von Hemptinne, *ib.*, **26**. 728, 1898 (decomposition potassium iodide).

[3] E. Cohen, *Zeit. phys. Chem.*, **23**. 442, 1897.

corresponding volumes of the sugar molecules in the solution. Obviously, $b_{40} = 2b_{20}$; $2a_{20} = a_{40}$. From Ostwald's data, therefore, we get $b_{20} = 17{\cdot}7$; similarly, $b_{10} = 8{\cdot}85$; $b_4 = 3{\cdot}54$. We now calculate from Cohen's equation, $k_{10} : k_4 = 2{\cdot}64$, while we get 2·78 by using the experimental data.

Arrhenius[1] has drawn attention to the fact that the increase of the rate of inversion coincides with the increase in the osmotic pressure per gram-molecule of the solution, and he shows that the experimental results agree with Wilhelmy's law of mass action if we substitute "osmotic pressure" for the "active mass," so that the law reads, "*the velocity of a chemical reaction is proportional to the osmotic pressure of the substance taking part in the reaction.*" It is easy to see that this must be so.

The osmotic pressure of cane sugar in solution, kept at a constant temperature, is proportional to the number of collisions of the sugar molecule with the "semipermeable" walls of the containing vessel. Again, the amount of sugar inverted in unit time will be proportional to the number of collisions of the sugar molecule with the molecules, or rather the ions, of the acid. But the amount of acid in the solution is constant, and consequently the number of collisions of the molecules of sugar with the molecules of the acid will be proportional to the osmotic pressure of the sugar molecule. In other words, the velocity of the reaction will be proportional to the osmotic pressure of the sugar molecules.

It is here interesting to note how dependent we are upon atoms, molecules, and the kinetic theory whenever we want to obtain a mental picture of a chemical process.

§ 87. Action of Foreign Substances upon Catalytic Processes.

If this view be correct, those conditions which affect the osmotic pressure will also modify the velocity of a reaction. These conditions are—

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[1] S. Arrhenius, *Zeit. phys. Chem.*, **28**. 317, 1899; **2**. 495, 1888.

1. The osmotic pressure of a solution increases more rapidly than it would do on the assumption that it is proportional to the concentration. This agrees with the observations made on the influence of the concentration of cane sugar on the rates of inversion by Spohr and by Ostwald. If subsequent work establishes the inter-dependence of osmotic pressure, and the velocity of a reaction with increasing concentration, the "abnormal" increase of the osmotic pressure of concentrated solutions will have to be explained.

2. R. Abegg[1] has shown that the osmotic pressure of a mixture of two substances is often greater than the sum of the osmotic pressures of the individual substances. Hence the partial osmotic pressure of a substance will be greater in the presence of another substance than it would be if it were alone dissolved in water. Hence it would follow that the osmotic pressure of a sugar solution will be increased by the addition of another substance. Thus Tammann[2] found that a solution containing a mixture of copper sulphate and cane sugar has an osmotic pressure greater than the sum of the individual values for cane sugar and copper sulphate. The addition of 0·4 gram-molecules of sodium chloride increases the rate of inversion of cane sugar 26 per cent. The addition of invert sugar also accelerates the velocity the same as if the concentration of the cane sugar were increased. Thus, the velocity is accelerated 10 per cent. beyond the value calculated according to the law of mass action, by a mixture containing 10 per cent. of cane sugar and 10 per cent. of invert sugar, and also by a 20 per cent. solution of cane sugar.

It is further found that the acceleration of the velocity with increasing concentration is greatest with those salts which "induce" the greatest rise of osmotic pressure when mixed with other salts.

The addition of foreign substances (K_2SO_4, Na_2SO_4, etc.)

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[1] R. Abegg, *Zeit. phys. Chem.*, **15**. 256, 1896.

[2] G. Tammann, *Zeit. phys. Chem.*, **9**. 106, 1892; P. Steiner, *Wied. Ann.*, **52**. 275, 1894; V. Gordon, *Zeit. phys. Chem.*, **18**. 1, 1895; W. Roth, *ib.*, **24**. 114, 1897; H. Euler, *ib.*, **31**. 360, 1900; V. Rothmund, *ib.*, **33**, 401, 1900.

does not accelerate the rate of hydrolysis of an ester by a 0·025 N-solution of alkaline hydroxide quite so much as the inversion of cane sugar.[1] The behaviour of the haloids and nitrates is exceptional, for the velocity of hydrolysis of an ester is retarded, not accelerated, by the addition of these salts. The hydrolysis of ethyl acetate is also retarded by the addition of non-electrolytes like cane sugar, glycerine, acetone, etc.[2] The retardation—negative catalysis—has been explained, with more or less success, by assuming—

1. The degree of ionization of the ester or catalyzer is diminished, or else the catalyzer combines with the "foreign substance" so that the quantity of the available catalytic agent is diminished.[3]

2. The combination of the ester with the retarding salt by which the active mass of the ester is diminished. Freezing-point (osmotic pressure) determinations of mixed solutions of retarding salts (like sodium iodide) and ester (ethyl acetate) does not agree with this assumption, although it is supported by the fact that such compounds have been isolated, and the retarding influence of such salts diminishes as the temperature rises, owing to the decomposition of the compound of the ester and salt.[4]

§ 88. Joint Effect of Two Catalytic Agents.

In some cases two catalytic agents induce the same reaction, and their joint effect is the same as if each was acting alone. This, for example, is the case when a mixture of colloidal gold and platinum acts upon hydrogen peroxide.[5]

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[1] H. Trey, *Journ. prakt. Chem.* [2], **34**. 353, 1886.

[2] C. Kullgren, *Zeit. phys. Chem.*, **37**. 612, 1901.

[3] S. Arrhenius, *Zeit. phys. Chem.*, **1**. 120, 1887; **2**. 289, 1888; **5**. 6, 1890; J. Spohr, *Journ. prakt. Chem.* [2], **33**. 272, 1886; H. Trey, *ib.*, **34**. 353, 1886; K. Arndt, *Zeit. anorg. Chem.*, **28**. 364, 1901.

[4] J. Spohr, *Journ. prakt. Chem.* [2], **32**. 51, 1885; *Zeit. phys. Chem.*, **2**. 216, 1888.

[5] M. et Mme. V. Henri, *Compt. Rend. Soc. Biol.*, **55**. 864, 1903.

But very often *the joint effect of two catalytic agents is not the sum of their separate effects.*[1] In the following table the relative effects of different mixtures of catalytic agents upon the reaction between hydrogen peroxide and potassium iodide are arranged side by side with the effects calculated on the assumption that their joint effect is the sum of their separate effects :—

Mixture.	Calc.	Obs.
$FeSO_4 + H_2MoO_4$	314	321 (normal)
$CuSO_4 + H_2MoO_4$	247	250 (normal)
$FeSO_4 + H_2WO_4$	369	270 (retard)
$FeSO_4 + CuSO_4$	315	350 (accelerate)
$H_2SO_4 + H_2WO_4$	275	370 (accelerate)

A mixture of copper and mercuric sulphates also exerts a greater catalytic influence upon the oxidation of aniline or naphthalene by concentrated sulphuric acid than the sum of their separate effects.[2]

Brode thinks that these results do not agree with the suggestion of Noyes[3] that "the catalytic agent does not affect the reaction as a whole, but only exerts a specific action on each substance taking part in the reaction." See also p. 324.

§ 89. Ionic Theories of Homogeneous Catalyses.

The above-mentioned experiments on the velocity of inversion of cane sugar show that Wilhelmy's law of mass action does not hold unless we understand for the "active mass," not the concentration, but the "osmotic pressure" of the reacting substance. We shall also see, in § 115, how the influence of temperature upon the velocity of chemical reactions led Arrhenius

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[1] J. Brode, *Zeit. phys. Chem.*, **37**. 257, 1901 ; A. Titoff, *ib.*, **45**. 641, 1903 ; T. S. Price, *ib.*, **27**. 474, 1898.

[2] G. Bredig and J. W. Brown, *Zeit. phys. Chem.*, **46**. 502, 1903.

[3] A. A. Noyes, *Zeit. phys. Chem.*, **19**. 599, 1896.

to assume that when a reaction takes place with a measurable velocity only a small fraction of the total number of molecules takes part in the reaction. An increase of temperature is supposed to increase the number of "active molecules" at the expense of the "inactive" ones, just as the degree of ionization of water is augmented by an increase of temperature. This has led Euler[1] to put forward the hypothesis that Arrhenius' "active molecules" are the ions of the dissociated reacting substance. Euler assumes that "all substances, without exception, are split up into ions, although the part ionized is frequently a very small fraction of the whole . . . all reactions are ion reactions . . . only collisions between ions are chemically fruitful." While another fervid supporter of the theory claims that "most chemical reactions, if not all, are reactions between ions; molecules, as such, do not enter into the reaction at all."[2]

To suit this theory a molecule of cane sugar in aqueous solution is supposed to be split up into two imaginary ions—

$$C_{12}H_{22}O_{11} \rightleftharpoons A^{\cdot} + B'.$$

The products of the concentrations of these ions with the concentrations of the ions of the dissociated water, HO and H, determines the velocity of inversion. For equilibrium—

$$k_1 C_{\text{cane sugar}} C_{\text{water}} = k_2 C_{\text{dextrose}} C_{\text{levulose}},$$

hence—

$$\frac{dx}{dt} = k_1 C_{A^{\cdot}} C_{B'} C_{OH'} C_{H^{\cdot}} - k_2 C_{\text{dextrose}} C_{\text{levulose}}.$$

"Granting these premises," any cause which tends to increase the product $C_{A^{\cdot}} C_{B'} C_{OH'} C_{H^{\cdot}}$ will increase the velocity of the reaction. Neutral salts are supposed to act in this way, and consequently Euler defines a catalytic agent as a *substance which*

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[1] H. Euler, *Zeit. phys. Chem.*, **36**. 641, 405, 1901; **40**. 498, 1902; **47**. 353, 1904; *Ber.*, **33**. 3202, 1900; R. Henriques, *Zeit. angew. Chem.*, **11**. 338, 697, 1898; F. Goldschmidt, *Zeit. Elektrochem.*, **10**. 221, 1904; R. Abegg, *ib.*, **10**. 185, 1904.

[2] H. C. Jones, *Amer. Chem. Journ.*, **25**. 349, 1901; *Chem. News*, **84**. 160, 1901.

modifies the velocity of chemical reactions by changing the concentration of the ions of the reacting substances.[1] In other words, the assumption is made that the ions are present in unknown concentrations, and these are assumed to change in accord with theoretical requirements!

In the hydrolysis of ethyl acetate—

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH,$$

the condition for equilibrium is that—

$$C_{\text{ester}}C_{\text{water}} = KC_{\text{acid}}C_{\text{alcohol}},$$

analogous with the regular—

$$C_{\text{salt}}C_{\text{water}} = KC_{\text{acid}}C_{\text{base}}.$$

Euler assumes that the ethyl alcohol, acetic acid, ethyl acetate, and water are all more or less dissociated, and that for equilibrium—

$$C_{\mathrm{H}^{\cdot}}C_{\mathrm{OH}'} = K_1C_{\mathrm{H_2O}};\ C_{\mathrm{C_2H_5O}'}C_{\mathrm{H}^{\cdot}} = K_2C_{\mathrm{C_2H_5OH}};$$

$$C_{\mathrm{CH_3CO}^{\cdot}}C_{\mathrm{OH}'} = K_3C_{\mathrm{CH_3COOH}};\ C_{\mathrm{C_2H_5O}'}C_{\mathrm{CH_3CO}^{\cdot}} = K_4C_{\mathrm{CH_3COOC_2H_5}};$$

and writes—

$$K_4C_{\mathrm{CH_3COOC_2H_5}}K_1C_{\mathrm{H_2O}} = K_2C_{\mathrm{C_2H_5OH}}C_{\mathrm{CH_3COOH}};$$

or—

$$C_{\mathrm{C_2H_5O}'}C_{\mathrm{CH_3CO}^{\cdot}}C_{\mathrm{H}^{\cdot}}C_{\mathrm{OH}'} = KC_{\mathrm{C_2H_5O}'}C_{\mathrm{H}^{\cdot}}C_{\mathrm{CH_3CO}^{\cdot}}C_{\mathrm{OH}'}.$$

Euler sets up the velocity equations by equating the difference of the opposing reactions to the usual dx/dt. Wegscheider[2] has pointed out that the last relation is a "self-evident identity," unless we make the unpermissible assumption that there are different kinds of H·, OH', and other ions. "Euler's equation," says Wegscheider, "does not express a chemical process, and it cannot be used to represent the velocity of a chemical reaction." Euler's hypothesis may mean that the reaction is between the ions—

$$CH_3CO^{\cdot} + C_2H_5O' \rightleftharpoons CH_3COOC_2H_5.$$

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[1] H. Euler says, "All catalytic agents increase the concentration of the reacting ions."

[2] R. Wegscheider, *Zeit. phys. Chem.*, **39**. 257, 1901; **41**. 62, 1902.

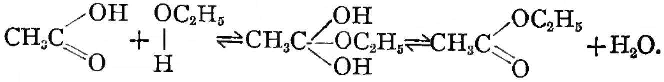
What ions are formed is, at present, outside the range of experimental verification, and we are therefore at liberty to suggest other more or less plausible schemes. Five years before Euler's publication, C. Zengelis[1] suggested the scheme symbolized by the equations—

$$C_2H_5OH \rightleftharpoons C_2H_5^{\cdot} + OH'; \; C_2H_5COOH \rightleftharpoons C_2H_5COO' + H^{\cdot};$$

followed by—

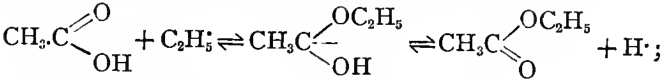
$$C_2H_5' + CH_3COO^{\cdot} \rightleftharpoons CH_3COOC_2H_5.$$

Another view is to represent the change as the result of a process of association—



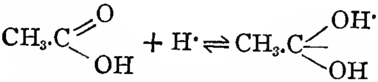
$$CH_3C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown O\end{matrix} + \begin{matrix}OC_2H_5\\ |\\ H\end{matrix} \rightleftharpoons CH_3C\begin{matrix}\diagup OH\\ -OC_2H_5\\ \diagdown OH\end{matrix} \rightleftharpoons CH_3C\begin{matrix}\diagup OC_2H_5\\ \diagdown\!\!\diagdown O\end{matrix} + H_2O.$$

None of these expressions take account of the accelerating influence of hydrogen ions, and A. Lapworth,[2] in consequence, has proposed a compromise between the ionic theory and the association hypothesis, namely, that "the production of complex ions is at the bottom of a large number of organic reactions." He suggests for the esterification of alcohol—



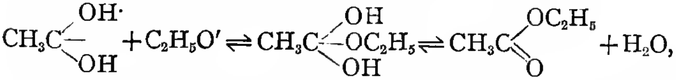
$$CH_3.C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OH\end{matrix} + C_2H_5^{\cdot} \rightleftharpoons CH_3C\begin{matrix}\diagup OC_2H_5\\ -\\ \diagdown OH\end{matrix} \rightleftharpoons CH_3C\begin{matrix}\diagup OC_2H_5\\ \diagdown\!\!\diagdown O\end{matrix} + H^{\cdot};$$

or, the alternative—



$$CH_3.C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OH\end{matrix} + H^{\cdot} \rightleftharpoons CH_3.C\begin{matrix}\diagup OH^{\cdot}\\ -\\ \diagdown OH\end{matrix}$$

a slow reaction, followed by the more rapid changes—



$$CH_3C\begin{matrix}\diagup OH^{\cdot}\\ -\\ \diagdown OH\end{matrix} + C_2H_5O' \rightleftharpoons CH_3C\begin{matrix}\diagup OH\\ -OC_2H_5\\ \diagdown OH\end{matrix} \rightleftharpoons CH_3C\begin{matrix}\diagup OC_2H_5\\ \diagdown\!\!\diagdown O\end{matrix} + H_2O,$$

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[1] C. Zengelis' Περὶ Χημίζης Ευγγενείας ὑπὸ (*On Chemical Affinity*), Athens, 1896; *Ber.*, **34**. 198, 1901.

[2] Private communication. See also A. Lapworth, *Journ. Chem. Soc.*, **73**. 445, 1898; **79**. 1265, 1901; **83**. 995, 1903; **85**. 1206, 1904; A. Lapworth and A. C. O. Hann, *ib.*, **81**. 1508, 1902.

which are in harmony with the observation that the velocity of hydrolysis of ethyl acetate is directly proportional to the concentration of the hydrogen ions.

The validity of the fundamental assumption that the chemical activity of an electrolyte is due to the ions has been seriously questioned by L. Kahlenberg,[1] who found that chemical reactions may proceed very rapidly in solutions which do not conduct electricity, and consequently are free from ions. For example, dry hydrogen chloride precipitates chlorides from benzene solutions of oleates of cobalt, nickel, and copper; and dry hydrogen sulphide precipitates sulphides from similar solutions in spite of the fact that solutions of these substances in benzene do not conduct electricity. Similarly, dry hydrogen sulphide precipitates sulphides from benzene solutions of arsenic trichloride and stannic chloride, and a dry petroleum ether solution of arsenic trichloride. Again, although dry ammonia does not unite with dry hydrogen chloride, union does take place if a trace of dry non-conducting benzene vapour be present.

Walker[2] also has shown that when certain reacting substances are mixed together, ionization takes place *after*, not before, chemical action. "In metathetic reactions between the alkyl iodides in the presence of aluminium chloride," says Walker, "reaction is not dependent upon antecedent ionization."

The velocity of many chemical reactions is not affected to any appreciable extent by a partial ionization of the reacting substances. The rate of combination of hydrogen and chlorine, for example, is in no way affected when ions are produced by external means, *e.g.* Röntgen rays, thorium, and radium radiations, etc.[3] J. J. Thomson could detect no free ions

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[1] L. Kahlenberg, *Journ. phys. Chem.*, **6.** 1, 1902; *Chem. News*, **88.** 312, 1903; *Zeit. phys. Chem.*, **46.** 68, 1903; *Journ. Amer. Chem. Soc.*, **25.** 380, 1903; C. F. Roberts and L. Brown, *ib.*, **25.** 801, 1903; H. E. Patten, *Journ. phys. Chem.*, **7.** 153, 1903; K. G. Falk and C. E. Waters, *Amer. Chem. Journ.*, **31.** 398, 1904 (action of benzene sol. of dry HCl upon Zn).

[2] D. Konowaloff, *Wied. Ann.*, **49.** 733, 1893; J. W. Walker, *Journ. Chem. Soc.*, **85.** 1082, 1904; with D. McIntosh, and E. Archibald, *ib.*, **85.** 1098, 1904; P. Walden, *Zeit. phys. Chem.*, **43.** 394, 1903.

[3] H. B. Dixon and H. B. Baker, *Journ. Chem. Soc.*, **69.** 1308, 1896;

when the gases were in active combination, with instruments capable of detecting the ionization of one molecule per 10^{14} of the molecules present; nor could Hemptinne detect any sign of free ions during the explosion of a mixture of hydrogen and chlorine, and of carbon monoxide and oxygen. Of course we can fall back upon the assumption that the ions of gases are not the same as the corresponding ions of solutions.

§ 90. Autocatalysis—Positive and Negative.

The hydrolysis of ethyl acetate is greatly accelerated by acids, and it has been observed that the acid which is formed during the hydrolysis of the ester itself acts catalytically. This explains why the action of water on an ester proceeds at first slowly and rapidly develops as the acid product of the hydrolysis accumulates in the system. When one of the substances taking part in the reaction acts as a catalyst the phenomenon is called, by Ostwald,[1] **autocatalysis.** Numerous illustrations might be quoted.

A simple example occurs during the inversion of an aqueous solution of cane sugar at 100°. The product of the reaction —invert sugar—appears to decompose, producing an unknown acid, which accelerates the rate of inversion.[2] The rate of formation of this acid is proportional to the amount of invert sugar present, x. Hence, if x denote the amount of invert sugar formed during the hydrolysis, x will also be proportional to the amount of acid produced, and the velocity of the reaction will therefore be—

$$\frac{dx}{dt} = kx(a - x)\text{ ; or, }\frac{1}{at}\log\frac{ax}{a - x} = k. \quad . \quad . \quad (1)$$

A. Rzewuski, *Naturwiss. Rundsch.*, **11**. 419, 1896; *Wied. Beibl.*, **20**. 1016, 1896; A. von Hemptinne, *Zeit. phys. Chem.*, **21**. 493, 1896; **39**. 345, 1902; J. J. Thomson, *Proc. Camb. Phil. Soc.*, **11**. 90, 1901; G. Bredig and W. Pemsel, *Phot. Archiv.*, **1**. 83, 1900; P. V. Bevan, *Phil. Trans.*, **202**. 71, 1903; F. Lengfeld and J. H. Ransom, *Journ. Phys. Chem.*, **5**. 502, 1901.

[1] W. Ostwald, *Ber. über d. Verhandl. d. Konig. Sachs. Ges. d. Wissen.*, 189, 1890.

[2] C. Kullgren, *Zeit. phys. Chem.*, **41**. 407, 1902.

In one experiment the influence of the acid only began to be perceptible after the reaction had been in progress 900 minutes. At that time $x = 0{\cdot}45$. This makes the integral of the velocity equation assume the form—

$$\frac{1}{(t - 900)a}\log\frac{x}{a - x} + 0{\cdot}11485 = k.$$

Data derived from Kullgren's experiments are as follows:—

t	$a - x$	$k \times 10^6$
0	12·43	—
900	11·95	—
1200	11·20	122
1400	10·24	121
1800	7·01	117
2200	2·77	122

One product of the hydrolysis of methyl acetate is acetic acid. If acetic acid be used as the catalytic acid, the speed of hydrolysis is proportional to the amount (a) of acetic acid present at any moment. Then—

$$\frac{dx_1}{dt} = k_1a(b - x). \quad . \quad . \quad . \quad . \qquad (2)$$

Let x of acetic acid have been set free during the reaction at the time t. This also acts catalytically on the ethyl acetate, thus increasing the velocity of the reaction. Hence—

$$\frac{dx_2}{dt} = k_1x(b - x). \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

The true velocity of the whole reaction will be the sum of these two separate velocities, or—

$$\frac{dx}{dt} = \frac{dx_1}{dt} - \frac{dx_2}{dt} = k_1(a + x)(b - x), \quad . \quad . \quad . \qquad (4)$$

which on integration becomes—

$$\frac{1}{t}\log\frac{b(a + x)}{a(b - x)} = k_1(a + b) = \text{constant}. \quad . \quad . \quad . \qquad (5)$$

The following measurements of the rates of hydrolysis of b

units of methyl acetate in the presence of *a* units of acetic acid will illustrate the principle[1] ($a = 1338$, $b = 1370$):—

t	x	constant $= k_1(a + b)$
7200	195	0·0863
14400	377	0·0853
21600	542	0·0839
28800	687	0·0827
34500	783	0·0812[2]

The hydrolysis of diacetamide[3] and of bromosuccinic acid furnish other examples. The latter reaction is unimolecular—

$$C_2H_3Br(COOH)_2 = C_2H_2(COOH)_2 + HBr.$$

The hydrobromic acid produced during the reaction acts catalytically. Müller[4] obtained satisfactory results on the assumption that the velocity is inversely proportional to the amount of hydrobromic acid present.

If the catalytic acid originally employed is different from that liberated during the reaction, the corresponding equations will be—

$$\frac{dx}{dt} = (k_1a + k_2x)(b - x)\,; \quad . \quad . \quad . \quad . \quad (6)$$

where k_1 is the velocity constant for the hydrolysis of methyl acetate by acetic acid, and k_2 the velocity constant for the added acid. By integration—

$$\frac{1}{t}\log\frac{b(k_1a + k_2x)}{k_1a(b - x)} = k_1a + k_2b. \quad . \quad . \quad . \quad (7)$$

As an example take Ostwald's measurements of the rate of hydrolysis of methyl acetate in the presence of *b* units of oxyisobutyric acid $C_3H_6OH.COOH$ ($a = 1308$; $b = 1370$).

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[1] W. Ostwald, *Journ. prakt. Chem.* [2], **28**. 449, 1883.

[2] Owing to the great length of time occupied by the experiments, there is a continual loss of methyl acetate, and this accounts for the gradual decrease of the numbers in the third column.

[3] W. Hentschel, *Ber.*, **23**. 2394, 1890.

[4] W. Müller, *Zeit. phys. Chem.*, **41**. 483, 1902.

Now write $k_2/k_1a = K$, and equation (7) may be written in the form—

$$\frac{1}{t}\log\frac{b}{b-x} + \log(1 + Kx) = k_1a(1 + Kb),$$

which contains two unknowns, K and k_1. By substituting experimental values of a, b, t, and of x from two sets of experiments, approximate numerical values for K and k_1 may be readily calculated. In this way it was found that $k_1a = 0·2221$, and $K = 0·000211$.

t	x	constant $= k_1a + k_2b$
1440	106	0·307
5760	380	0·303
11520	686	0·307
12960	732	0·299
17280	882	0·303

It is interesting to notice that if strong acids like hydrochloric or sulphuric acids be employed as the original catalyst, and if a feeble acid like acetic acid be liberated during the hydrolysis, k_2 will be vanishingly small in comparison with k_1. In that case the above expression reduces to the simple form—

$$\frac{1}{t}\log\frac{b}{b-x} = k_1a = \text{constant}. \quad . \quad . \quad . \quad (8)$$

For the hydrolysis of methyl acetate in the presence of hydrochloric acid, Ostwald obtained the following numbers ($a = 1338$, $b = 1370$):—

t	x	k_1a = constant
60	202	11·33
180	523	11·37
300	759	11·40
480	1006	11·62
900	1264	11·51

Müller's experiments on the decomposition of bromosuccinic acid in the presence of strong mineral acids are in harmony with this conclusion.[1]

Autocatalysis also occurs in the bimolecular reaction between ethyl alcohol and various acids, say, hydrochloric acid.[2]

V. Henry[3] has verified expression (7) for the inversion of cane sugar by invertase, which is much more rapid than it should be if the reaction were a case of simple catalysis. The rate of inversion is decreased by the presence of one of the decomposition products, levulose. Here $a = 1$, and bk_2/k_1 is put equal to ϵ. Hence, from (7)—

$$\frac{1}{t}\log\frac{b+\epsilon x}{b-x} = k_1(1+\epsilon), \quad . \quad . \quad . \quad . \quad (9)$$

an equation containing two constants. For a series of corresponding values of t, b, and x, it was found that $\epsilon = 1{\cdot}02$, $1{\cdot}04$, $0{\cdot}98$, $1{\cdot}05$, $1{\cdot}01$, *i.e.* very nearly unity; therefore—

$$\frac{1}{t}\log\frac{b+x}{b-x} = 2k_1. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This expression gave results in harmony with actual measurements.

Autocatalysis has also been studied in connection with the transformation of γ-oxyvaleric acid into γ-oxyvalerolactone,[4] and of (1 : 2) oxymethylbenzoic acid into phthalide[5] from the point of view of the ionic theory. The rate of transformation was supposed to be proportional to the concentration of the ions derived from the acid, as well as to the active

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[1] *L.c.* See W. Kistiakowsky, *Zeit. phys. Chem.*, **27**. 250, 1898.

[2] A. Villiers, *Ann. Chim. Phys.*, [5], **21**. 72, 1880; J. C. Cain, *Zeit. phys. Chem.*, **12**. 751, 1898; O. Knoblauch, *ib.*, **22**. 268, 1897; H. Goldschmidt, *ib.*, **31**. 343, 1899; *Ber.*, **28**. 3218, 1895; **29**. 2208, 1896; T. S. Price, *Journ. Chem. Soc.*, **79**. 303, 1901. For the decomposition of nitrosulphonic acids, M. Wagner, *Zeit. phys. Chem.*, **19**. 668, 1896; **20**. 334, 1896.

[3] V. Henry, *Zeit. phys. Chem.*, **39**. 194, 1902.

[4] P. Henry, *Zeit. phys. Chem.*, **10**. 96, 1892.

[5] U. Collan, *Zeit. phys. Chem.*, **10**. 130, 1892.

masses of the substances taking part in the reaction. Consequently—

$$\frac{dx}{dt} = k\alpha(a - x)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If $a - x$ denotes the concentration of the acid, and α that fraction of the acid which is split up into ions, we have by Ostwald's dilution law—

$$\frac{\alpha^2(a - x)}{1 - \alpha} = K; \ \alpha = \frac{1}{2(a - x)}(\sqrt{4K(a - x) + K^2} - K). \ (12)$$

Substituting this value of α in the preceding equation, and integrating in the usual way, we get—

$$\frac{1}{t}\left\{\frac{Q - P}{(P - K)(Q - K)} + \frac{1}{2K}\log\frac{(P + K)(Q - K)}{(P - K)(Q + K)}\right\} = k, \ (13)$$

where $\sqrt{4K(a - x) + K^2} = P$; $\sqrt{4Ka + K^2} = Q$. The value of K can be calculated from measurements of the conductivity of the acid in the usual way. Thus for γ-oxyvaleric acid, $K = 0{\cdot}0000202$. Henry applied this equation to the direct transformation of this acid into the corresponding lactone, and of γ-oxybutyric acid into its lactone; Collan applied the equation to some measurements of the rate of transformation of oxymethylbenzoic acid into phthalide both alone and in the presence of a different catalyzing acid.

Hitherto we have only discussed reactions which are accelerated by the gradual accumulation of the catalytic agent in the system. We now consider reactions in which the catalytic agent is gradually withdrawn from the system. Hence the reaction slows down at a greater rate than the simple law of mass action would lead us to suppose. This occurs during the transformation of γ-oxybutyrolactone, and of γ-oxyvalerolactone into their respective acids. With our former notation, the velocity of the reaction *without* the catalytic agent is—

$$\frac{dx_1}{dt} = k_1(b - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If y denotes the number of gram-molecules of the catalytic agent put out of action at the time t, owing to some secondary change, then $a - y$ of the catalytic agent will be present at the time t. Hence (2) assumes the form—

$$\frac{dx_2}{dt} = k_2(a - y)(b - x) ; \quad . \quad . \quad . \quad . \quad (15)$$

the resultant velocity will therefore be—

$$\frac{dx}{dt} = \{k_1 + k_2(a - y)\}(b - x) \quad . \quad . \quad . \quad (16)$$

Let us further assume that the amount of catalytic agent put out of action by combination with the products of the reaction is given by an algebraic expression containing x, which, for brevity's sake, we write $f_1(x)$,[1] then—

$$\frac{dx}{dt} = \{k_1 + k_2a - k_2f_1(x)\}(b - x). \quad . \quad . \quad (17)$$

When all the catalyst is consumed, $a - f_1(x) = 0$, and the velocity of the reaction will be given by equation (14).

If the products of the reaction slow down the main reaction, say, by a secondary action on the intermediate compound or on one of the reacting substances, then—

$$\frac{dx}{dt} = - k_3f_2(x)(b - x), \quad . \quad . \quad . \quad . \quad (18)$$

and the velocity of the whole reaction will be—

$$\frac{dx}{dt} = \{k_1 + k_2a - k_2f_1(x) - k_3f_2(x)\}(b - x).$$

For the sake of brevity put $f(x)$ in place of $k_2f_1(x) + k_3f_2(x)$, and—

$$\frac{dx}{dt} = \{k_1 + k_2a - f(x)\}(b - x), \quad . \quad . \quad (19)$$

when x is great enough to make—

$$f(x) = k_1 + k_2a ; \ \frac{dx}{dt} = 0.$$

This means that a state of **false equilibrium** will set in, and the reaction will come to a standstill before the available

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[1] In many cases $f_1(x) = x$, and (17) assumes the typical form for a reaction of the second order.

energy has run down to its lowest potential. In other words, the reaction will not proceed so far in the presence of the catalytic agent as it does in its absence. Such a state of "false equilibrium" occurs during the hydrolysis of salicine by emulsin.[1]

§ 91. The Kinetic Theory of Chemical Reactions.

Just as in the reversible reaction, $A_1 \rightleftharpoons A_2$, the system is said to be in equilibrium when the amount of A_1 transformed into A_2 in a given time is the same as the amount of A_2 converted into A_1 in the same time, so it has been supposed that the atoms which compose the molecules of a gas are continually "changing partners" in such a way that in, say, a mass of hydrogen chloride, "each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing partners with the other atoms of hydrogen."[2] In the same way with a mass of chlorine or of hydrogen, the molecules are continually splitting up into atoms, and the atoms so produced are continually recombining. A state of equilibrium is reached when the number of molecules decomposed into atoms in a given time is equal to the number of molecules reformed from the atoms in the same time.

With this hypothesis, and the kinetic theory of gases, J. J. Thomson[3] has calculated the conditions of equilibrium for the dissociation of gases like iodine, phosphorus pentachloride, methyl oxide hydrochloride, the combination of hydrogen and

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[1] A. A. Noyes and W. J. Hall, *Zeit. phys. Chem.*, **18**. 240, 1895; G. Tammann, *Zeit. physiol. Chem.*, **16**. 285, 1892; **18**. 428, 1895.

[2] A. W. Williamson, *B. A. Reports*, ii., 65, 1850; *Phil. Mag.* [3], **37**. 350, 1850; *Journ. Chem. Soc.*, **4**. 229, 1852; *Alembic Club Reprints*, No. 16; *Liebig's Ann.*, **77**. 37, 1851; "Atomic Motion," *Chem. News*, **56**. 5, 1887; L. Pfaundler, *Pogg. Ann.*, **131**. 353, 1867; *Jubelband*, 182, 1874; R. Clausius, *Pogg. Ann.*, **100**. 353, 1857; **101**. 338, 1857.

[3] J. J. Thomson, *Phil. Mag.* [5], **18**. 233, 1884; see also same journal, **23**. 379, 472, 1887; H. F. Morley and M. M. P. Muir's *Watts' Dict. of Chem.*, London, **2**. 434, 1889.

iodine, of hydrogen and oxygen, etc., which are in harmony with the published experiments upon these reactions.

How, then, can we explain why mixtures of gases like hydrogen and chlorine may remain in contact an indefinite time under ordinary atmospheric conditions without evincing any sign of chemical combination? The system, we well know, is not in a true state of equilibrium, there is a "struggle for existence" among the molecules hydrogen, chlorine, and hydrogen chloride. The result of the contest ought to be the same whether we start with a mixture of hydrogen chloride, or with equal volumes of hydrogen and chlorine. We must therefore either assume that the mixture of hydrogen and chlorine is continually approaching a state of true equilibrium, in other words, that the hydrogen and chlorine are slowly combining at ordinary temperatures, or else we must assume that the conditions necessary for the decomposition and reformation of the molecules are wanting. This latter state of "partial equilibrium" is postulated by J. J. Thomson.

The theory of false equilibrium superadded to Williamson's hypothesis presents formidable difficulties. We may still retain the kinetic theory and imagine that when two molecules collide or approach within the sphere of each other's attraction the mechanical shock of the collision might disintegrate the molecules into atoms, which enter into combination when they meet;[1] or we may assume that there is a momentary juxtaposition of the two colliding molecules, say, of hydrogen and chlorine, which results in the hydrogen and chlorine atoms going off in combination as two molecules of hydrogen chloride. It is conceivable that these alternative hypotheses might be distinguished by measurements of the rate of combination of these gases. If union takes place between the *atoms*, the velocity of the reaction will be proportional to the pressure of the gas, for obviously we shall have—

$$\frac{dx}{dt} = k_1 p_1^{\frac{1}{2}} p_2^{\frac{1}{2}}; \text{ or, } \frac{dx}{dt} = k_1 p,$$

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[1] W. M. Hicks, *Phil. Mag.* [5], **3**. 401, 1877; **4**. 174, 1877; for the vortex ring theory, see J. J. Thomson, *l.c.*; also *A Treatise on the Motion of Vortex Rings*, London, 1883.

if $p_1 = p_2$. If union takes place during the collision of *molecules* the velocity of the reaction will be proportional to the square of the pressure of the gas. Thus—

$$\frac{dx}{dt} = k_2 p_1 p_2 ; \text{ or, } \frac{dx}{dt} = k_2 p^2,$$

if $p_1 = p_2$. No suitable measurements are available. It is indeed found that the rate of combination of the gases is nearly always proportional to the pressure of the gas, but this may mean that union only takes place on the walls of the containing vessel.

T. Ewan[1] found that the rate of oxidation of aldehyde was represented by the equation—

$$\frac{dx}{dt} = k p_1 p_2^{\frac{1}{2}},$$

where p_1 denotes the partial pressure of the aldehyde, and p_2 that of the oxygen. Hence it was inferred that the reaction takes place between aldehyde molecules and oxygen atoms.

Since a great number of chemical reactions appear to take place only in the presence of a third substance, many chemists seem to think that a third substance—catalytic agent—must always be present before chemical action can take place. This hypothesis involves the assumption that man cannot prepare pure substances, because reactions are known which do take place between substances purified by the most refined methods.

§ 92. The Water Problem.

Up to the middle of the seventeenth century combustion was explained by the aid of Plato's assumption that all combustible substances, in common, contained a principle which enabled them to burn. Geber (*c.* 1529) thought that this inflammable principle must be sulphur—*Ubi ignis et calor, ibi sulphur*. J. J. Becher (*c.* 1669) pointed out that many com-

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[1] T. Ewan, *Zeit. phys. Chem.*, **16.** 315, 1895 : *Phil. Mag.* [5], **38.** 512, 1894.

bustible substances were known which did not contain sulphur, and he was led to postulate the existence of another principle which he termed "*terra pingua*"—inflammable earth. Becher's inflammable earth became Stahl's phlogiston. G. E. Stahl (*c.* 1697) taught that in the act of combustion the phlogiston, previously united with the combustible body, was set at liberty. "Oxidation" was said to be equivalent to the escape of phlogiston, "reduction" to the absorption of phlogiston.

The phlogiston theory did not give a reasonable account of the increase in weight acquired by a substance during the act of combustion. A. L. Lavoisier (1775) then showed that the increase in weight of a body during combustion was equal to the weight of oxygen consumed, and he was led to the belief that a combustible substance is one which has the power of uniting directly with the oxygen gas. The combustion of carbon monoxide, for instance, was said to be explained by the equation—

$$2CO + O_2 = 2CO_2,$$

in which two molecules of carbon monoxide unite with one molecule of oxygen.[1] This view was generally accepted until H. B. Dixon's announcement to the B. A. meeting at Swansea[2] in 1880 that the union only takes place in the presence of water vapour. The reaction thus necessitates an entirely different explanation. Water plays an important part in the reaction. It is easy to invent explanations of the mechanism of particular reactions, but it is not easy to show what *rôle* water plays in the process.

The influence of water on chemical change was suspected quite a century before Dixon's discovery. T. O. Bergmann,[3] for example, in 1780, noticed that "regulus of manganese" only retained its bright appearance in dry air, and that phosphorus oxidizes more slowly in dry than in moist air.

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[1] Using current symbols. For full historical details, see some text-book on Historical Chemistry.

[2] H. B. Dixon, *B. A. Reports*, 593, 1880; *Chem. News*, **46**. 151, 1882.

[3] T. O. Bergmann's *Opuscula physica et chimica*, Upsala, **2**. 206, 1780; *Physical and Chemical Essays*, London, **2**. 206, 1784.

Six years later, the illustrious Scheele[1] showed that pyrophorus will not oxidize in air dried by quicklime, and hence he inferred that "the water usually present in the atmosphere is the chief cause of the burning of pyrophorus."

Mrs. Fulhame[2] appears to have been the first to give a clear statement of the influence of water on chemical transformation. In a remarkable "Essay on Combustion" she proves "beyond the power of contradiction" that water is necessary for the reduction of the metallic oxides and for the oxidation of the metals. She found, for example, that gold chloride cannot be reduced by hydrogen gas if moisture be excluded. The effect of moisture is not to promote the reduction by breaking up the salt into minute particles, nor by condensing the gas and so bringing the hydrogen into closer contact with the metallic oxide; for if either of these views were correct, ethereal and alcoholic solutions of the metallic salt should prove as effective as water. This is not the case. Neither ether nor alcohol promote the reduction if water be absent. Mrs. Fulhame believed that the reaction—oxidation or reduction—took place in two stages. In the first place, carbon monoxide decomposed the water, forming carbon dioxide and liberating hydrogen; thus—

$$CO + H_2O = CO_2 + H_2 \text{ (nascent)};$$

finally, the nascent hydrogen united directly with the free oxygen, reforming water—

$$2H_2 \text{ (nascent)} + O_2 = 2H_2O.$$

Consequently, the oxygen which unites with the carbon monoxide to form carbon dioxide is not obtained directly from the oxygen gas mixed with the carbon monoxide, but from the water. "Water," said this gifted woman, "is essential for the oxidation, and it is always decomposed in the process

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[1] C. W. Scheele, *Crell's Ann.*, **1**. 483, 1786; *Experiments on Fire and Air*, London, 112, 1780; *Sämmtliche physische und chemische Werke*, Berlin, **1**. 183, 1793; see J. Priestley, *On Air*, **6**. 443, 1786.

[2] Mrs. Fulhame, *An Essay on Combustion*, London, 1794; see *Annales de Chimie*, **26**. 58, 1798; J. W. Mellor, *Journ. Phys. Chem.*, **7**. 557, 1903.

. . . carbon monoxide unites with the oxygen of the water, while the hydrogen of the latter seizes the oxygen of the air."[1]

§ 93. Dixon's Theory of Combustion.

This is precisely the theory suggested independently by H. B. Dixon (1880).[2] The water vapour acts the part of a "carrier of oxygen," as indicated in the last two equations. M. Traube[3] discredited Dixon's view of the process, and tried to show that steam would not react with carbon monoxide, and imagined that "the reaction would be impossible, because the reverse action would take place under the same conditions." Traube also noticed that a trace of hydrogen peroxide was always found on the sides of a moistened jar held over a lighted jet of carbon monoxide; hence he was led to suppose that the mechanism of the reaction was that indicated by the following equations:—

$$CO + H_2O + O_2 = CO_2 + H_2O_2; \text{ and } CO + H_2O_2 = CO_2 + H_2O$$

or, as Mendeléeff[4] puts it—

$$CO + H_2O = CO_2 + H_2 \text{ (nascent)}; \; H_2 + O_2 = H_2O_2;$$
$$H_2O_2 + CO = CO_2 + H_2O.$$

In a later paper,[5] Dixon refuted Traube's arguments; he demonstrated that carbon monoxide is oxidized by steam with the liberation of hydrogen,[6] and that hydrogen unites with oxygen to reform steam. These results make it probable that

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[1] For bibliographical lists of the published observations on the influence of moisture on chemical change, see H. B. Baker, *Journ. Chem. Soc.*, **65**. 611, 1894; J. W. Mellor and E. J. Russell, *ib.*, **81**. 1272, 1902.

[2] H. B. Dixon, *Phil. Trans.*, **175**. 630, 1884; *B. A. Reports*, 593, 1880; *The Gas World*, **40**. 1052, 1904.

[3] M. Traube, *Ber.*, **15**. 666, 1882.

[4] D. Mendeléeff's *The Principles of Chemistry*, London, **1**. 207, 305, 391, 1891.

[5] H. B. Dixon, *Journ. Chem. Soc.*, **49**. 95, 1886.

[6] W. R. Grove, *Phil. Trans.*, **138**. 617, 1847; H. L. Buff and A. W. Hofmann, *Liebig's Ann.*, **113**. 129, 1860; *Journ. Chem. Soc.*, **12**. 273, 1860; A. Naumann and C. Pistor, *Ber.*, **18**. 2894, 1885; L. Maquenne, *Compt. Rend.*, **96**. 63, 1882.

steam does really undergo "a cycle of chemical reactions, whereby it gives up oxygen to carbon monoxide and returns to its original state." Dixon also proved that other gases like hydrogen sulphide, ethylene, formic acid, ammonia, pentane, and hydrogen chloride, will determine the explosion of carbon monoxide and oxygen; while sulphur dioxide, carbon disulphide, carbon dioxide, nitrogen monoxide, cyanogen, and carbon tetrachloride, are quite ineffective. Hence he inferred that *not only steam, but all substances which will form steam under the conditions of the experiment, are capable of determining the explosion.*

Dixon showed that hydrogen peroxide is produced when the flame of carbon monoxide and cyanogen burns in air, although in the latter case "the presence of water is not necessary for combustion." Hence the hydrogen peroxide found by Traube is a by-product arising from a secondary reaction, and one might just as reasonably conclude that the carbon monoxide is oxidized by the alternate formation and decomposition of formic acid—

$$CO + H_2O = H.COOH; \ 2H.COOH + O_2 = 2CO_2 + 2H_2O,$$

because formic acid is produced when induction sparks are passed through moist carbon monoxide gas.

Remsen, Keiser, and Jones [1] have also shown that carbon monoxide has no apparent action on hydrogen peroxide at ordinary temperatures or at the temperature of the decomposition of hydrogen peroxide. On the other hand, carbon dioxide is produced when a mixture of air and carbon monoxide is passed over moist phosphorus. The oxidation is indeed effected by ozone, but not by hydrogen peroxide.[2]

§ 94. Slow Combustion, or Autoxidation.

A study of the slower oxidations which take place at ordinary temperatures has not only shown that the process of

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[1] I. Remsen, *Amer. Chem. Journ.*, **4**. 50, 1882; I. Remsen and E. H. Keiser, *ib.*, **4**. 50, 454, 1882; W. A. Jones, *ib.*, **30**. 40, 1903.

[2] C. E. Waters, *Amer. Chem. Journ.*, **30**. 50, 1903.

oxidation is complicated by the presence of water, but the question has been raised whether just so much oxygen takes part in the reaction as combines with the substance undergoing oxidation. In other words, if a certain quantity of oxygen be required for the formation of an oxide, is another portion of the oxygen, which does not unite with the oxidizing substance, sympathetically affected by the process?

Schönbein[1] first noticed that when certain substances are oxidized spontaneously by atmospheric oxygen, one part of the oxygen present combines directly with the substance undergoing oxidation, while another part of the oxygen may be converted into ozone, hydrogen peroxide, or simultaneously oxidize some other substance. For example—

(i.) Ozone is formed during the oxidation of phosphorus.

(ii.) Hydrogen peroxide is formed during the oxidation of zinc, lead, etc.

(iii.) Indigo blue is simultaneously oxidized to colourless isatin when benzaldehyde or turpentine is oxidized; sodium arsenite is likewise oxidized in the presence of oxidizing sodium sulphite etc.

That part of the oxygen which unites with the substance undergoing oxidation is sometimes called **bound oxygen,** while the oxygen which is consumed in the formation of ozone, hydrogen peroxide, is called **active oxygen,** and the oxygen is said to be "activated" or "rendered active" during the process of oxidation. Engler calls the substance undergoing oxidation the "autoxidizer," and the substance which unites simultaneously with the active oxygen, the "acceptor."

Schönbein still further demonstrated that just so much oxygen is rendered active as is consumed by the oxidizing substance; or, in all slow oxidations the same amount of oxygen is required for the oxidation of the substance as is consumed in the formation of hydrogen peroxide from water, ozone from oxygen, etc. The hydrogen peroxide is generally decomposed into water and oxygen, so that an exact proof of

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[1] C. F. Schönbein, *Journ. prakt. Chem.*, **75**. 99, 1858; **77**. 137, 1859; **78**. 69, 1859; **79**. 87, 1860; **93**. 25, 1864; **105**. 226, 1868.

the above deduction can only be obtained under favourable conditions.

Thus, one gram of lead was mixed with 200 grams of mercury and shaken with 300 c.c. of standard sulphuric acid (1 : 55) in the presence of oxygen. The lead sulphate formed was filtered off, and the amount of sulphate still remaining was determined by titration of an aliquot part of the filtrate. This furnished data for the calculation of the amount of bound oxygen consumed in the formation of lead monoxide (*i.e.* $PbSO_4$), for we may symbolize the reactions by the equations—

$$Pb + H_2O + O_2 = PbO + H_2O_2 ; \; PbO + H_2SO_4 = PbSO_4 + H_2O.$$

The amount of hydrogen peroxide was determined by titration of an aliquot part of the filtered solution with potassium permanganate. The following will illustrate the results obtained—

Bound oxygen : Active oxygen = 1·46 : 1·39 mgrm.

Schönbein's law has also been verified by van't Hoff[1] for the oxidation of phosphorus; by Jorissen[2] and by Engler and his co-workers[3] for the autoxidation of aldehyde, triethylphosphine, turpentine, amylene, hexylene, styrol, cyclopentane, diallyl ether, benzylallyl ether, dimethyl fulvene, methylethyl fulvene, sodium sulphite; by Manchot[4] for the autoxidation of hydroanthraquinone, chrysene, phenanthrene, hydrazotoazol, hydrazomethyltriazol; ammoniacal cuprous oxide, etc.[5]

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[1] J. H. van't Hoff, *Zeit. phys. Chem.*, **16.** 411, 1895.

[2] W. P. Jorissen, *Zeit. phys. Chem.*, **23.** 667, 1897; *Ber.*, **29.** 1951, 1896; **30.** 1051, 1897.

[3] C. Engler and W. Wild, *Ber.*, **30.** 1669, 1897; **33.** 1109, 1900; C. Engler and J. Weissberg, *Ber.*, **31.** 3046, 3055, 1898; **33.** 1090, 1097, 1900; *Kritische Studien über die Autoxydationsvorgänge*, Braunschweig, 1903; C. Engler and W. Frankenstein, *Ber.*, **34.** 2933, 1901; C. Engler, *Ber.*, **30.** 2358, 1897; **36.** 2642, 1903; with T. Ginsberg, *ib.*, **36.** 2645, 1903.

[4] W. Manchot, *Liebig's Ann.*, **314.** 177, 1899; *Habilitatschrift*, Göttingen 1899; with J. Thiele, *Liebig's Ann.*, **303.** 49, 1898; with J. Herzog, *ib.*, **316.** 318, 331, 1901 (indigo white, and hydrazobenzene); *Ber.*, **33.** 1742, 1900; *Zeit. anorg. Chem.*, **27.** 297, 1901; with F. Glaser, *ib.*, **27.** 420, 1901 (iron oxide and cobalt cyanide); with O. Wilhelms, *Ber.*, **34.** 2479, 1901; E. Bamberger, *ib.*, **33.** 113, 1900 (acrylhydroxylamine).

[5] J Meyer, *Ber.*, **35.** 3952, 1902. For bibliography, see G. Bodländer's

§ 95. The Brodie-Schönbein Theory.

To explain the phenomenon of autoxidation, Schönbein has adopted a suggestion favoured by Brodie,[1] and assumed that during the process ordinary oxygen is split up into two parts, which take up electric charges of opposite sign. The part which had a positive charge was called *antozone*—symbol: $\oplus$; and the other part, with a negative charge, was called *ozone*—symbol: $\ominus$. Hence two varieties of active oxygen are postulated—ozone and antozone, and—

$$\overbrace{\text{Ordinary oxygen}}^{\text{Inactive oxygen}} = \overbrace{\text{antozone} + \text{ozone}}^{\text{Active oxygen}}$$

The substance undergoing oxidation was supposed to have a preference for oxygen carrying one kind of charge, while the remaining variety of active oxygen was consumed in a secondary reaction, such as the formation of ozone and hydrogen peroxide from water, isatin from indigo, etc. Oxides produced by antozone were called **antozonides**, while those derived from ozone were called **ozonides**. For example—

Antozonides:—Hydrogen peroxide, peroxides of potassium, sodium, barium, calcium, and strontium.

Ozonides:—Ozone, peroxides of manganese, lead, nickel, bismuth, and silver; permanganates, chromates, vanadates, and hypochlorites.

According to this theory—

Water + antozone = hydrogen peroxide;
Manganese monoxide + ozone = manganese peroxide.

A mixture of the two last-named peroxides give ordinary oxygen, owing to the neutralization of the positive oxygen of

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Ueber langsame Verbrennung (Ahrens') *Sammlung*, **3**. 385, 1899; E. Baur, *Zeit. angew Chem.*, **15**. 53, 1902.

[1] B. C. Brodie, *Phil. Trans.*, **141**. 759, 1850; **151**. 837, 1862; **152**. 407, 1863; *Proc. Roy. Soc.*, **9**. 361, 1858; **11**. 442, 1861; *Journ. Chem. Soc.*, **4**. 194, 1852; **7**. 304, 1855; **16**. 316, 1863; **17**. 266, 281, 1864.

the one with the negative oxygen of the other. The activity of the so-called "nascent" oxygen is not really due to the nascent state of the oxygen, but to the fact that the oxygen has been liberated in one of its two active states, ⊕ or ⊖. In support of this, Schönbein points out that although both the ⊕ from hydrogen peroxide and the ⊖ from potassium permanganate will decolourize a solution of indigo blue, yet the oxygen, as it is liberated from a mixture of hydrogen peroxide and potassium permanganate, has no action on the colouring matter, because the two forms of active oxygen neutralize one another. It must, however, be mentioned that there is no direct experimental evidence of the existence of antozone,[1] and Hoppe-Seyler[2] says there is no difference, materially or electrically, between bound and active oxygen. Hoppe-Seyler assumes that one atom of oxygen unites with the substance undergoing oxidation, while the other atom of oxygen is liberated in the nascent state. But this view does not account for the fact that water is more readily oxidized than oxalic acid, carbon monoxide, or indigo blue, when these substances are shaken up with oxygen in presence of metallic zinc or lead.

In order to test whether dry nascent oxygen is more chemically active than ordinary oxygen towards carbon monoxide, Dixon[3] exploded dry mixtures of carbon monoxide and of chlorine peroxide, with the result that the greater part of the carbon monoxide remained unburnt as when ordinary dry oxygen was employed. The chief chemical reaction was the ordinary explosive decomposition of chlorine peroxide—

$$2ClO_2 = Cl_2 + 2O_2.$$

Similar results were obtained with chlorine monoxide. At the moment of explosion, when the oxygen is in the atomic

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[1] G. Meissner, *Untersuchung über den Sauerstoff*, Hanover, 20, 218, 1863; *Neue Untersuchungen über den Elektrischen Sauerstoff*, 1869; C. Engler and O. Nasse, *Liebig's Ann.*, **154**. 215, 1870; C. Engler and W. Wild, *Ber.*, **29**. 1929, 1896; **33**. 1109, 1900.

[2] E. Hoppe-Seyler, *Zeit. physiol. Chem.*, **2**. 22, 1878.

[3] H. B. Dixon and E. J. Russell, *Journ. Chem. Soc.*, **71**. 605, 1897; E. J. Russell, *ib.*, **77**. 361, 1900.

condition and in excess, it only oxidized a part of the carbon monoxide.[1]

Schönbein does not appear to have regarded his positive and negative varieties of oxygen in the modern sense of atoms with positive and negative charges, but rather from the Berzelian point of view, in which hydrogen and the metals are said to be electropositive because they appear during electrolysis at the negative pole, and chlorine and bromine are said to be electronegative because they appear at the positive pole.

Various modifications of Schönbein's hypothesis have been suggested by Clausius, van't Hoff, etc. R. Clausius [2] supposed that the oxygen molecule was resolved on contact with, say, "phosphorus, into two atoms of opposite electrical states, one of which combines with the phosphorus and the other is removed from the sphere of action." Von Helmholtz and Richarz [3] show that the condensation of aqueous vapour into "clouds" is not only caused by the ionization of the gas, but also by the purely chemical processes of slow and rapid combustion, and they propose a "jet of aqueous vapour as a test for chemical action." The condensation of the vapour is either caused by free atoms of oxygen -O- or by unsaturated molecules -O-O-. Neither ozone, nitrous acid, nor hydrogen peroxide exercise any action. Elster and Geitel [4] noticed that moist air in which

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[1] G. Pickel, *Zeit. anorg. Chem.*, **38**. 307, 1904 (ozone will oxidize hydrogen below 100°); C. E. Waters, *Amer. Chem. Journ.*, **30**. 50, 1903 (ozone will oxidize carbon monoxide); W. A. Bone and J. Drugman, *Proc. Chem. Soc.*, **20**. 127, 1904 (ozone will oxidize ethane to ethyl alcohol); L'abbé Mailfert, *Compt. Rend.*, **94**. 860, 1882.

[2] R. Clausius, *Pogg. Ann.*, **103**. 644, 1858; **121**. 250, 1864.

[3] H. L. F. von Helmholtz, *Journ. Chem. Soc.*, **39**. 277, 1881; *Nature*, **23**. 535, 1881; *Vorträge und Reden*, **2**. 275, 1884; R. von. Helmholtz, *Wied. Ann.*, **32**. 1, 1887; with F. Richarz, **40**. 161, 1890; F. Richarz, *Ber.*, **21**. 1678, 1888; J. J. Thomson, *Phil. Mag.* [5], **36**. 313, 1893.

[4] J. Elster and H. Geitel, *Wied. Ann.*, **37**. 324, 1889; **39**. 326, 1890; *Phys. Zeit.*, **16**. 457, 1903; W. Giese, *Wied. Ann.*, **17**. 1, 236, 519, 1882; **38**. 404, 1889; A. Schuster, *Proc. Roy. Soc.*, **37**. 317, 1884; F. Richarz, *Wied. Ann.*, **52**. 389, 1894; J. J. Thomson's *Applications of Dynamics to Physics and Chemistry*, London, 291, 1888; *Phil. Mag.* [5], **29**. 359, 1890; *Conduction of Electricity through Gases*, Cambridge, 155, 1903; G. C.

phosphorus is oxidizing will conduct electricity, while ozone itself is a non-conductor. The conductivity is supposed to be caused by the splitting of the oxygen molecule into ions during the process of oxidation, and "the presence of ozone may be regarded as evidence of the previous dissociation of the oxygen molecule."[1] Schmidt, however, maintains that the conductivity observed by Elster and Geitel is really due to the "convection of electricity by cloud-forming conducting oxidation products," and not to the ionization of oxygen.

T. Ewan,[2] working under the direction of van't Hoff, found that the rate of oxidation of phosphorus in dry oxygen is proportional to the square root of the pressure (p) of the oxygen, and to the rate of evaporation of the phosphorus at the temperature of the experiment. The latter, according to Stefan, is equivalent to a constant multiplied by log $P/(P-p_1)$, where P denotes the total pressure of the oxygen and phosphorus vapour, and p_1 the partial pressure of the phosphorus vapour only. Hence—

$$-\frac{dp}{dt} = k\sqrt{p}\log\frac{P}{P-p_1},$$

where k is constant. Now, the concentration of the oxygen molecules will be proportional to the pressure of the gas, while the concentration of the oxygen atoms will be proportional to the square root of the pressure. Hence, if the atoms of oxygen alone take part in the oxidation, the rate of oxidation must be proportional to the square root of the pressure. From this,

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Schmidt, *Drude's Ann.*, **10**. 704, 1903; *Phys. Zeit.*, **4**. 111, 1903; A. Gockel, *ib.*, **4**. 604, 1903.

[1] The rise of potential which accompanies the formation of ozone must be accompanied by a fall of potential elsewhere. By *assuming* that the chemical energy of one system is not available for another totally different reaction, W. Ostwald (*Zeit. phys. Chem.*, **34**. 248, 1900) is able to show that the energy degraded during the oxidation of phosphorus cannot be utilized for producing ozone. To get over the difficulty, Ostwald assumed that a peroxide of phosphorus is first formed, which subsequently breaks up into ozone and a stable oxide. See § 99.

[2] T. Ewan, *Zeit. phys. Chem.*, **16**. 315, 1895; *Phil. Mag.* [5], **38**. 512, 1894.

van't Hoff[1] concludes that "the dissociation of the oxygen molecule is not a consequence of the oxidation, but antecedent to it," as suggested by Loew[2] in 1870. Oxygen atoms are supposed to exist normally in the gas, so that we are really dealing with the equilibrium—

$$O_2 \rightleftharpoons 2O\,;$$

and if the atoms have charges of opposite sign we have—

$$O_2 \rightleftharpoons O^+ + O^-.$$

The phosphorus "prefers" ions with one kind of charge, while the remaining ions enter into secondary reactions, namely, the formation of ozone, decolorization of indigo, etc. This view is obviously Schönbein's hypothesis in another guise. Too much appears to have been made of the rate of oxidation of the phosphorus, for Russell has shown that the regularity found by Ewan only applies to a limited range of pressures.

When phosphorus is oxidized in darkness in the presence of a solution of indigo, the luminosity, which is a sign that phosphorus is undergoing oxidation, gradually disappears; if the contents of the vessel be now shaken up, the luminosity reappears. Hence something which retards the further oxidation is formed, and this product is destroyed by shaking up with indigo solution. The alternate appearance and disappearance of the luminosity may be produced again and again. At the same time the blue colour of the indigo solution gradually disappears, showing that the primary product of the oxidation of phosphorus is absorbed by the indigo solution.

From this experiment, van't Hoff thinks that the primary product of the action cannot be ozone, because the presence of ozone would accelerate the oxidation.[3] Something which retards the oxidation must be present. Merely shaking up the water, without the indigo, will not remove the primary product of the oxidation. Van't Hoff suggests that this product is an

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[1] J. H. van't Hoff, *Zeit. phys. Chem.*, **16**. 411, 1895; E. J. Russell, *Journ. Chem. Soc.*, **83**. 1263, 1903.

[2] O. Loew, *Zeit. für Chemie*, **6**. 65, 1870; H. Fudakowsky, *Ber.*, **6**. 108, 1873.

[3] J. Chappuis, *Bull. Soc. Chim.* [2], **35**. 419, 1881.

excess of positive or negative oxygen ions. The white fumes formed during the oxidation of the phosphorus are supposed to be clouds of condensed steam induced by the presence of charged ions, since it is well known that charged ions serve as nuclei for the condensation of steam.

Whatever may be the product which prevents oxidation, it gradually disappears when the flask is left alone, and the luminosity, in consequence, reappears in a few hours; again oxidation ceases, to begin anew on standing a few hours. This explains the "periodic phosphorescence" noticed by Joubert[1] in 1874.

§ 96. Traube's Theory.

Moritz Traube,[2] as we have seen, takes quite a different view of the process. He does not believe that the oxygen molecule is split up into true atoms possessing different properties, but suggests the alternative process, that the oxygen molecule, as a whole, combines directly with the substance undergoing oxidation. If hydrogen, for example, be undergoing oxidation, hydrogen peroxide, not water, is the primary product. The oxygen used in the autoxidation is derived from the hydrogen peroxide. Hydrogen peroxide is not a product of the oxidation of water, but is an intermediate stage of the oxidation.[3]

On the other hand, Schönbein's "antozonides" are, in general, the only oxidizing agents which form hydrogen peroxide in the presence of free oxygen and water. But the antozonides are far more feeble oxidizing agents than ozonides like permanganates and chromates, which do not oxidize water. Traube thinks that the explanation lies in the assumption that

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[1] J. Joubert, *Thése sur la Phosphorescence du Phosphore*, Paris, 1874.

[2] M. Traube, *Ber.*, **15**. 663, 2325, 2854, 1882; **16**. 123, 1883; **17**. 1062, 295 ref., 1884; **18**. 1887, 1894, 1885; **19**. 1111, 1886; **20**. 2, 3345, 1887; **22**. 1496, 3057, 1889; **26**. 1471, 1893; *Gesammelte Abhandlungen*, Berlin, 1899.

[3] F. Haber, *Zeit. phys. Chem.*, **34**. 513, 1900; **35**. 609, 1900; with F. Bran, *ib.*, **35**. 80, 1900.

hydrogen peroxide is not produced by the oxidation of water, but by the reduction of free oxygen. In support of this hypothesis, Traube points out that hydrogen peroxide is always produced when strong reducing agents act on gaseous oxygen, but never by the action of oxidizing agents upon hydrogen or water. The formation of hydrogen peroxide has been observed during the combustion of illuminating gas, alcohol, ether, carbon disulphide, etc. Hydrogen peroxide also appears during electrolysis at the cathode or the pole where hydrogen is evolved, never at the anode.[1] It is therefore suggested again that hydrogen peroxide is formed by the direct union of free hydrogen and oxygen—

$$H_2 + O_2 = H_2O_2.$$

If this view be correct, it follows that the oxidation of carbon monoxide in the presence of platinum proceeds according to the equation—

$$\boxed{CO + O}H_2 + O_2 = CO_2 + H_2O_2\,;$$

similarly, when the metals zinc, lead, or copper are oxidized in the presence of water (p. 306), we have—

$$\boxed{Zn + O}H_2 + O_2 = ZnO + H_2O_2.$$

This is said to be followed by the reactions—

$$ZnO + H_2O = Zn(OH)_2\,;\; Zn + H_2O_2 = Zn(OH)_2.$$[2]

Since one molecule of hydrogen peroxide is formed for every atom of zinc or lead oxidized, Traube thinks that the hydrogen peroxide is not an accidental side product of the slow oxidation of the metal, but that it is the chief primary product.

Traube also infers that hydrogen peroxide is the primary product of the oxidation when hydrogen burns in the air; if

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[1] F. Richarz, *Wied. Ann.*, **24**. 183, 1885; *Verh. d. physik. Ges.*, Berlin, 116, 1886.

[2] According to B. B. Kurilow (*Journ. Russ. Phys. Chem. Ges.*, **22**. 180, 1900; *Compt. Rend.*, **137**. 618, 1903), zinc peroxide is formed by the action of $Zn(OH)_2$ upon H_2O_2.

so, it is easy to see why the presence of water is necessary for the action.

Traube thinks that the oxygen in hydrogen peroxide is associated with the hydrogen as a whole molecule, and not split up, as commonly supposed, so as to form two hydroxyl groups (HO-OH), just as in oxyhæmaglobin the oxygen is supposed to be united with the hæmaglobin in whole molecules.[1]

Oxides in which the oxygen enters as whole molecules are called **holoxides**, to distinguish them from the usual peroxides. The former are sometimes called "true," the latter "false" peroxides. Traube's holoxides are Schönbein's antozonides; Traube's peroxides are Schönbein's ozonides.

The feeble oxidizing powers of the holoxides are supposed to be due to their liberating molecular, not atomic, oxygen. This theory of the constitution of hydrogen peroxide also explains why this compound is a reducing agent, reducing, as it does, the higher oxides of manganese and lead to simpler oxides, and the oxides of silver, gold, etc., to the metallic state—

$$Ag_2\boxed{O + H_2}O_2 = O_2 + 2Ag + H_2O.$$

More recent investigations by W. Spring[2] and by Brühl appear to lend support to Traube's view of the constitution of hydrogen peroxide, but the question is not by any means settled.[3]

§ 97. Bach's Theory.

A. Bach's[4] study of the process of oxidation has led him to the belief that the substance undergoing oxidation *itself*

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[1] F. C. Donders, *Pflüger's Archiv.*, **5**. 20, 1872; G. Hüfner, *Zeit. physiol. Chem.*, **10**. 218, 1886; **12**. 568, 1888; **13**. 285, 1889; E. du Bois-Reymond's *Archiv. Physiol.*, 1, 1890; 130, 1894; 39, 1900; *ib.*, *Suppl.*, 187, 1901.

[2] W. Spring, *Zeit. anorg. Chem.*, **8**. 424, 1895; J. W. Brühl, *Ber.*, **28**. 2847, 1895; **33**. 1709, 1900; see E. Bose, *Zeit. phys. Chem.*, **39**. 1, 1901.

[3] S. Tanater, *Ber.*, **33**. 205, 1900; **36**. 1893, 1903.

[4] A. Bach, *Compt. Rend.*, **124**. 2, 951, 1897; *Moniteur Scientifique* [4], **11**. ii., 479, 1897; see also R. Ihle, *Zeit. phys. Chem.*, **22**. 114, 1897;

unites with the oxygen to form a *peroxide.* Manchot[1] also has expressed the opinion that "in every process of oxidation there is first formed a *primary oxide*, which in general has the character of a peroxide." Traube, as we have just seen, refers the presence of hydrogen peroxide to the combination of the substance undergoing oxidation with the oxygen of the water, and the subsequent union of the hydrogen of the water with free oxygen to reform water. Bach, on the other hand, assumes that the free oxygen unites directly with the substance undergoing oxidation to form a holoxide, and that the latter interacts with water to form hydrogen peroxide.[2] "The transformation of passive into active oxygen is effected by the preliminary formation of peroxides. . . . Active oxygen is not oxygen in the state of free atoms, but it is oxygen which is easily liberated from the holoxide."

In the combustion of carbon monoxide it is supposed that percarbonic acid[3] is first formed, and that this subsequently decomposes into carbon dioxide and water. In support of this hypothesis, Bach points out that when a flame of carbon dioxide is made to impinge upon water containing a little potassium hydroxide and cobalt chloride, a precipitate is obtained identical with that produced by potassium percarbonate with a solution of cobalt chloride. The test, however, loses its decisive character when we remember that Durrant[4] has shown that a similar precipitate is obtained with potassium hydrogen carbonate in the presence of hydrogen peroxide and cobalt chloride.

Bach's theory has been more successfully applied to other reactions. But let us make a digression.

A. Villiers, *Compt. Rend.*, **124**. 1349, 1897; A. Livache, *ib.*, **124**. 1520, 1897; G. Bertrand, *ib.*, **124**. 1032, 1355, 1897.

[1] W. Manchot, *Liebig's Ann.*, **325**. 95, 1902; C. C. Benson, *Journ. Phys. Chem.*, **7**. 356, 1903.

[2] A. M. Glover and G. F. Richmond, *Amer. Chem. Journ.*, **29**. 179, 1903.

[3] E. J. Constam and A. von Hansen, *Zeit. Elektrochem.*, **3**. 137, 445, 1896–7.

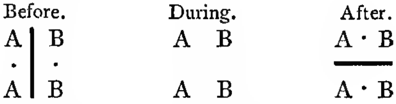
[4] R. G. Durrant, *Chem. News*, **73**. 228, 1896; **75**. 43, 1897.

§ 98. The Association Theory of Chemical Reactions.

Suppose that one molecule of a substance A interacts with one molecule of a substance B to form two molecules of a substance AB, that is to say, in chemical symbols—

$$A_2 + B_2 = 2AB.$$

In order that A and B may interact, the two molecules A_2 and B_2 must come within the sphere of one another's activity.[1] The forces which hold the molecules intact will then be modified. We assume, with Bergmann, that if the attraction of A towards B is greater than the attraction of A towards A, or of B towards B, then the molecules of A and B will be broken up to reform two molecules of AB. "Residual affinities," says Armstrong,[2] "are in all probability the forces by which the various components are led to associate and to take up compatible positions." Kekulé[3] represents this sequence of changes by the following symbols :—



Three distinct operations are thus involved.

Stage 1.—The formation of a new molecule by the direct addition of A_2 and B_2, such as occurs in the formation of ammonium chloride from hydrogen chloride and ammonia, or of phosphorus pentachloride from phosphorus trichloride and chlorine.

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[1] This seems to be true with a great many reactions which are commonly supposed to take place between ions, for sometimes chemical action precedes ionization, as indicated on p. 290.

[2] H. E. Armstrong, *Encyc. Brit.*, **26**. 740, 1902. The idea is, I believe, due to J. Mercer (*B.A. Reports*, 32, 1842), and was accepted by L. Playfair (*Phil. Mag.* [3], **31**. 192, 1847). J. W. Walker, *Journ. Chem. Soc.*, **85**. 1082, 1904, also accepts the idea of residual affinities or "potential valencies." See S. Young's *Stoichiometry* for particulars of this phase of the subject ; O. J. Lodge, *Technics*, **2**. 217, 1904.

[3] A. Kekulé, *Liebig's Ann.*, **106**. 129, 1858.

Stage 2.—Intramolecular change, such as the conversion of ammonium cyanate into urea—

$$NH_4.CNO = (NH_2)_2CO.$$

Stage 3.—The breaking up of the complex molecule into simpler substances, usually called the "products of the reaction." For example, by heating the addition compound which zinc chloride forms with ethyl alcohol, we get both ethene and ethyl ether.

The nature of the compounds formed in each operation—

$$\text{Additive compound} \rightarrow \text{intermediate compound} \rightarrow \text{final product}$$

depends on the conditions of temperature and pressure under which the reacting substances are brought into contact. In some cases the intermediate compounds are well defined, possibly owing to their stability under the conditions of the experiment. Such is the intermediate compound formed when zinc chloride is brought in contact with ethyl alcohol in the reaction—

$$ZnCl_2 + C_2H_5OH = ZnCl_2C_2H_6O = ZnCl_2.H_2O + C_2H_4.$$

At other times the intermediate stage is over so quickly that the formation of such a compound is quite a mental process. A and B are then said to enter into direct combination without the formation of intermediate stages. See § 91, p. 298.

If a chemical process takes place with the formation of a consecutive series of intermediate compounds, that compound which involves the smallest loss of free energy will be formed first, then the one which involves the next smallest loss of free energy will be produced second, etc.—**Ostwald's law of successive reactions.**[1] Whether the intermediate stages can be demonstrated or not, depends upon the stability of the intermediate compound under the conditions of the experiment. When a hot solution of potassium hydroxide is added to a hot solution of copper sulphate, dark brown copper oxide

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[1] W. Ostwald's *Lehrbuch*, Leipzig, 2. i., 514, 1893; *Grundlinen der anorganische Chemie*, Leipzig, 215, 1900; A. Findlay's trans., 207, 1902; *Zeit. phys. Chem.*, 22. 306, 1897.

is precipitated at once; but if the experiment be conducted at ordinary temperatures, the intermediate compound $Cu(OH)_2$ is precipitated. This compound is supposed to be instantaneously decomposed in the first experiment, and to be relatively stable in the second experiment. Hence, the reaction—

$$CuSO_4 + 2KOH = K_2SO_4 + CuO + H_2O$$

is said to take place in two stages—

$$CuSO_4 \rightarrow Cu(OH)_2 \rightarrow CuO.$$

The resolution of the intermediate compounds into simpler elements is greatly modified by the conditions under which the experiment is performed. A reaction might take place in steps with the formation of one intermediate compound under one set of conditions, and another intermediate compound under another set of conditions. In the same way the intermediate compound may give rise to different products, according to the conditions under which the reaction takes place. For example, ammonium nitrate, which is produced when ammonia and nitric acid are brought into contact, decomposes on heating in various ways.

At a low temperature we have simple dissociation—

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3; \quad . \quad . \quad . \quad I.$$

by carefully raising the temperature, nitrogen monoxide and steam are produced—

$$NH_4NO_3 = 2H_2O + N_2O; \quad . \quad . \quad . \quad II.$$

while if the ammonium nitrate is heated rapidly, the following reaction goes on with explosive violence[1]—

$$2NH_4NO_3 = 4H_2O + 2N_2 + O_2; \quad . \quad . \quad III.$$

traces of other nitrogen oxides, nitrogen dioxide, and tetroxide, are also produced during the decomposition of ammonium nitrate by heat.

I. and III. are extreme cases. It is probable that under no conditions would it be possible to get one reaction to go

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[1] M. Berthelot, *Sur la Force des Matèrieres Explosivs d'après la Thermochemie*, Paris, 1. 20, 1883.

with the exclusion of the others. At high temperatures III. represents the main reaction, I. and II. are side reactions; at moderate temperatures II. is the main reaction, I. and III. side reactions.

Bone and his co-workers[1] have studied the oxidation of methane at about 500°, and they find that the final products of the reaction "consist simply of carbon monoxide, carbon dioxide, and steam . . . with the transient formation of formaldehyde as an intermediate product. In one experiment, for instance, 13 per cent., and in another as much as 22 per cent., of the methane burnt was accounted for as formaldehyde removed from the sphere of the reaction before it had been further oxidized."

Does this interesting result prove that the "transient intermediate product" formaldehyde is necessarily the course of the main reaction when methane burns in air? Bone suggests two equations to account for his results—

(i.) The direct interaction of one molecule of methane with a molecule of oxygen—

$$CH_4 + O_2 = H.CO.H + H_2O;$$

(ii.) The formation and rapid decomposition of an hypothetical $CH_2(OH)_2$—

$$CH_4 + O_2 = CH_2(OH)_2 = H.CO.H + H_2O.$$

As indicated above, two or more molecules of methane and oxygen must be within the sphere of one another's attraction before interaction can take place. All we can say is that the molecular complex so formed decomposes at about 500° with the production of formaldehyde. Under other conditions the complex molecule $(CH_4)_nO_m$ might decompose directly into other products, say, for example, carbon dioxide and hydrogen. Thus Bone himself[2] represents the reaction which

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[1] W. A. Bone and R. V. Wheeler, *Journ. Chem. Soc.*, **81**. 535, 1902; **83**. 1074, 1903; W. A. Bone and W. E. Stockings, *ib.*, **85**. 693, 1904 (oxidation of ethane); see also Armstrong, references on p. 274.

[2] B. Lean and W. A. Bone, *Journ. Chem. Soc.*, **61**. 873, 1892; W. A. Bone and J. C. Cain, *ib.*, **71**. 26, 1897.

takes place when equal volumes of ethylene and oxygen are fired by the electric spark by the equation—

$$C_2H_4 + O_2 = 2CO + 2H_2,$$

although methane and oxygen furnish no free hydrogen at about 500°. We have no more right to say that formaldehyde is *always* produced as a transient intermediate compound in the oxidation of methane than we have to say that nitrogen monoxide is always produced as a transient intermediate compound in the decomposition of ammonium nitrate.

Similarly, the oxidation of sulphur dioxide in the "lead chamber" might take place in several different ways, one of which is known to involve the formation of "chamber crystals"—nitrosulphonic acid. But whether the main reaction goes, under normal conditions, *viâ* nitrosulphonic acid,[1] has not been definitely established. This reaction is most interesting historically. It was one of the first catalytic processes to be explained by the intermediate compound theory.[2]

H. B. Dixon[3] long ago pointed out that the isolation of a product which might act as an intermediate compound does not demonstrate that the main reaction goes in that way. The assumed intermediate compound may be, in reality, a by-product of the reaction. W. Ostwald[4] thinks that it is also necessary to show that "the intermediate reactions actually take place more rapidly than the direct reaction under the given conditions . . . because, if a reaction goes more slowly *viâ* the intermediate product than in the direct path, it will take the latter, and the possibility of intermediate products has no influence on the process." Hence, adds Ostwald, "I see no

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[1] E. Péligot, *Ann. Chim. Phys.* [3], **12**. 266, 1844; G. Lunge, *Zeit. angew. Chem.*, **16**. 145, 581, 1902; E. Haagn, *ib.*, **16**. 583, 1902; M. Trautz, *Zeit. phys. Chem.*, **47**. 513, 1904.

[2] J. B. Désormes and Clément, *Annales de Chemie*, **59**. 329, 1806; *Nicholson's Journ.*, **17**. 41, 1807.

[3] H. B. Dixon, *Journ. Chem. Soc.*, **49**. 94, 1886.

[4] W. Ostwald, *Ueber Katalyse*, Leipzig, 21, 1902; *Grundriss der allgem. Chem.*, Leipzig, 517, 1899; *Zeit. Elektrochem.*, **7**. 995, 1901; *Nature*, **65**. 522, 1902.

possibility of explaining retarding catalytic influences by the assumption of intermediate products."[1]

Ostwald here refers to the explanations of catalytic reactions as the result of an association of the molecules of A and B with a third substance. These explanations fall naturally into two classes—

Class 1.—The three molecules come simultaneously within the sphere of one another's attraction before interaction takes place; or any two might come into contact and remain associated together until the third molecule comes within the sphere of their attraction. The whole system then breaks up into simpler molecules.

Why does the rearrangement of the molecules of A and B go on better if they are associated with a third substance? In answer, Bunsen and Roscoe[2] say, "all chemists are agreed that the phenomena of affinity depend upon the specific attractions which exist between the particles of bodies of different natures. These attractions must necessarily exist when the particles are prevented from following them to form a chemical compound. Let us suppose the particles A and B so brought together that a chemical attraction is exerted between them; and let us suppose a third body, C, brought into the sphere of attraction of the other two; this third body will then also exert an attraction upon A and B. The attraction between A and B will not remain the same as it originally was, but it will be the resultant of all the forces originating in A, B, and C. It is thus easily seen that the attractions which tend either to effect or support a chemical combination between two bodies, must be altered in the sphere of action of a third body; and that the presence of a third body may therefore, according to circumstances, effect or prevent the formation of a chemical compound."

The action of sulphur dioxide upon chlorine is an interesting example. Union takes place very slowly, if at all, in

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[1] F. Riedel, *Zeit. angew. Chem.*, **16**. 493, 1903; G. Bredig and F. Haber, *ib.*, **16**. 557, 1903; A. Skrabel, *ib.*, **16**. 621, 1903.

[2] R. Bunsen and H. E. Roscoe, *Phil. Trans.*, **146**. 381, 1857.

darkness, even when the liquefied gases are mixed together. In the presence of camphor, sulphuryl chloride is formed very quickly. Camphor alone has no action on chlorine, but with sulphur dioxide it forms a liquid which rapidly absorbs chlorine. The final product is a solution of camphor in sulphuryl chloride.[1]

Class 2.—Two or more molecules associate and break up into other molecules (or atoms), which react with a third molecule to produce the final products of the reaction. The association may take the form of a collision. The colliding molecules may thus be broken up into atoms in the so-called nascent condition. When these atoms come in contact with suitable molecules the final stage of the reaction sets in.

Illustrations of catalyses in which the catalyst unites with one or more of the reacting substances are very common in organic chemistry. The use of aluminium chloride in the Friedel-Crafts reaction is a well-known type.[2] For others the reader should consult Lassar-Cohn's *Arbeitsmethoden für organisch-chemische Laboratorien*,[3] and also Conroy's *Catalysis and its Applications*.[4]

Armstrong's theory of chemical reaction is a modification of the first hypothesis; Bach's, Traube's, and Dixon's are modifications of the second.

This sketch will show how futile have been our efforts to establish a satisfactory theory of catalysis, and of chemical change in general. Perhaps we are doing wrong to search for a general theory. At any rate, up to the present time, we have found that the hypotheses which have been set up to

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[1] H. Schulze, *Journ. prakt. Chem.* [2], **24.** 168, 1881.

[2] C. Friedel and J. M. Crafts, *Bull. Soc. Chim.* [2], **29.** 2, 1878; O. Ruff, *Ber.*, **34.** 1749, 1901; B. D. Steele, *Journ. Chem. Soc.*, **83.** 1470, 1903; A. Slator, *ib.*, **83.** 729, 1903; L. Meyer, *Ber.*, **20.** 3058, 1887 (oxygen carriers); E. Bamberger, *ib.*, **35.** 4293, 1902 (oxidation ethylamine); with R. Seligman, *ib.*, **35.** 4299, 1902 (oxidation methylamine); and a number of investigations already mentioned.

[3] Hamburg, 1904; A. Smith's trans., *A Manual of Organic Chemistry*, London, 1895.

[4] J. T. Conroy, *Journ. Soc. Chem. Ind.*, **21.** 302, 1902.

explain one set of facts break down completely when extended to other sets; and, so far as our knowledge goes, the phenomena admit of many interpretations. We plead, therefore, with Lord Rayleigh, not for the quest of new reactions, but for a closer investigation of the "old" ones.

It may indeed be questioned whether a reaction will always go that path by which the final products of the reaction are produced in the shortest possible time. Let me illustrate by the following analogy. *AOC* (Fig. 16) is an inclined plane. If a ball be placed at *A*, it will obviously "prefer" to roll down the steeper path *AB* than along *AC*. But when the ball reaches *O*, its velocity will slacken down as it rolls slowly from *O* to *C*. It thus appears as if the ball prefers to travel the roundabout path *AOC* than along the direct path *AC*, in spite of the fact that the course along *AOC* occupies more time.

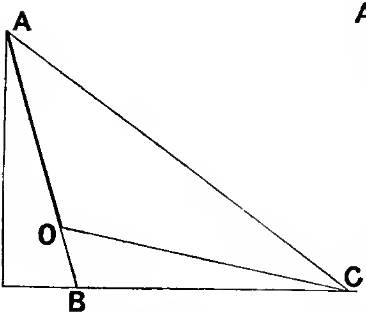

FIG. 16.

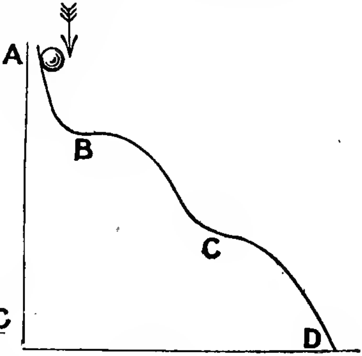

FIG. 17.

Whether the intermediate products are transitory or not depends, as we have seen, on the conditions of the experiment. The action of potassium hydroxide upon chlorine may be represented by a ball rolling down the curve *ABCD*, "Liveing's switchback"[1] (Fig. 17). The ball will be in the

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[1] G. D. Liveing's *Chemical Equilibrium*, Cambridge, 35, 1885; W. Ostwald's *Lehrbuch*, Leipzig, 2. i., 515, 1893.

most stable state of equilibrium possible when it reaches *D*. So will the mixture of potassium hydroxide and chlorine be in its most stable state of equilibrium when the potassium has all been converted into chloride. If the velocity of the ball be not too great, it will come to rest when it reaches the ledge *B*, so, if the temperature is low enough, say 0°, the system $Cl_2.2KOH$ will be converted into $KCl + KOCl + H_2O$; if the ball be rolling a little more quickly, it might pass *B* and come to rest at *C*; so, if the temperature of the KOH and the Cl_2 mixture be about 100°, we shall have potassium chlorate but no potassium hypochlorite remaining at the end of the reaction.

This analogy is misleading if it suggests that KOCl is the *sole* intermediate stage in the formation of $KClO_3$, because potassium chlorate may not only be a product of the decomposition of potassium hypochlorite, but it may also be formed by other more or less direct reactions, just as ethyl chloride is formed when alcohol is treated with hydrogen chloride in the presence of zinc chloride,[1] not only by the direct action of hydrogen chloride upon the alcohol, but also by the union of nascent ethylene (p. 328) with the hydrogen chloride. The final stage may thus be reached by a number of *different* side reactions,[2] and *among a number of possible side reactions those will predominate which progress, under the conditions of the experiment, with the greatest initial velocity.* Tafel[3] has shown that the formation of methyl chloride is too slow to serve as the intermediate link in the esterification of methyl alcohol by the fatty acids—formic, acetic, etc.—in the presence of the catalyst hydrochloric acid, as is postulated by the so-called theory of "indirect esterification."[4]

The function of the catalytic agent is to direct the transformation along one path in preference to another. This comes out in an interesting way during the formation of

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[1] C. E. Groves, *Journ. Chem. Soc.*, **25**. 636, 1874.

[2] Any one of which might be followed by a series of consecutive reactions.

[3] J. Tafel, *Zeit. phys. Chem.*, **19**. 592, 1896.

[4] E. Petersen, *Zeit. phys. Chem.*, **16**. 385, 1895; **20**. 331, 1896.

pentacetyl-*d*-glucose from *d*-glucose and acetic anhydride. If zinc chloride be the catalytic agent, the transformation goes *viâ* the α-isomer; while if dry sodium acetate be employed, the β-isomer is produced. In either case equilibrium occurs when the system contains 88 per cent. of α-pentacetyl-*d*-glucose, and 12 per cent. of β-pentacetyl-*d*-glucose.[1] Slator,[2] too, has noticed that chlorine and benzene react in the presence of iodine chloride with the formation of both addition and substitution products; but if tin tetrachloride, or ferric chloride are employed as catalytic agents, only the substitution products are formed; in light, without catalytic agent, only the addition product is formed. The velocity of the "main" reaction between hydrogen iodide and hydrogen peroxide agrees with the expression—

$$-\frac{dC}{dt} = k_1C_1C_2,$$

where C_1 and C_2 denote the respective concentrations of the hydrogen peroxide and hydrogen iodide; if C_3 of molybdic acid or an iron salt be present, the predominating reaction[3] is in harmony with the equation—

$$-\frac{dC}{dt} = k_1(C_1 + k_2C_3)C_2.$$

The function of aluminium chloride in the preparation of sulphur monochloride from sulphur and sulphuryl chloride is to facilitate the decomposition of the latter ("dissociation catalysis"),[4] so that the reaction goes *viâ* the path—

$$AlCl_3 + SO_2Cl_2 \rightleftharpoons AlCl_3.SO_2 + Cl_2;\ Cl_2 + 2S \rightleftharpoons S_2Cl_2$$
$$AlCl_3.SO_2 \rightleftharpoons AlCl_3 + SO_2.$$

If a certain resistance is to be overcome before the reaction can be started, that process which requires the least energy for

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[1] A. P. N. Franchimont, *Ber.*, **12**. 1940, 1881; A. Herzfeld, *ib.*, **13**. 265, 1882; E. Erwig and W. Königs, *ib.*, **22**. 1464, 1889; C. L. Jungius, *Koninklijke Akad. van Wetenschappen*, 779, 1904.

[2] A. Slator, *Journ. Chem. Soc.*, **83**. 729, 1903.

[3] J. Brode, *Zeit. phys. Chem.*, **37**. 290, 1901; **49**. 208, 1904.

[4] O. Ruff, *Ber.*, **34**. 1749, 3509, 1901; **35**. 4453, 1902.

its initiation will be produced in preference.[1] If the two reactions have actually started side by side, what reaction is produced in preference will depend on the relative velocities of the two reactions.

§ 99. Specific Illustrations of the Association Theory.

We may now consider a few chemical reactions which have all been "explained" by theories in agreement with the above views.

I. Oxidation of benzaldehyde.—In the oxidation of benzyl or propyl aldehyde, just as much oxygen is consumed in the oxidation as is required for the formation of benzoic acid in accord with the equation—

$$2C_6H_5.CO.H + O_2 = 2C_6H_5COOH.$$

If, however, acetic or benzoic anhydrides, or some oxidizable substance like an aqueous solution of sodium sulphindigotate, be also present, twice as much oxygen will be consumed as when these substances are absent. Two molecules of acyl[2] peroxide are formed at the same time.

Jorissen[3] assumes that one atom of oxygen unites with the aldehyde to form first the acid—C_6H_5COOH—and then the peroxide—$(C_6H_5CO)_2O_2$—with the liberation of free atomic oxygen or ozone—

$$2C_6H_5COH + 2O_2 = (C_6H_5CO)_2O_2 + H_2O + O.$$

The ozone or atomic oxygen is then supposed to attack the acid anhydride present to form a molecule of peroxide—

$$(CH_3CO)_2O + O = (CH_3CO)_2O_2;$$

or—

$$(CH_3CO)_2O + O_3 = (CH_3CO)_2O_2 + O_2.$$

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[1] See p. 414. D. Tommasi, *The Electrical Review*, **53**. 373, 1903; *Journ. Phys. Chem.*, **2**. 229, 1898.

[2] "Acyl" is a general term for any organic acid radical. Acetyl $(CH_3CO)_2O_2$ and benzoyl $(C_6H_5CO)_2O_2$ peroxides, or the mixed acetyl benzoyl $(CH_3CO)(C_6H_5CO)O_2$ peroxide, are all "acyl" peroxides.

[3] W. P. Jorissen, *Zeit. phys. Chem.*, **22**. 56, 1897; *Ber.*, **30**. 1951, 1897.

Hence two molecules of benzaldehyde produce in all two molecules of acyl peroxide. Engler and Wild[1] do not agree with Jorissen's views of the process of oxidation. They hold that the reaction takes place in two stages. *First*—

$$2C_6H_5COH + 2O_2 = (C_6H_5CO)_2O_2 + H_2O_2.$$

Second, (*a*) if the aldehyde be alone exposed to the oxygen, there will follow—

$$(C_6H_5CO)_2O_2 + H_2O_2 = 2C_6H_5COOH + O_2,$$

as recognized by Brodie in 1864;[2] or, (*b*) if acetic or benzoic anhydrides be present, the hydrogen peroxide will attack it in preference to benzoyl peroxide, so that—

$$(C_6H_5CO)_2O + H_2O_2 = (C_6H_5CO)_2O_2 + H_2O,$$

corresponding with the formation of two molecules of peroxide from two molecules of benzaldehyde.

J. U. Nef[3] assumes that "in the absence of a trace of water, benzaldehyde will not be oxidized to benzoic acid in air or in oxygen gas," and he builds up a set of equations for the oxidation of benzaldehyde in agreement with the views of Traube. Jorissen,[4] however, has shown that oxidation takes place even though the benzaldehyde and oxygen be well dried by means of phosphorus pentoxide.[5]

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[1] C. Engler and W. Wild, *Ber.*, **30**. 1669, 1897.

[2] B. C. Brodie, *Phil. Trans.*, **153**. 407, 1863.

[3] J. U. Nef, *Liebig's Ann.*, **298**. 280, 1897.

[4] W. P. Jorissen, *Maandblad voor Naturwetenschapen*, **22**. 109, 1898; C. Engler and J. Weissberg, *Ber.*, **31**. 3044, 1898.

[5] This appears to be a convenient place to point out that it would give chemists much more confidence in discussing questions on the influence of moisture in chemical reactions if investigators would state definitely that their phosphorus pentoxide had been specially purified by slow distillation over platinized asbestos or pumice, say, as indicated by W. A. Shenstone and C. B. Beck (*Journ. Chem. Soc.*, **63**. 475, 1893). Negative results with *ordinary* phosphorus pentoxide are not of much value. See, for example, S. Gutmann's error (*Liebig's Ann.*, **299**. 267, 1898) and H. B. Baker's reply (*Journ. Chem. Soc.*, **73**. 422, 1898); or K. Böttsch (*Liebig's Ann.*, **210**. 213, 1881) and H. B. Dixon (*Phil. Trans.*, **175**. 633, 1884).

When benzaldehyde is oxidized in the presence of a solution of indigo-sulphonic acid, the oxygen consumed is equally divided between the indigo sulphonic acid and the benzaldehyde. Traube has shown that, in the absence of a catalyzer, hydrogen peroxide only oxidizes an acid solution of indigo sulphonic acid "very slowly, if at all." "Hence," says Jorissen, "if hydrogen peroxide be formed in the first stage of the oxidation, the active oxygen it contains cannot decolorize the indigo-sulphonic acid in the time available." But what is against the assumption that the atoms in the newly formed molecule of hydrogen peroxide do not settle down into their normal state instantaneously, and that "nascent" hydrogen peroxide, so to speak, can really oxidize indigo-sulphonic acid? To take a particular illustration, we know that ordinary nitrous acid has no action on nitroethane, but in the presence of any reagent capable of producing nitrous acid, nitroethane is at once converted into ethylnitrolic acid.[1]

In 1889 G. Bodländer[2] assumed that an addition product is formed when benzaldehyde is exposed to oxygen gas.

$$C_6H_5COH + O_2 = C_6H_5CO.O.OH \text{ (benzoyl hydrogen peroxide).}$$

If benzaldehyde be *alone* exposed to the action of oxygen, one more molecule reacts with the hypothetical benzoyl hydrogen peroxide to form two molecules of benzoic acid.

$$C_6H_5CO.O.OH + C_6H_5COH = 2C_6H_5COOH.$$

On the other hand, if the benzaldehyde be exposed to the

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[1] See M. M. P. Muir's *Principles of Chem.*, 99, 1899. It is well enough known that hydrogen *in statu nascendi* is more chemically active than the ordinary gas. Some think the nascent hydrogen is in an atomic condition, others (D. Tommasi, *Ber.*, **12**. 1701, 1879) hold that the energy set free during the reaction is available for doing chemical work before it has run down to heat, so that the difference between nascent and ordinary hydrogen lies in the greater available energy of the former. See also T. L. Phipson, *Chem. News*, **40**. 184, 1879; D. Tommasi, *ib.*, **40**. 245, 1879; S. Kern, *ib.*, **31**. 112, 236, 1875; J. Thomsen, *Ber.*, **12**. 2030, 1879; F. Fittica's *Jahresbericht*, 187, 1879.

[2] G. Bodländer, *Ahrens' Sammulung*, **3**. 470, 1899.

action of oxygen gas in the presence of, say, benzoic anhydride, the peroxide decomposes, giving up one atom of oxygen to the anhydride—

$$C_6H_5CO.O.OH + (C_6H_5CO)_2O = (C_6H_5CO)_2O_2 + C_6H_5COOH;$$

while if a solution of indigo-sulphonic acid be present, the intermediate compound gives up an atom of oxygen to the indigo, and we may write—

$$C_6H_5CO.O.OH + \text{indigo} = C_6H_5COOH + \text{oxidized indigo}.$$

A year later, the hypothetical peroxide was actually prepared by A. Baeyer and V. Villiger,[1] and shown to form benzoic acid with benzaldehyde, as Bodländer had predicted. We must, however, bear in mind that the sensation surrounding the discovery of Bodländer's peroxide does not in any way influence the actual course of the reaction. We can only say that Bodländer's theory is a possible and rational view of the process. The final interpretation of the experimental material is still in the throes of disputation.

II. Oxidation of the metals.—Engler and Wild[2] quote many experiments in support of the view that in the oxidation of the alkali metals there is a direct combination of the metal with the oxygen molecule so as to break up only one of the bonds uniting the two oxygen atoms together, and the peroxide so formed afterwards unites with water to form hydrogen peroxide and an hydroxide of the metal. During the combustion of sodium on an aluminium plate, for example, sodium peroxide is formed. Erdmann and Köthner[3] have also shown that rubidium passes almost quantitatively into the peroxide. In the presence of water the latter is slowly converted into rubidium hydroxide and hydrogen peroxide. Similar changes have been observed during the oxidation of magnesium, lead, and copper.

III. Oxidation of triethylphosphine.—According to Engler

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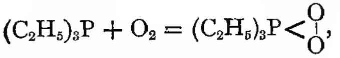
[1] A. Baeyer and V. Villiger, *Ber.*, **33**. 858, 2480, 1900.

[2] C. Engler and W. Wild, *Ber.*, **30**. 1669, 1897.

[3] H. Erdmann and P. Köthner, *Liebig's Ann.*, **294**. 66, 1896; K. Frenzel, S. Fritz, and V. Meyer, *Ber.*, **30**. 2515, 1897.

and Wild,[1] one molecule of triethylphosphine combines directly with one molecule of oxygen to form the solid triethylphosphine peroxide—



$$(C_2H_5)_3P + O_2 = (C_2H_5)_3P<\begin{matrix}O\\ |\\ O\end{matrix},$$

in accordance with the theory of Bach—

(1) If water be absent, the subsequent changes are somewhat complex. Side reactions are set up. Some of the peroxide remains unchanged; a little combines with another molecule of the triethylphosphine to form $(C_2H_5)_3PO$; but the main reaction is an intramolecular change, resulting in the formation of $(C_2H_5)_2PO.O.C_2H_5$.

(2) If water be present, the molecule of triethylphosphine first formed unites with another molecule of triethylphosphine to form $(C_2H_5)_3PO$. Hence only two molecules of triethylphosphine combine with one molecule of oxygen, and when triethylphosphine oxidizes in presence of water, only half as much oxygen is consumed as when water is absent.

(3) If indigo solution be present, one half of the oxygen molecule remains united with the triethylphosphine, and the other half is consumed in the oxidation of the indigo.

IV. Oxidation of phosphorus.—Engler and Wild[2] also state that the first product of the oxidation of phosphorus is a peroxide, which in the presence of water furnishes hydrogen peroxide. It is also supposed that under diminished pressure this peroxide can dissociate into ordinary phosphoric oxide and atomic oxygen, which with ordinary oxygen gives ozone. The phenomenon observed during the oxidation of phosphorus under diminished pressure is supposed to occur at the limits of the dissociation of phosphorus peroxide.

Van't Hoff[3] has shown that for every atom of phosphorus 0·436 to 0·60 atoms of oxygen are rendered active. If P_2O_2 be

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[1] C. Engler and W. Wild, *Ber.*, **30**. 1669, 1897; C. Engler and J. Weissberg, *Ber.*, **31**. 3055, 1898; W. P. Jorissen, *Zeit. phys. Chem.*, **22**. 34, 1897.

[2] C. Engler and W. Wild, *Ber.*, **30**. 1669, 1897.

[3] J. H. van't Hoff, *Zeit. phys. Chem.*, **16**. 413, 1895.

the peroxide first formed which decomposes into active oxygen and Besson's[1] oxide—P_2O—we should have just 0·5 atoms of oxygen activated for every atom of phosphorus oxidized, a result in close agreement with experiment. The reactions would be expressed in symbols—

$$2P + O_2 = P_2O_2;\ P_2O_2 = P_2O + O;\ O + O_2 = O_3.$$

The following equations also agree with the experimental results—

$$2P + 2O_2 = P_2O_4;\ P_2O_4 = P_2O + O_3.^{2}$$

V. Oxidations by hydrogen peroxide.—Kastle and Loevenhart[3] believe that the oxidizing actions of hydrogen peroxide are adequately explained by the assumption that the hydrogen peroxide unites with the substance undergoing oxidation to form an addition product. The hydrogen peroxide gives up its oxygen to the compound associated with it more readily than hydrogen peroxide could do alone. There is abundant evidence of the formation of addition products of hydrogen peroxide with other substances.[4] Job also ascribed the oxidizing action of cerous salts in the presence of hydrogen peroxide to the alternate formation and decomposition of cerium peroxide.

When the oxidation is effected without the aid of a catalytic agent and without the evolution of oxygen gas, it is

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[1] A. Besson, *Compt. Rend.*, **124**. 763, 1897.

[2] W. Ostwald, *Zeit. phys. Chem.*, **34**. 250, 1900.

[3] H. Kastle and A. S. Loevenhart, *Amer. Chem. Journ.*, **29**. 397, 517, 1903.

[4] E. Schöne, *Liebig's Ann.*, **192**. 257, 1878; **193**. 241, 1878; R. de Forcrand, *Compt. Rend.*, **130**. 716, 1900; M. Berthelot, *ib.*, **108**. 477, 1899; H. Moissan, *ib.*, **97**. 96, 1883; H. C. Jones and C. G. Carroll, *Amer. Chem. Journ.*, **27**. 22, 1902; *ib.*, **28**. 284, 1902; G. Petrenko, *Journ. Russ. phys. Chem. Soc.*, **34**. 391, 1902; P. Kasanezky, *ib.*, **34**. 388, 1902; W. Staedel, *Zeit. angew. Chem.*, **15**. 642, 1902; F. Wiede, *Ber.*, **31**. 516, 1898; **32**. 378, 1899; S. Tanatar, *Ber.*, **32**. 1544, 1899; *Zeit. anorg. Chem.*, **28**. 255, 1901; P. Melikoff and L. Pissarshewsky, *Ber.*, **31**. 953, 1898; R. Willstätter, *Ber.*, **36**. 1828, 1903; A. Job, *Compt. Rend.*, **134**. 1052, 1902; **136**. 45, 1903; *Ann. Chim. Phys.* [7], **20**. 205, 1900; R. Kissling, *Zeit. angew. Chem.*, **14**. 395, 1891.

supposed that there is first a direct addition of hydrogen peroxide and a subsequent decomposition into water and the highest stable oxidation product of the substance in question. The oxidation of sulphur dioxide, of ammonium thiocyanate, of phenolphthaleïn, and of formic aldehyde, are typical examples. In symbols, we should have—

$$H_2SO_3 + H_2O_2 = H_2SO_3.H_2O_2 = H_2SO_4 + H_2O;$$
$$H.CO.H + H_2O_2 = H_2COH.H_2O_2 = H.COOH + H_2O.$$

In some cases more hydrogen peroxide combines with the substance undergoing oxidation than is actually required for the oxidation to the highest stable oxide, and the latter may then act as a carrier of oxygen to another substance or decompose with the evolution of oxygen. We can thus explain Radziszewski's[1] experiments on the oxidation of the nitriles by hydrogen peroxide in alkaline solution. The action is—

$$RCN + 2H_2O_2 = R.CONH_2 + H_2O + O_2.$$

Since a little alkali is necessary for the reaction, it is probable that one of Schöne's peroxides—$H_4K_2O_6$—is first formed. This unites with the nitriles, and the product formed decomposes at once into amide, water, molecular oxygen, and K_2O_2. The latter reforms $H_4K_2O_6$ by uniting with more hydrogen peroxide. The cycle is repeated until all the nitrile is oxidized.

The action of hydrogen peroxide upon silver or silver oxide has been explained in a similar manner.[2] The theory may also be employed to explain those oxidations which cannot be effected by hydrogen peroxide alone, and yet take place readily if a catalyst be present. For example, formic, tartaric, glycollic, lactic, and other organic acids are readily oxidized in the presence of ferrous iron;[3] sugars are oxidized in the presence of ferric chloride;[4] and the oxidation of

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[1] B. Radziszewski, *Ber.*, **17.** 355, 1884.

[2] A. Baeyer and V. Villiger, *Ber.*, **34.** 749, 1901; M. Berthelot, *Ann. Chim. Phys.* [7], **11.** 223, 1897.

[3] H. J. H. Fenton and J. H. Jackson, *Journ. Chem. Soc.*, **75.** 1, 1899; H. J. H. Fenton and H. O. Jones, *ib.*, **77.** 69, 1900.

[4] O. Fischer and M. Busch, *Ber.*, **24.** 1871, 1891.

hydriodic acid by hydrogen peroxide is hastened by the presence of ferrous sulphate, molybdic acid, or tungstic acid.[1]

§ 100. Induced or Sympathetic Reactions.

While an aqueous solution of sodium arsenite does not undergo any perceptible change when shaken up with air, a solution of sodium sulphite is rapidly oxidized; and when a mixture of sodium arsenite and sodium sulphite is treated in the same manner, both salts are oxidized.[2] In agreement with Jorissen's [3] observation that as much oxygen is rendered active as is consumed in the oxidation of the sodium sulphite, we can represent the actions according to Traube's theory, by the symbols—

$$Na_2SO_3 + H_2O + O_2 = Na_2SO_4 + H_2O_2,$$

followed by—

$$Na_3AsO_3 + H_2O_2 = Na_3AsO_4 + H_2O;$$

or, according to Bach—

$$Na_2SO_3 + O_2 = Na_2SO_5,$$

followed by—

$$Na_2SO_5 + Na_3AsO_3 = Na_2SO_4 + Na_3AsO_4.$$

It has not yet been decided which of these reactions, or indeed whether others which might be suggested, represents the course of the reaction.

Although the above reaction might well have been included among the examples of "autoxidation," yet it is a convenient example to introduce a class of chemical processes in which a slow reaction between two substances, A and B, is accelerated

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[1] J. Brode, *Zeit. phys. Chem.*, **37**. 257, 1901. See also B. C. Brodie's explanation of the action of hydrogen peroxide upon potassium permanganate (*Journ. Chem. Soc.*, **17**. 281, 1864).

[2] F. Mohr's *Lehrbuch der chem. anal. Titriermethode*, Braunschweig, 271, 1855.

[3] W. P. Jorissen, *Zeit. phys. Chem.*, **23**. 667, 1897; P. Schützenberger and C. Risler, *Compt. Rend.*, **76**. 1214, 1873.

by a simultaneous rapid reaction between A and C, where A, B, and C are three different substances. Ostwald[1] calls these **coupled reactions**. We might call them "sympathetic reactions," because the reaction between A and B appears to be sympathetically accelerated by the reaction between A and C. I shall adopt Kessler's original designation,[2] "induced reactions."

Induced reactions are not confined to oxidation processes, they include chlorinations, reductions, and various organic syntheses, so that the phenomenon appears to be pretty general.

The fastest reaction is called the **primary reaction**; that which appears to be forced along or induced by contact with the primary change is called the **secondary reaction.** The substance which takes part in both reactions is called the **actor**; the substance which takes part in the primary reaction is called the **inductor**; and the substance which takes part in the secondary reaction is called the **acceptor.** In the preceding example oxygen is the actor, sodium sulphite the inductor, and sodium arsenite the acceptor.

Kessler[3] appears to have been the first to study the subject systematically, and in 1863 he compiled about three dozen examples. The following may be taken as typical cases[4]:—

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[1] W. Ostwald, *Zeit. phys. Chem.*, **34**. 248, 1900.

[2] F. Kessler, *Pogg. Ann.*, **119**. 218, 1863. To avoid confusion with Bunsen and Roscoe's prior use of the term "chemical induction" (*Pogg. Ann.*, **100**. 482, 1857) for another phenomenon, Kessler proposed the term "idiochemischen induction," which might be rendered "autochemical induction."

[3] F. Kessler, *Pogg. Ann.*, **95**. 216, 1855; **96**. 332, 1855; **113**. 142, 1861; **118**. 44, 60, 1863; **119**. 218, 1863.

[4] From the writings of J. von Liebig (*Chemische Briefe*, Heidelberg, 131, 1865), C. Wicke (*Zeit. Chem.*, **8**. 89, 1865), J. Thiele (*Liebig's Ann.*, **273**. 160, 1893), W. Manchot (*Ber.*, **34**. 2479, 1901; *Liebig's Ann.*, **325**. 93, 105, 1902), E. Schaer (*Liebig's Ann.*, **323**. 32, 1901), N. Schilow (*Zeit. phys. Chem.*, **42**. 641, 1903). See also E. A. G. Baumann (*Zeit. physiol. Chem.*, **8**. 244, 1881) on the simultaneous oxidation of carbon monoxide and hydrogen; and E. Baur (*Zeit. anorg. Chem.*, **30**. 251, 1902) on simultaneous oxidation of a cerium salt and potassium arsenite; A.

Primary reaction.	Secondary reaction.	Actor.	Inductor.	Acceptor.
$SO_2 + HBrO_3$	$HBrO_3 + As_2O_3$	$HBrO_3$	SO_2	As_2O_3
$Na_2SO_3 + O_2$	$O_2 + Na_3AsO_3$	O_2	Na_2SO_3	Na_3AsO_3
$H_2CrO_4 + As_2O_3$	$As_2O_3 + HBrO_3$	As_2O_3	H_2CrO_4	$HBrO_3$
$FeSO_4 + H_2O_2$	$H_2O_2 + HI$	H_2O_2	$FeSO_4$	HI
$As_2O_3 + KMnO_4$	$KMnO_4 + MnSO_4$	$KMnO_4$	As_2O_3	$MnSO_4$
$CrSO_4 + O_2$	$O_2 + C_2H_5OH$	O_2	$CrSO_4$	C_2H_5OH
$FeSO_4 + HClO_3$	$HClO_3$ + indigo blue	$FeSO_4$	$HClO_3$	indigo blue
$Sb_4O_6 + KMnO_4$	$KMnO_4 + HCl$	$KMnO_4$	Sb_4O_6	HCl

Another interesting example which occurs during the titration of stannous chloride with potassium permanganate, used to puzzle the older chemists. The greater the amount of water employed for a given amount of stannous chloride, the less the amount of permanganate required for the titration.[1] If air-free water be used, this phenomenon is not observed. The same amount of permanganate is required however much water is employed. It was hence inferred that the oxygen dissolved in the water, as well as the permanganate, oxidizes the stannous salt. But dissolved oxygen has no perceptible action on the stannous salt alone; it can only oxidize the stannous chloride *simultaneously* with the permanganate.

The proportion in which the actor divides itself between the inductor and the acceptor is called the **induction factor,** written I—

$$I = \frac{\text{Amount of acceptor transformed}}{\text{Amount of inductor transformed}}.$$

Skrabel, *Oesterreichische Chemiker-Ztg.* [2], **6**. 533, 1903; G. von Georgievics, *Zeit. Farb. Textilchemie,* **1**. 594, 1902; W. P. Jorissen, *Chem. Zeit.,* **1**. 1174, 1902; M. Prud'homme, *Bull. Soc. Chim.* [3], **29**. 306, 1903; R. Luther, *Zeit. Elektrochem.,* **8**. 645, 1902; *Zeit. phys. Chem.,* **34**. 488, 1902; **36**. 385, 1901; with J. K. H. Inglis, *ib.,* **43**. 203, 1903; with F. J. Brislee, *ib.,* **45**. 216, 1903; E. Müller, *Zeit. Elektrochem.,* **7**. 516, 1900–1; K. Elbs and A. W. Schönherr, *ib.,* **2**. 245, 1895; N. Zelinsky, *Journ. Russ. Phys.-chem. Gesell.,* **35**. 399, 1903.

[1] A. V. Harcourt, *B. A. Reports,* ii., 43, 1863.

Kessler did not himself suggest any explanation of induced reactions, but two tenable hypotheses might be suggested—

I. The catalytic theory.—The inductor acts as a catalytic agent in the reaction between the actor and the acceptor, but at the same time the catalytic agent (inductor) is chemically transformed by a simultaneous independent reaction. For instance, sulphurous acid may act as a catalytic agent in the reaction between bromic acid and arsenious acid, and be itself oxidized to sulphuric acid at the same time.

II. The intermediate compound theory.—Here the inductor is supposed to form an intermediate compound with either the acceptor or the actor (or both), and this then reacts with the remaining component to form the final products of the reaction. In illustration, sulphurous acid may first reduce bromic acid to bromous acid, which then oxidizes the arsenious acid—

$$\begin{aligned}
&\text{(i.)}\ HBrO_3 + SO_2 = HBrO_2 + SO_3\,;\\
&\phantom{\text{(i.)}}\ HBrO_2 + As_2O_3 = HBr + As_2O_5\,;
\end{aligned}$$

or, we might have either of the processes—

$$\begin{aligned}
&\text{(ii.)}\ HBrO_3 + SO_2 = SO_5 + HBr\,;\\
&\phantom{\text{(ii.)}}\ SO_5 + As_2O_3 = SO_3 + As_2O_5\,;\\
&\text{(iii.)}\ As_2O_3 + SO_2 = As_2O_3.SO_2\,;\\
&\phantom{\text{(iii.)}}\ As_2O_3.SO_2 + HBrO_3 = As_2O_5 + SO_3 + HBr.
\end{aligned}$$

Many other possible schemes might here be suggested.

Qualitative experiments do not give us much help in the discrimination of these hypotheses.[1] If the induction be a catalytic process, the induction factor can be made as great as we please by increasing the initial concentration of the acceptor, or decreasing the initial concentration of the inductor. Let C_1, C_2, C_3, respectively denote the concentrations of sulphurous, bromic, and of arsenious acids at the time t, and C_{10}, C_{20}, C_{30}, the corresponding concentrations at the beginning of the reaction, then, if we are dealing with an ordinary catalytic

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[1] R. Luther and N. Schilow, *Zeit. phys. Chem.*, **46.** 777, 1903.

process in which the velocity of the action is proportional to the amount of catalytic agent present at the time t—

$$-\frac{dC_3}{dt} = k_1C_1C_2C_3\,;\ -\frac{dC_1}{dt} = k_2C_1C_2.$$

By integration—

$$I = \frac{C_{30}}{C_{10}}(1 - e^{-KC_{10}}),$$

where $K = k_1/k_2$. Or, we might have—

$$-\frac{dC_3}{dt} = k_1C_1C_2C_3\,;\ -\frac{dC_1}{dt} = k_2C_1^2C_2,$$

in which case—

$$I = \frac{C_{30}}{C_{10}}.$$

The student should have no difficulty in setting up the chemical equations corresponding with these velocity equations. Other schemes furnish similar results.

With consecutive reactions, the induction factor increases asymptotically up to a limiting value as the ratio $C_{\text{acceptor}} : C_{\text{inductor}}$ increases in magnitude. This will be seen directly on plotting corresponding values of $C_{\text{acceptor}} : C_{\text{inductor}}$ with the induction factor—

when $C_{As_2O_3} : C_{SO_2} = 2{\cdot}2,\ 3{\cdot}5,\ 4{\cdot}0,\ 7{\cdot}2,\ 17{\cdot}8,\ 35{\cdot}6;$
$I = 0{\cdot}4,\ 0{\cdot}5,\ 0{\cdot}6,\ 0{\cdot}8,\ 1{\cdot}5,\ 1{\cdot}8.$

The maximum limiting value, which is generally small, can be readily calculated for any given set of chemical equations. For (i), above, it follows that the inductor—SO_2—will receive two oxygen units ($2 \times \frac{1}{2}O$), while the acceptor—As_2O_3—receives four units ($4 \times \frac{1}{2}O$). The maximum value of the induction factor is therefore = 2. If the assumed chemical equations do not furnish this induction factor, they need not be considered to represent the mechanism of the reaction. Of course quite a number of possible sets of equations might furnish the same induction factor.

If the induction takes place by the formation of intermediate compounds, the velocity equations will have to be treated as a series of consecutive reactions. Information on this subject might be obtained by varying the nature of the substances taking part in the formation of the suspected intermediate compound. It is assumed that only chemically related substances will be able to act in the required manner. In this way it will often be possible to find which of the three components—actor, inductor, acceptor—plays a specific *rôle* in the formation of the "intermediate compound."

In illustration, ferrous salts (inductor) play the most important *rôle* in the oxidation of various organic compounds. Thus:—

Actor.	Inductor.	Acceptor.
$KMnO_4$	Fe''	tartaric acid
H_2CrO_4	Fe''	potassium iodide
Persulphates	Fe''	indigo
$HBrO_4$	Fe''	arsenious acid

Manchot (*l.c.*) explains the phenomenon on the assumption that ferrous iron is oxidized to a peroxide, which oxidizes the acceptor according to the scheme—

$$\text{Actor} + Fe'' = Fe^{v} + \text{reduced actor};$$
$$Fe^{v} + \text{acceptor} = Fe''' + \text{oxidized acceptor.}$$

We have also Bach's (*l.c.*) explanation of a similar group of inductions with sulphur dioxide where it is supposed that an intermediate persulphite is formed.

When the inductor is independent of the specific nature of the acceptor and the inductor, the actor is supposed to form an intermediate stage in the reaction. Thus, in the oxidation of hydriodic acid (acceptor) by nitric acid (actor) in the presence of zinc or cadmium (inductor), we are supposed to have—

$$HNO_3 + Zn = ZnO + HNO_2; \quad 2HNO_2 + 2HI = I_2 + 2NO + H_2O.$$

In Haber's general scheme[1] for oxidizing and reducing actions, we have—

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[1] F. Haber, *Zeit. phys. Chem.*, **34**. 513, 1900; **35**. 81, 1900; *Zeit. Elektrochem.*, **7**. 441, 1901.

1. *Oxidations.*

(i.) Actor + acceptor = intermediate actor + acceptor reduced.
(ii.) Intermediate actor + inductor = reduced actor + oxidized inductor.

A specific example occurs in the oxidations induced by activated oxygen previously discussed; hydrogen peroxide is the intermediate form of the actor.

2. *Reductions.*

(i.) Actor + acceptor = intermediate actor + reduced acceptor.
(ii.) Intermediate actor + inductor = oxidized actor + reduced inductor.

Then we have inductions in which the process is independent of the specific nature of the actor, of the inductor, and of the acceptor. In this case, a complex may be formed between two components, say, between the inductor and acceptor, the actor and acceptor, or the actor and inductor.

Thus Wagner[1] explained the oxidation of ferrous iron (inductor) by permanganates (actor) in the presence of chlorides (acceptor) by the preliminary formation of a complex—ferrohydrochloric acid; many other examples have been mentioned in discussing the theories of Engler, Bach, Bodländer, etc.

Luther and Schilow (*l.c.*) propose to classify induced reactions from the results obtained by varying the nature of the three components of the system. There may be—

I. One specific component, the nature of the other components may be varied within certain limits. The specific component may be (i.) the inductor, (ii.) the actor, (iii.) the acceptor.

II. Two specific components, the nature of only one component may then be varied. This may be (i.) the inductor, (ii.) the actor, (iii.) the acceptor.

Much work remains to be done upon this subject. The examples quoted can only be regarded as so much raw material to be worked up by subsequent investigators.[2]

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[1] J. Wagner's *Maassanalytische Studien*, Leipzig, 105, 1898; *Zeit. phys. Chem.*, **28**. 33, 1899.

[2] In the phenomenon of "co-fermentation" (R. Magnus, *Zeit. physiol. Chem.*, **42**. 149, 1904) one enzyme is only able to do its own special work in the presence of another enzyme.

§ 101. Influence of Solvent on the Velocity of Chemical Reactions.

The velocity of a chemical reaction is so sensitive to external influences that many reactions have hitherto resisted all attempts to reduce them to "order." The influence of the nature of the medium in which the reacting substances are dissolved is evidently a potent factor. For example, owing to the different solubilities of salts in different solvents, reactions may go in different directions.[1] Thus in aqueous solution mercury iodide precipitates, and potassium chloride goes into solution; while in acetone, potassium chloride precipitates, and mercury iodide goes into solution.

The state of equilibrium of gases, as we have seen, is not affected by the presence of a foreign inert gas, and E. Cohen[2] has shown that the presence of neither hydrogen, nitrogen, nor carbon dioxide exercise any perceptible influence on the rate of decomposition of gaseous arsine. With solutions, on the other hand, any variation in the composition of the solvent medium may have a marked influence on the velocity of the reaction. This fact was early recognized by Berthelot and Gilles,[3] but we are indebted to Menschutkin[4] for an extended series of investigations upon this subject. The following table contains a selection of values of k in different solvents from the lists published by Menschutkin, and by Hemptinne and Bekaert.[5] The second column refers to the action of ethylamine on ethyl iodide, and the third column to the action of ethylamine on ethyl bromide:—

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[1] N. Menschutkin, *Zeit. phys. Chem.*, **34**. 157, 1900; P. Rohland, *Zeit. anorg. Chem.*, **18**. 322, 1898.

[2] E. Cohen, *Zeit. phys. Chem.*, **25**. 481, 1898.

[3] M. Berthelot and L. Péan de St. Gilles, *Ann. Chim. Phys.* [3], **66**. 90, 1862; F. Lengfeld, *Amer. Chem. Journ.*, **11**. 40, 1889; W. Ostwald, *Journ. prakt. Chem.* [2], **28**. 449, 1883.

[4] N. Menschutkin, *Ber.*, **15**. 1818, 1882; *Zeit. phys. Chem.*, **1**. 611, 1887; **5**. 589, 1890; **6**. 41, 1890.

[5] A. von Hemptinne and A. Bekaert, *Zeit. phys. Chem.*, **28**. 225, 1899.

Solvent.	Formation of $N(C_2H_5)_4I$.	Formation of $N(C_2H_5)_4Br$.	Dielectric constant (15° to 20°).
Benzyl alcohol ...	0·29925	0·008294	10·6
Acetone	0·13655	0·002400	21·8
Methyl alcohol ...	0·11610	0·002500	32·5
Ethyl alcohol ...	0·08235	0·001970	21·7
Chlorobenzene ...	0·05197	0·000843	—
Benzene	0·01314	0·000228	2·6
Xylene	0·00646	0·000103	2·6

In spite of many coincidences, it is not found feasible to refer the differences in the velocities to the ionization powers of the different solvents, for the differences in the velocities are often greater than the differences in the dissociation powers of the same solvents. Thus, the rate of transformation of ammonium cyanate into urea is thirty times as fast in ethyl alcohol as it is in water,[1] and yet the dissociating power of water is about four times as great as ethyl alcohol.[2]

In view of the close agreement between the dielectric constant and the ionizing power of the solvent, naturally the attempt has been made to refer changes in the velocity of the reaction to the dielectric constant of the medium. In many cases the velocity is greatest in media which possess the highest dielectric constant, as shown in the preceding table. It has also been observed that the velocity in mixtures of different solvents is in many cases in agreement with the mean value calculated from the velocities in the separate components.[3] Larger deviations occur with many mixtures—for instance, ethyl alcohol and benzene—which also possess a greater dielectric constant than that calculated from its components.[4]

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[1] J. Walker and S. A. Kay, *Journ. Chem. Soc.*, **71**. 489, 1897.

[2] H. C. Jones, *Zeit. phys. Chem.*, **31**. 114, 1899.

[3] A. von Hemptinne and A. Bekaert, *Zeit. phys. Chem.*, **28**. 225, 1899; A. von Hemptinne, *ib.*, **31**. 35, 1899; I. Kablukoff and A. Zacconi, *Ber.*, **25**. 499, 1892; E. Cohen, *Zeit. phys. Chem.*, **28**. 145, 1899; **37**. 69, 1901; A. J. Wakeman, *ib.*, **11**. 49, 1893; W. C. Kistiakowsky, *ib.*, **27**. 250, 1898.

[4] J. C. Philip, *Zeit. phys. Chem.*, **24**. 18, 1897.

The influence of the medium differs from simple catalytic action in that the effects are not due to the presence of small quantities of the catalytic agent, and the state of equilibrium of the reacting system is different in different solvents. Van't Hoff[1] has set up a theory of the action which is of great importance. The disturbing effects of the medium may be divided into two parts—

1. *A catalytic action* affecting the two opposing actions of a reversible reaction in the same way, and having no influence on the final state of equilibrium.

2. *A specific action* dependent upon the relation between the solvent and each of the reacting substances. Van't Hoff has shown how the disturbing effects on the state of equilibrium may be eliminated.

It is easy to see that the conditions of equilibrium for the two reversible reactions—

$$n_1A_1 \rightleftharpoons n_2A_2\text{; and } n_1B_1 \rightleftharpoons n_2B_2,$$

may be written—

$$k_1C_{A_1}^{n_1} = k_2C_{A_2}^{n_2}\text{; or, } n_1 \log C_{A_1} - n_2 \log C_{A_2} = \text{constant, say, } K_a;$$

$$k_1'C_{B_1}^{n_1} = k'C_{B_2}^{n_2}\text{; or, } n_1 \log C_{B_1} - n_2 \log C_{B_2} = \text{constant, say, } K_b;$$

or, more simply—

$$\Sigma n \log C_A = K_a;\ \Sigma n \log C_B = K_b. \quad . \quad . \quad (1)$$

If a substance is in the same molecular state in two different solvents, the partition coefficient tells us that there is a fixed ratio between the concentrations of the substance in each solvent, and it is further found that for slightly soluble substances this ratio is proportional to the solubility of the substance in each solvent. Hence, if C_a, C_b, and S_a, S_b, respectively denote the concentration and solubility of the substance in each solvent, A and B, we have—

$$C_aS_b = C_bS_a. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[1] J. H. van't Hoff's *Vorlesungen über Chemie*, Braunschweig, **1**. 218, 1898; R. A. Lehfeldt's trans., **1**. 221, 1899.

Subtracting equations (1) and substituting equations (2) in the result, we get—

$$K_a - K_b = \Sigma n \log \frac{C_A}{C_B} = \Sigma n \log \frac{S_a}{S_b}. \quad . \quad . \quad (3)$$

$$\therefore K_a - \Sigma n \log S_a = K_b - \Sigma n \log S_b = K, \quad . \quad (4)$$

which means that K is the same whatever solvent we use. Again, it follows that—

$$\Sigma n \log \frac{C}{S} = K, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which means that if the concentration of the reacting substances be expressed in terms of the concentration of a saturated solution, the equilibrium constant K will be independent of the solvent. And, if we choose the concentration of a saturated solution as the unit of concentration, the velocity of a chemical reaction, say—

$$COS + H_2O \text{ (in excess)} = CO_2 + H_2S,$$

will be written—

$$-\frac{dC}{dt} = k'\frac{C}{S}, \text{ instead of } -\frac{dC}{dt} = kC,$$

where C denotes the concentration defined in the ordinary way, and S the amount of the reacting substance which stands in equilibrium in the different solutions.

$$\therefore k' = kS,$$

where k' denoted the amount of reacting substance which is transformed in unit volume of the different solvents in unit time when the dissolved salt is distributed between the different solutions in the proportions required for equilibrium. The value of k' can be calculated from the velocity constants and the partition coefficient or solubility of the reacting substances in the different solvents.

G. Buchböck has determined velocity coefficients[1] for the decomposition of carbonyl sulphide in an excess of an aqueous isohydric solution of various salts, and also determined the coefficients of absorption of carbonyl sulphide in the same

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[1] G. Buchböck, *Zeit. phys. Chem.*, **23**. 123, 1897; **34**. 229, 1900.

solutions. The results agree fairly well with the above theory, provided we confine our attention to particular groups of salts. This will be evident from the fifth column of the following table:—

Added substance.	Isohydric solution contains grm., eq. per litre.	$k \times 10^6$	Absorption coefficient S.	Velocity in saturated solution $k \times S \times 10^6$	Viscosity η.	$k \times S \times \eta \times 10^6$.
KI	1·143	571	0·0174	9·94	0·929	9·23
KNO_3	1·355	668	0·0165	11·02	0·978	10·78
KCl	1·151	632	0·0156	9·86	0·997	9·83
HBr	0·968	371	0·0218	8·09	1·028	8·31
HCl	1·000	391	0·0209	8·17	1·062	8·68
$NaNO_3$	1·317	542	0·0156	8·45	1·093	9·23
NaCl	1·119	534	0·0148	7·90	1·105	8·73
LiCl	1·141	436	0·0164	7·15	1·157	8·28
H_2SO_4	1·908	415	0·0180	7·47	1·191	8·90
$BaCl_2$	1·507	503	0·0136	6·84	1·200	8·21
$SrCl_2$	1·459	476	0·0141	6·71	1·225	8·21
$CaCl_2$	1·401	452	0·0146	6·60	1·226	8·09
$MgCl_2$	1·358	422	0·0153	6·46	1·307	8·44
HCOOH	2·073	501	0·0219	10·97	1·062	11·64
CH_3COOH	2·069	479	0·0243	11·64	1·249	14·53
$CH_2ClCOOH$	2·245	488	0·0231	11·27	1·390	15·66
CCl_3COOH	1·117	403	0·0236	9·51	1·462	13·90
$CHCl_2COOH$	1·860	414	0·0255	10·56	1·533	16·91
H_2O	—	534	0·0216	11·53	1·00	11·53

Attempts to refer the velocity of the reaction in different solutions to the viscosity of the medium[1] have not been successful, in spite of Buchböck's view to the contrary. This will be evident from the results given in column 7. Again, salts which lower the viscosity accelerate the rate of inversion of cane sugar, but so do salts which raise the viscosity of the medium. Arrhenius[2] has discussed this question with reference to the influence of neutral salts on the rate of inversion of cane sugar. The addition of electrolytes does not appear to alter the velocity of the reaction very much, although the

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[1] A. Guyard, *Bull. Soc. Chim.* [2], **31.** 354, 1879.

[2] S. Arrhenius, *Zeit. phys. Chem.*, **2.** 284, 1888; **28.** 326, 1899.

viscosity changes in a very marked manner. Moreover, the influence of salts on the hydrolysis of ethyl acetate is just the opposite to what it should be according to Buchböch's hypothesis;[1] and Reformatsky[2] and Levi[3] have shown that the velocity of a reaction is not lessened when the viscosity of the solution is increased by the addition of gelatine, agar-agar, or silicic acid.

§ 102. Passivity of the Metals.

Ordinary nitric acid acts energetically upon metallic iron with the evolution of various gases. Wenzel (*l.c.*) in 1782, and Kier[4] in 1790, noticed that when iron is placed in contact with nitric acid of sp. gr. 1·45, it assumes a passive condition; this is also the case when iron is placed in contact with the more powerful oxidizing agents—chloric and chromic acids. In this condition iron is not only "insoluble" in dilute nitric acid, but it no longer precipitates copper from solutions of copper sulphate or nitrate, metallic silver from silver nitrate, or metallic lead from lead nitrate. Nearly all the experiments which have been made upon this subject refer to iron containing carbon as an impurity. Electrolytically prepared iron, however, is converted into the passive state under the same conditions.[5] Iron also becomes passive when it is touched with a piece of gold or platinum while dissolving in an acid of sp. gr. 1·35.

The temperature at which iron becomes passive depends upon the concentration of the acid; thus, with nitric acid of sp. gr. 1·38, the temperature is 31°; with an acid of sp. gr. 1·42, 55°. Renard[6] found that the heating of iron for a second

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[1] H. Euler, *Zeit. phys. Chem.*, **36**. 641, 1901.

[2] S. Reformatsky, *Zeit. phys. Chem.*, **7**. 34, 1891.

[3] M. G. Levi, *Chim. Gaz. Ital.*, **30**. ii., 64, 1900; J. T. Dunn, *Chem. News*, **36**. 88, 1877; G. Lunge, *Ber.*, **9**. 1315, 1876; J. S. Maclaurin, *Journ. Chem. Soc.*, **63**. 724, 1893; **67**. 199, 1895 (rate of attack of gold plates by solutions of potassium cyanide in presence of oxygen).

[4] J. Kier, *Phil. Trans.*, **80**. 359, 1790; *Schweigger's Journ.*, **53**. 151, 1828; G. Wetzlar, *ib.*, **49**. 470, 1827; **53**. 141, 1828.

[5] R. Lenz, *Journ. prakt. Chem.* [1], **108**. 438, 1869.

[6] A. Renard, *Compt. Rend.*, **79**. 159, 1874.

in air is sufficient to render the metal passive, and according to Raman,[1] the same condition is produced by making it the positive electrode in an electrolyte containing oxygen.

A sufficient explanation of the passivity of iron has not yet been published. The following suggestions have been made.

I. Faraday and Schönbein, and Beetz,[2] explain the phenomenon by assuming that a protective film of oxide is formed on the metal when it is dipped into the oxidizing agent. Raman thinks that the film is magnetic oxide, Fe_3O_4, which is known to be soluble in dilute nitric acid, but not in the concentrated acid. The passivity of the iron may be removed by strong rubbing, by heating in reducing gases, and by bringing it in contact with zinc in dilute acid; a minute scratch will often activate passive iron, and the passivity disappears when iron is placed in a magnetic field.[3]

II. The view is often held that the passivity is due to an adhering surface-film of gas, which protects the iron from the action of the acid. Varenne[4] found that no gas is evolved when iron is dipped in a 100 per cent. solution of nitric acid; with a 63 per cent. acid, nitric oxide is given off for from two to twenty seconds, and then ceases. In both cases the iron becomes passive. A 43 per cent. nitric acid (sp. gr. 1·299) does not induce passivity. Gautier and Charpy, and Heathcote,[5] state that the action does not really cease even in strong

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[1] E. Ramann, *Ber.*, **14.** 1430, 1881.

[2] M. Faraday and C. F. Schönbein, *Phil. Mag.* [3], **9.** 53, 1836; **10.** 175, 1837; *Pogg. Ann.*, **39.** 342, 1836; C. F. Schönbein, *ib.*, **37.** 393, 1836; **41.** 42, 1838; **43.** 1, 1838; **59.** 149, 1843; W. Beetz, *ib.*, **62**, 234, 1844; **67.** 286, 365, 1846; A. von Martens, *ib.*, **61.** 121, 1844; G. Wetzlar, *Schweigger's Journ.*, **49.** 470, 1827; **50.** 88, 129, 1829; G. T. Fechner, *ib.*, **53.** 129, 1828.

[3] E. L. Nichols, *Amer Journ. Science* [3], **31.** 272, 1886; E. L. Nichols and W. S. Franklin, *ib.*, **34.** 419, 1887.

[4] L. Varenne, *Compt. Rend.*, **89.** 783, 1879; *Ann. Chim. Phys.* [5], **19.** 251, 1880; **20.** 240, 1880; L. Desruelles, *Compt. Rend.*, **89.** 870, 1879; A. Ditte, *ib.*, **127.** 919, 1898 (solution of aluminium in acids); C. Fredenhagen, *Zeit. phys. Chem.*, **43.** 1, 1903.

[5] A. Gautier and G. Charpy, *Compt. Rend.*, **112.** 1451, 1891; H. L. Heathcote, *Zeit. phys. Chem.*, **37.** 368, 1901.

acid; the action is said to go on slowly, without the evolution of gas. Herschel[1] and Schönbein have noticed a series of alternating periods of evolution of gas and cessation, lasting from $\frac{1}{2}$ to $\frac{1}{5}$ of a second during the earlier stages of the action. Fechner[2] noticed oscillations of the electromotive force when the metal is placed in nitric acid containing silver nitrate, in circuit with another suitable metal.

III. St. Edme[3] attributes the passivity to the formation of a layer of nitride on the surface of the metal, because if passive iron be heated in a current of dry hydrogen, ammonia gas is evolved.

IV. Senderens[4] thinks that passive iron is really an allotropic modification of iron. Hittorf, as we shall see in the succeeding section, appears to share the same view. Finkelstein's[5] measurements of the polarization capacity of passive iron show that it behaves like platinum, and not like aluminium, which is known to be covered with a layer of non-conducting oxide. Hence, the passivity is not due to a layer of oxide Since the electromotive force of an iron electrode dipping in a solution of an iron salt varies with the ratio of ferric to ferrous iron in the solution, Finkelstein inclines to the belief that "passive" iron is trivalent metallic iron, while "active" iron is divalent metallic iron.

Other metals—cobalt, nickel, copper, bismuth,[6] chromium—exhibit passivity. According to St. Edme,[7] commercial sheet nickel is passive in ordinary nitric acid. Passive nickel remains passive even when heated to bright redness in a current

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[1] J. F. W. Herschel, *Ann. Chim. Phys.* [2], **54.** 87, 1833; C. F. Schönbein, *Pogg. Ann.*, **38.** 444, 1836.

[2] G. T. Fechner, *Pogg. Ann.*, **47.** 1, 1839; C. F. Schönbein, *Archives de l'electricité*, **2.** 269, 1842; J. P. Joule, *Phil. Mag.* [3], **24.** 106, 1844.

[3] E. St. Edme, *Compt. Rend.*, **52.** 930, 1861.

[4] J. B. Senderens, *Bull. Soc. Chim.* [3], **15.** 691, 1896.

[5] A. Finkelstein, *Zeit. phys. Chem.*, **39.** 91, 1901; W. J. Müller, *ib.*, **48.** 577, 1904.

[6] T. Andrews, *Phil. Mag.* [3], **12.** 305, 1838; *Pogg. Ann.*, **45.** 121, 1838; for nickel, see W. A. Hollis, *Proc. Camb. Phil. Soc.*, **12.** 253, 1904; M. le Blanc and M. G. Levi, *Boltzmann's Festschrift*, 183, 1904.

[7] E. St. Edme, *Compt. Rend.*, **106.** 1079, 1886.

of hydrogen. Iron, under the same conditions, loses its passivity. Iron dissolving in nitric acid becomes passive when touched with passive nickel.

§ 103. Periodic Chemical Changes.

Chromium prepared by Goldschmidt's "thermite" process[1] is in a passive condition with respect to sulphuric and hydrochloric acids. If inactive chromium be heated with either of these acids, it begins to dissolve, so that—

$$Cr + 2HCl = CrCl_2 + H_2.$$

The chromium thus enters into an active condition, for the evolution of gas continues even though the metal be cooled down to the temperature of the room; moreover, the metal may be removed from the acid, rinsed in water, and introduced into cold dilute hydrochloric acid. If a galvanometer cell is fitted up, as indicated in Fig. 18, so that the platinum dips in a solution of silver nitrate, and the chromium in hydrochloric acid, the electromotive force is—

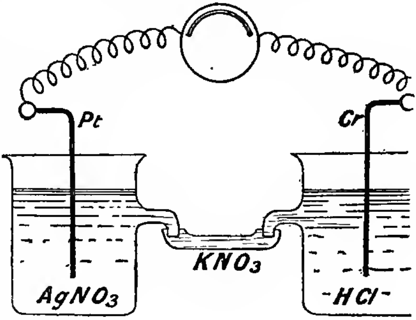

FIG. 18.

Active chromium = 1·8 volt; inactive chromium = 0·3 volt.

Although the inactivity might be ascribed to the formation of a layer of oxide on the surface of the metal, a layer which is removed by warming with hydrochloric acid, yet it is found that warming with a solution of an alkaline haloid effects the

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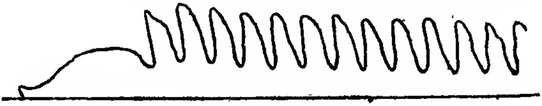
[1] H. Goldschmidt, *Liebig's Ann.*, **301.** 19, 1898.

same result. Hittorf[1] thinks that two allotropic modifications exist—active and inactive.

Ostwald[2] has observed some remarkable phenomena in connection with the solution of certain varieties of active chromium in dilute hydrochloric and sulphuric acids.

1. The rate of solution as measured by the evolution of gas is not continuous, but periodic. The reaction starts in the usual way, rate of evolution increases till the maximum is reached and the rate of evolution begins to diminish, but instead of dropping continually to zero, the rate of evolution of gas begins to rise again, then it slows down, and starts again after a few more minutes have elapsed, and so the cycle begins anew. Ostwald has designed an ingenious instrument for automatically recording the rate of evolution of gas from the dissolving metal. The beginning of such a record is shown in Fig. 19, where the ordinates are very nearly proportional to the rate of evolution of the gas, abscissæ, to the time.



Solvent HCl

FIG. 19.

2. At the same time periodic changes of the electromotive force are set up.[3]

3. The character of the oscillations is very sensitive to the presence of foreign substances in the solvent. As a general rule, oxidizing agents (nitric acid, nitrates, chlorates, bromates, etc.) shorten the length of the period of the oscillation, that is, hasten the recurrence of the maxima, as shown in Fig. 20;

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[1] W. Hittorf, *Zeit. phys. Chem.*, **25**. 729, 1898; **30**. 481, 1899; **34**. 385, 1900; *Zeit. Elektrochem.*, **4**. 482, 1898; **6**. 6, 1899; **7**. 168, 1900.

[2] W. Ostwald, *Königl. Sachs. Akad. d. Wiss.*, 25, 1899; *Zeit. phys. Chem.*, **35**. 33, 204, 1900.

[3] E. Brauer, *Zeit. phys. Chem.*, **38**. 441, 1901; C. Fredenhagen, *ib.*, **43**. 1, 1903; K. Koelichen, *Zeit. Elektrochem.*, **7**. 1, 1901.

while reducing agents (formaldehyde, cyanides, thiocyanates, iodides, hydrogen peroxide, etc.) lengthen the period, as indicated in Fig. 21. The presence of dextrine, starch, and organic substances of a similar nature, favour the "vibratory" action.

4. The presence of impurities in the metal greatly affects the character of the curves. The pure metal does not show the phenomenon. Sometimes a piece of metal will lose its activity in the process of solution, but if such a piece be removed from the solution and brought into contact with an active piece, the activity is restored.

FIG. 20.

5. Rise of temperature accelerates the action by shortening the periods.

No satisfactory explanation has been presented. Ostwald thinks that the "cause" lies in the substance of the metal, and not on its surface. It is, however, possible for such a state of things to be produced by the alternate formation and dissolution of the film of, say, oxide, on the surface of the metal. It is worthy of notice that, with the exception of an unverified experiment of Hofmann and Buff, in all the periodic phenomena, so far observed, there is a limiting surface between the reacting substance upon which the "protecting" film might be formed.

FIG. 21.

The periodic phenomenon has also been observed during the earlier stages of the "passivating" of iron, as mentioned in the preceding section. Malaguti's curves representing the action of barium carbonate upon sodium sulphate, and the reciprocal action of sodium carbonate upon barium sulphate, present "staircases"—*echelles*—as shown in Fig. 22;[1] Hofmann and Buff[2] state that when the sparks from a powerful induction coil are sent in a constant stream through carbon dioxide, decomposition takes place with the formation of carbon monoxide and oxygen, but after a time the latter unite again with a slight explosion to reform carbon dioxide; again, the gas is decomposed and the cycle is repeated over and over again. Joubert[3] noticed that when phosphorus is confined in a eudiometer containing oxygen gas over water, the luminosity gradually disappears, and after an interval of a few hours the luminosity reappears. The alternate appearance and disappearance of the luminosity recur at intervals of a few hours. An explanation of the latter phenomenon was given on p. 311, but I am not aware that the two observations immediately preceding—by Malaguti, and by Hofmann and Buff—have yet been explained or verified. Malaguti's is probably an accidental grouping of the experimental errors.

FIG. 22.

Bredig and Weinmayr[4] have recently investigated the decomposition of hydrogen peroxide in contact with a surface of mercury, which they believe to be of a periodic nature. A 1 per cent. solution of hydrogen peroxide was placed in contact with a clean surface of mercury 7·7 cm. in diameter, at 25°.

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[1] J. Malaguti, *Ann. Chim. Phys.* [3], **51**. 342, 1857.

[2] A. W. Hofmann and H. L. Buff, *Liebig's Ann.*, **113**. 1291, 1860; *Journ. Chem. Soc.*, **12**. 273, 1860.

[3] J. Joubert, *Thèse sur la Phosphorescence*, Paris, 1874.

[4] G. Bredig and J. Weinmayr, *Zeit. phys. Chem.*, **42**. 601, 1903; *Boltzmann's Festschrift*, 839, 1904; J. Weinmayr's *Die Quicksilberkatalyse des Wasserstoffsuperoxyds*, Heidelberg, 1903.

The amount of hydrogen peroxide in solution was determined from time to time by titration with standard potassium permanganate, and the results expressed in c.c. of permanganate. The results were—

Time = 0, 10, 20, 30, 40, 50, 60, 70, 80 min.
H_2O_2 = 10·79, 10·55, 10·00, 9·67, 8·83, 8·65, 7·60, 7·43, 6·6.

When these results are plotted in the usual way, a curve similar to that shown in Fig. 22 is obtained.

The alternate formation and dissolution[1] of a bronze-coloured film of mercury oxide appears to explain the periodic variation in the rate of decomposition of the hydrogen peroxide in contact with mercury.

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[1] Mercury oxide is reduced by a 10 per cent. solution of hydrogen peroxide.

CHAPTER XI

FERMENTATION

§ 104. Organic Ferments—Organized and Unorganized.

THE term "fermentation" was formerly applied to all chemical processes accompanied by the evolution of gas, so that the frothing of carbonates in acid, as well as the alcoholic fermentation of must or wort, were regarded as fermentations. The word now includes those changes in organic substances which are induced by certain living organisms, or by certain substances derived from animal or vegetable sources.

1. *Organized ferments.*—Many fermentations take place during the growth and reproduction of living organisms, special fermentations being induced by specific organisms. For example, the "yeast plant" converts sugar into alcohol; the "vinegar plant" transforms ethyl alcohol into acetic acid; the "lactic ferment" changes milk sugar into lactic acid; and the "nitric and nitrous ferments" effect the oxidation of ammoniacal products into nitrates. The putrefaction of animal and vegetable nitrogeneous matter is also the work of living organisms. The plants effecting these changes are called micro-organisms, microbes, or bacteria.

2. *Unorganized or soluble ferments; enzymes.*—These ferments are secreted by the protoplasm of living organisms, and they may be extracted from the cells in which they have been formed. Enzymes are able to excite the same specific fermentation as the cell from which they were derived.

Payen and Persoz[1] isolated the first enzyme, diastase, from barley malt, in 1832. The enzymes diastase, ptyalin of saliva,

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[1] J. Persoz and A. Payen, *Ann. Chim. Phys.* [2], 53. 73, 1833.

and amylopepsin of the pancreatic juice, have the power of bringing about the transformation of insoluble starch and other carbohydrates into soluble sugar. Again, pepsin of the gastric juice breaks up complex albuminous products into simpler substances, and thus transforms insoluble albumenoid food products into a fit state for digestion. Similar ferments have been separated from various parts of plants, moulds, and bacteria, and particularly from the embryos of seeds and the secretions of carnivorous plants. It also appears as if the immunity of animals from certain bacteria is due to the presence of proleolytic ferments which are capable of destroying the noxious bacteria as they invade the organism. Yeast contains an enzyme variously styled sucrase, invertin, or invertase, which transforms cane sugar into invert sugar. The enzyme emulsin is of historical interest, as it was the next enzyme to be isolated[1] after Persoz and Payen's diastase. It occurs in bitter almonds, and has the power of breaking up the glucoside amygdaline into glucose, benzaldehyde, and hydrogen cyanide.

This will be sufficient to show that the enzymes play a most important *rôle* in nature, particularly in the maintenance of animal life. The insoluble constituents of our food must be transformed into soluble products before they can be assimilated. This transformation appears to be mainly effected by the enzymes secreted in various parts of the alimentary canal. A detailed description of the characteristics of the enzymes belongs to the sphere of physiological chemistry; we are here mainly interested in the mechanism of the chemical changes which they invoke, because these changes are so closely allied to ordinary catalytic processes.

§ 105. Analogy between Fermentation and Catalysis.

One feature common to catalytic agents and ferments is that a very small quantity of the enzyme will transform a relatively large quantity of the fermentable substance. Thus one part of

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[1] J. von Liebig and F. Wöhler, *Liebig's Ann.*, **22**, 1, 1839.

rennet can decompose at least 400,000 times that amount of casein (Oppenheimer); and one part of invertase can transform 200,000 parts of cane sugar (O'Sullivan and Tompson). The action of ferments is very sensitive to the presence of foreign substances. The products of the reaction frequently react with the enzyme [1] itself so as to incapacitate the latter from further action. The speed of fermentation, like the rate of most catalytic processes, increases with the amount of enzyme.

Berzelius [2] long ago pointed out the analogy between catalytic action and fermentation. The idea runs all through Schönbein's writings on this and kindred subjects. The oxidation of sulphur dioxide,[3] of alcohol,[4] and of organic matter generally; the decomposition of calcium formate;[5] of dilute solutions of oxalic acid;[6] and of hydrogen peroxide;[7] the inversion of cane sugar;[8] the assimilation of nitrogen;[9] the reduction of nitrates;[10] the union of hydrogen and oxygen;[11]

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[1] C. O'Sullivan and F. W. Tompson, *Journ. Chem. Soc.*, **57**. 834, 1890; A. Brown, *ib.*, **81**. 373, 1902; G. Tammann, *Zeit. physiol. Chem.*, **16**. 291, 1892; A. C. Hill, *Journ. Chem. Soc.*, **73**. 634, 1898; **83**. 578, 1903; H. Müller-Thurgau, *Theil's Landwirthsch. Jahrb.*, 795, 1885.

[2] J. Berzelius, *Lehrbuch*, Dresden, **6**. 22, 1848.

[3] C. F. Schönbein, *Journ. prakt. Chem.* [1], **105**. 207, 1868.

[4] L. Pasteur, *Études sur le Vinaigre*, Paris, 1868.

[5] H. St. Claire Deville and H. Debray, *Compt. Rend.*, **78**. 1782, 1874; F. Hoppe-Seyler, *Zeit. physiol. Chem.*, **5**. 395, 1881; **11**. 566, 1887; *Pflüger's Archiv.*, **12**. 1, 1887.

[6] O. Šulc, *Zeit. phys. Chem.*, **28**. 719, 1899; W. P. Jorissen, *Maandblad voor natuurwetenschappen*, **22**. 100, 1898; *Zeit. angew. Chem.*, **13**. 521, 1899.

[7] J. Thénard, *Mem. de l'Acad. des Sciences*, **3**. 385, 1818; C. F. Schönbein, *Journ. prakt. Chem.* [1], **89**. 24, 325, 1863; E. Buchner, *Ber.*, **31**. 570, 1898; R. Neumeister's *Physiolog. Chemie*, Jena, 104, 1897.

[8] B. Raỳman and O. Šulc, *Zeit. phys. Chem.*, **21**. 481, 1896; **28**. 719, 1899; G. Bredig and R. Müller von Berneck, *ib.*, **31**. 262, 1899.

[9] O. Loew, *Ber.*, **23**. 1447, 3018, 1890; G. Bunge, *Lehrbuch d. physiol. und path. Chemie*, Leipzig, 24, 1898.

[10] C. F. Schönbein, *Journ. prakt. Chem.* [1], **105**. 206, 208, 1868; E. Griessmeyer, *Ber.*, **9**. 835, 1876; E. Schaer, *ib.*, **9**. 1068, 1876; **33**, 1232, 1900; O. Loew, *ib.*, **23**. 675, 1890; J. H. Gladstone and A. Tribe, *ib.*, **12**. 390, 1879.

[11] T. de Saussure, *Journ. prakt. Chem.* [1], **14**. 152, 1838.

the bleaching of indigo solutions;[1] and the blueing of tincture of guaiacum,[2] are all alike accelerated by the presence of finely divided platinum, by organic ferments, redblood corpuscles, bacteria, and moulds. Schönbein says, "it seems to me a most remarkable fact that the organic ferments should, like platinum, possess the power of decomposing hydrogen peroxide. These coincidences have led me to suspect that they are founded upon similar causes. . . . The results of my latest investigations have but strengthened my old oft-repeated suspicion, that the decomposition of hydrogen peroxide by platinum is the prototype of all fermentations."[3] The analogy has also led C. Ludwig to express the view that "physiological chemistry will, in time, be a branch of catalysis;"[4] while the remarkable results which have recently been obtained in the study of ferments has brought the idea still more into prominence.

It might be questioned whether we are yet prepared for a general theory of the mode of action of ferments, seeing that the literature of the subject is strewn with contradictory statements, and we are yet in total darkness with regard to the constitution of the substances taking part in the action. I may here refer to a few guesses that have been suggested to explain the mode of action of ferments.

§ 106. Vibration Theory of Fermentation and of Catalysis.

T. Willis (1659), and G. E. Stahl (1697), of phlogiston fame, believed that the ferment possessed a peculiar internal motion which it could communicate to neighbouring substances and thus set them in a state of decomposition. The ferment, so to speak, is the centre of a disturbance which is conveyed, by contact, to surrounding substances. The idea was revived a

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[1] C. F. Schönbein, *Journ. prakt. Chem.* [1], **75**. 79, 1858; **78**. 90, 1859.

[2] C. F. Schönbein, *Journ. prakt. Chem.* [1], **89**. 32, 325, 1863.

[3] C. F. Schönbein, *Journ. prakt. Chem.* [1], **89**. 335, 1863.

[4] C. Ludwig, *Lehrbuch der physiologie*, Wien, **1**. 50, 1858–60; G. Hüfner, *Journ. prakt. Chem.* [2], **10**. 156, 1874.

couple of centuries later by Liebig.[1] Although Liebig constantly modified the details of his theory, the central idea was that the motions taking place among the atoms of one body could be communicated, by contact, to another body and set up similar motions, just as one burning body is able to set another body on fire when the two are brought into contact. Liebig supposed that when yeast is added to a saccharine liquid, the yeast cells are decomposing, and, in the act of decomposition, induce a condition of unstable equilibrium in the motions of the atoms of the sugar molecules, so that the sugar is broken up into alcohol and carbon dioxide. Fermentation, therefore, is caused by the death, not the life, of the yeast cell.

Mendeléeff, Nägeli,[2] and others have modified the "vibration hypothesis" in various directions. It is often assumed that the vibration of the molecule, or atoms, of a substance can be increased by the corresponding vibrations of a second substance (catalytic agent), and by merely bringing the two substances into contact the molecules of the one substance can be broken up without affecting the molecules of the other (catalytic agent).

Some attempts have been made to test the point experimentally. Henri and Larguier,[3] for example, have shown that the hydrolysis of methyl acetate and the inversion of cane sugar by hydrochloric acid go with the same rapidity, whether the two systems are alone or in contact.

Liebig's one time popular vibration theory does not, after all, tell us very much. It is but one from an infinite number of more or less plausible guesses which might be suggested.

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[1] J. von Liebig, *Liebig's Ann.*, **30**. 241, 363, 1839; *Pogg. Ann.*, **48**. 106, 1839.

[2] C. von Nägeli's *Theorie der Gärung*, München, 1879; and in R. Neumeister's *Lehrbuch der Physiologischen Chemie*, Jena, 109, 1897; Z. H. Skraup, *Monatshefte für Chem.*, **12**. 110, 1891; **11**. 323, 1890; D. Mendeléeff, *Ber.*, **19**. 456, 1886; A. Irving, *Chem. News*, **58**. 153, 1888. See F. B. Ahrens on "Das Gärungsproblem" in his *Sammlung*, **7**. 445, 1902.

[3] V. Henri and Larguier des Bancels, *Compt. Rend. Soc. Biol.*, **53**. 784, 1901; M. et Mme. V. Henri, *ib.*, **55**. 864, 1903 (decomposition of hydrogen peroxide by colloidal gold and platinum); A. Coppadoro, *Gazz. Chim. Ital.*, **31**. i., 425, 1901.

Its peculiar virtue lies in its power of stretching over any new facts which might be discovered, and of retracting when the occasion should arise. It lies outside the range of experimental verification, and is consequently invulnerable; but, on the other hand, it is almost useless as a working hypothesis for suggesting new lines of investigation.

A somewhat similar theory has been propounded to explain the chemical action of light. It is supposed that "ether waves" of light will augment the vibrations of the material molecules just as a succession of puffs of air, which follow each other in periods identical with the period of vibration of a tuning-fork, will render the latter sonorous. "It is the heaping up of motion on the atoms, in consequence of their synchronism with the waves of light, which causes the atoms to part company."[1]

§ 107. Vital Theories of Fermentation.

In 1837 Schwann[2] showed that the alcoholic fermentation of sugar depends upon the growth and reproduction of living yeast cells, and in 1858 Pasteur[3] proved beyond all doubt that alcoholic fermentation and putrefaction are caused by the presence of certain low forms of life—micro-organisms, or bacteria. Liebig vigorously contested Pasteur's statement that "fermentation is a necessary consequence or manifestation of life," and even went so far as to deny the biological facts in some such words as these: "To suppose that putrefaction or fermentation is caused by the physiological action of such creatures can only be compared with the idea entertained by a child who would explain the rapid current of a river through a mill-wheel by supposing that the mill-wheel, by its force, drives the water down the stream." The beneficial result of Liebig's opposition was to call attention to the weak places in

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[1] J. Tyndall's *Heat a Mode of Motion*, London, 475, 1880.

[2] T. Schwann, *Pogg. Ann.*, **41**. 184, 1837.

[3] L. Pasteur, *Compt. Rend.*, **46**. 179, 1858; **48**. 640, 735, 1859; **50**. 1083, 1860.

Pasteur's early work. Subsequent experiments were all against Liebig's views.

Pasteur's theory is that the living yeast cells "break up, by their vital activity, either directly or through the agency of a soluble ferment, the sugar in which they grow." Some hold that all the sugar must pass through the cell walls of the yeast plant and become an integral part of the cell protoplasm before it can be resolved into its so-called products of fermentation—alcohol, carbon dioxide, etc. In other words, that the sugar must be digested, so to speak, by the yeast cells, and that the alcohol and carbon dioxide are "excretory products of the vegetable cells feeding upon a definite kind of nutritive material."

On the other hand, some believe that the process of fermentation is not directly due to the vital activity of the cell, but is rather a chemical process in which the enzymes capable of inducing the change are manufactured by the protoplasm. This view is supported by the fact that a liquid can be expressed from yeast which will induce alcoholic fermentation in saccharine liquids. Early in 1897 E. Buchner[1] published a paper on "Alcoholic Fermentation without Yeast Cells," in which he showed how this liquid might be obtained.

Fresh yeast, dehydrated under pressure, was ground up with quartz sand and "kiesselguhr," so as to break up the yeast cells. The resulting doughy mass was squeezed through cloth in a hydraulic press at 500 atmospheres. The filtrate is called "Hefepressaft" ("press juice," or "yeast juice").

Solutions of sugar undergo alcoholic fermentation in contact with "press juice," although no organism visible under a microscope magnifying 700 diameters can be detected in a solution which has been fermenting several days. Unlike enzymes, however, the "press juice" loses its activity in a short time. This, says Buchner, is due to the decomposition

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[1] E. Buchner, *Ber.*, **30.** 117, 1110, 2668, 1897; **31.** 209, 568, 1084, 1090, 1531, 1898; **32.** 127, 1899; E. Buchner and R. Albert, *ib.*, **33.** 266, 971, 1900.

of the active sugar ferment by the proleolytic ferments present in the "press juice." By adding a large volume of alcohol to "press juice" the enzyme is precipitated along with the albuminous matter present in the juice. The precipitate is still active, although all living protoplasm has been killed by the treatment. It is therefore inferred that alcoholic fermentation is the work of an enzyme present in "press juice." This hypothetical enzyme is called *zymase*, or *Buchnerase.*

Nasse [1] has advanced the theory of electrolytic dissociation to explain the specific activity of ferments. He found no difference in the electrical conductivity of a solution of fresh ferment, say diastase, and of the boiled ferment in water; but when the water was replaced by a solution of starch, the unboiled ferment had a greater conductivity than that in which the ferment had been "killed" by boiling. Hence, says Nasse, "the ferment is partially ionized at the time it is exerting its specific action." I do not know of any further experiments in support of this interesting observation.

There does not appear to be anything mutually exclusive in Pasteur's and Buchner's theories of the seat of the activity of the ferment. So far as we can say, both are just as likely to be right as either of them.

§ 108. Fermentability and Structure.[2]

While admitting the resemblances, we must not forget any possible differences between the action of ferments and of the catalytic action of, say, acids and alkalies upon substances like cane sugar, etc. One of the most popular arguments [3] against the view that fermentation is nothing more than a simple process of hydrolysis is that while starch, albuminoids, glucosides,

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[1] O. Nasse, *Maly's Jahrber.*, 718, 1894.

[2] The relation between the constitution of chemical compounds and their power of taking part in chemical changes is discussed in another volume of this series—S. Smiles' *The Relation between Chemical Constitution and Physical Properties;* see also R. A. Lehfeldt's *Electro-chemistry*, Part I., 93, 1904.

[3] But there may not be much in it after all.

and the sugars can be hydrolyzed by dilute acids, under approximately the same conditions, each ferment exerts its own specific action. The diastase which hydrolyzes starch will not "touch" albuminoids, maltose, nor cane sugar; and the ferment which breaks up albuminoids does not affect the carbohydrates or fats.

In 1860 Pasteur proved that while mould fungus readily induces the fermentation of dextrorotatory tartaric acid, it has no action on the lævo acid, and Emil Fischer has given us many examples of sugars, one isomer of which is susceptible to the attack of an enzyme while the optical isomer is "immune." Thus, *d*-fructose is attacked by certain yeasts, while *l*-fructose remains unaffected; compounds of *l*-leucine with amidopropionic acid are split up by trypsin, the compound formed by *d*-leucine remains intact (Fischer); lipase saponifies *l*-ethyl mandelate, but not the dextro compound.[1]

It is worthy of note that the four fermentable sugars, glucose, mannose, fructose, and galactose, exist in two optically isomeric forms usually represented on a plane surface by the schemes—

Fermentable.	CO.H	CO.H	CO.H	CH_2OH
	H.C.OH	HO.C.H	H.C.OH	CO
	HO.C.H (*l*)	HO.C.H (*l*)	HO.C.H (*l*)	HO.C.H (*l*)
	H.C.OH (*r*)	H.C.OH (*r*)	HO.C.H (*l*)	H.C.OH (*r*)
	H.C.OH (*r*)	H.C.OH (*r*)	H.C.OH (*r*)	H.C.OH (*r*)
	CH_2OH	CH_2OH	CH_2OH	CH_2OH
	d-glucose	*d*-mannose	*d*-galactose	*d*-fructose
Not fermentable.	CO.H	CO.H	CO.H	CH_2OH
	HO.C.H	H.C.OH	HO.C.H	CO
	H.C.OH	H.C.OH	H.C.OH	H.C.OH
	HO.C.H	HO.C.H	H.C.OH	HO.C.H
	HO.C.H	HO.C.H	HO.C.H	HO.C.H
	CH_2OH	CH_2OH	CH_2OH	CH_2OH
	l-glucose	*l*-mannose	*l*-galactose	*l*-fructose

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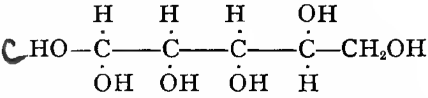
[1] H. D. Dakin, *Proc. Chem. Soc.*, 19. 161, 1903.

Of these, only the dextro varieties are fermentable,[1] and the close structural identity between *d*-glucose, *d*-mannose, and *d*-fructose is brought out by the fact that yeast attacks these sugars with approximately the same readiness, while *d*-galactose is less susceptible to the action. On the other hand, *d*-talose—



$$\mathrm{CHO}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2OH}$$

is not fermentable. Now, *d*-talose is related to *d*-galactose in the same way that *d*-mannose is related to *d*-glucose. The attachment of the two hydroxyls to the carbon atoms on the left is the same as in *d*-mannose, and the two middle hydroxyls resemble those in *d*-galactose; the bottom hydroxyl resembles that of three of the fermentable sugars. Hence, the immunity of these sugars does not depend upon the position of the individual hydroxyl groups. The only difference between the non-fermentable *d*-talose and the other fermentable sugars is the *relative* position of the OH-groups.

This conclusion is also confirmed by Fischer's investigation of the action of the enzyme emulsin and yeast upon the glucosides derived from the various sugars. In the first place, be it noted, only the glucosides of the non-fermentable sugars resist the action of the enzyme; and, in the second place, the relation between the enzyme and the structure of the substance which it attacks is brought out very clearly. Thus, yeast attacks dextro-α-methylglucoside and galactoside, but leaves the β-methyl compounds untouched. The following table illustrates the selective action of emulsin and yeast upon the substances named. The symbol " + " denotes hydrolysis; while " – " means that no action was observed :—

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[1] E. Fischer, *Ber.*, **27**. 2985, 3479, 1894; **28**. 1429, 1895; **23**. 2137, 1890; *Zeit. physiol. Chem.*, **26**. 60, 1898.

Glucoside.	Emulsin.	Yeast.
α-methyl *d*-glucoside . . .	−	+
β-methyl *d*-glucoside . . .	+	−
α-methyl *d*-galactoside . . .	−	+
β-methyl *d*-galactoside . . .	+	−

"The explanation of these phenomena," says Fischer, "probably lies in the structure of the enzyme . . . for the enzymes are doubtless optically active, and consequently possess an asymmetric molecular structure." This has led to the hypothesis that the molecular configuration of the enzyme and of the fermentable sugar are complementary, so that "the one may be said to fit the other as a key fits a lock" (Fischer), or "as male and female screw" (Pasteur). The action of yeast upon the sugars is just as if the ferment were "provided with three hands, in the order right, right, left (*r*, *r*, *l*, p. 361) to enable it to grip the sugar molecule and commence tearing it to pieces; with these three hands it grips the corresponding hands—also of the configuration and order right, right, left—of the first three sugars. The enzyme can only grip the *d*-galactose by two hands, and so it obtains a less firm hold. Owing to the greater incompatibility between zymase and *d*-talose, the former obtains too feeble a hold on the latter to enable it to make a successful assault, and the sugar therefore remains unfermented."[1]

The specific action of the toxines and antitoxines has also been referred by Ehrlich[2] to a similar relation between the configuration of the toxine and the protoplasm of the cell.

These suggestions remind us of the association theory of chemical changes, § 87. The decomposition of the sugars by fermentation is only possible when the enzyme can form a

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[1] W. J. Pope, *Nature*, **68**. 280, 1903.

[2] P. Ehrlich, *Das Sauerstoffbedürfnisse de Organismus*, Berlin, 1885; C. J. Martin and T. Cherry, *Proc. Roy. Soc.*, **63**. 420, 1898; C. J. Martin, *ib.*, **64**. 88, 1898–9. For description of Ehrlich's theory, see R. T. Hewlett's *Serum Therapy*, London, 1903.

"molecular complex" with the sugar. As a matter of fact, Szumowski[1] has shown that some enzymes have the power of combining with relatively large quantities of the substance upon which it is capable of acting; and Kastle and Loevenhart[2] have suggested the hypothesis that the so-called oxidases are "unstable organic peroxides" which are produced in the cell as first oxidation products, and, further, that the decomposing action of liver catalase on hydrogen peroxide is of the same type as other inorganic catalytic agents which affect the decomposition of hydrogen peroxide (see p. 331).

It is interesting to observe that only the dextro-sugars occur in nature, and that these are the only sugars which can be assimilated as food-stuffs by the yeast plant. No organism capable of digesting artificially synthesized lævo-sugars is known. "It would seem to follow, as a legitimate conclusion, that, whilst *d*-glucose is a valuable food-stuff, we should be incapable of digesting its enantiomorphously related isomeride *l*-glucose. Humanity is therefore composed of dextro men and dextro women. And just as we ourselves would probably starve if provided with food enantiomorphously related to that to which we are accustomed, so, if our enantiomorphously related isomerides, the lævo men, were to come among us now, at a time when we have not yet succeeded in preparing synthetically the more important food-stuffs, we should be unable to provide them with the food necessary to keep them alive."[3]

However attractive the theory, we must not lose sight of the tremendous leap we have taken from the little we know of the structure of the sugar molecule to our absolute ignorance of the configuration of the enzymes.

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[1] W. Szumowski, *Arch. d. physiol.*, 160, 1898.

[2] J. H. Kastle and A. S. Loevenhart, *Amer. Chem. Journ.*, **26**. 539, 1901.

[3] W. J. Pope, *Nature*, **68**. 280, 1903; see W. A. Bone and H. C. H. Carpenter, *Pharm. Journ.*, **66**. 106, 165, 463, 489, 1901.

§ 109. Inorganic Ferments.

Aqueous solutions of hydrogen peroxide are extremely sensitive to the presence of foreign substances; some accelerate, and some retard the rate of decomposition.[1] The organic ferments, as well as animal tissues, and vegetable extracts, all accelerate the decomposition of hydrogen peroxide in a vigorous manner.[2] So do the finely divided metals—platinum, gold, silver, etc. The activity of the metal is much enhanced when it is prepared in the following manner (Bredig's process):—

Two wires of the metal—say platinum—are dipped into pure water and an electric current of 10 amperes and 40 volts is passed through the wires; the latter are then separated 1–2 mm., so as to form an electric arc 1–2 cm. below the surface of the water. The general arrangement is shown in Fig. 23. Particles of the

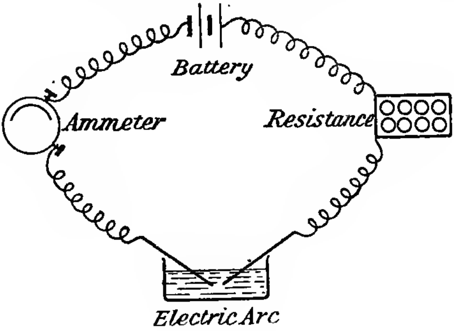

FIG. 23.

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[1] J. Thénard, *Ann. Chim. Phys.* [2], 9. 314, 1818.

[2] "Fibrin ferment" is an exception (Bergengrün, *Protoplasma*, Dorpat, 1888); emulsin which has been heated might still act upon amygdaline, but not upon H_2O_2 (J. Jacobsen, *Zeit. physiol. Chem.*, 16. 340, 1892). O. Loew has shown that the action of the substances mentioned in the text is due to the universal occurrence of an organic ferment, which he calls catalase, in all living tissues (*Catalase, a New Enzym of General Occurrence*, Washington, 1901; *U.S. Dept. Agric. Rep.*, No. 68, 1901).

metal are torn off in such a fine state of division that they do not subside after standing for months. The solution, too, appears homogeneous under the microscope.[1] The metal also passes through the finest filter paper. In spite of all this, the solution has not the usual physical properties of true solutions. It has, for example, no osmotic pressure; the freezing-point, boiling-point, and vapour pressure are the same as pure water. The metal does not diffuse through animal membranes, and it is therefore said to be in a *colloidal state*, or, to employ T. Graham's term, the metal is in the form of a *hydrosol.*

Solutions of platinsol, or "colloidal platinum," present so many analogies with the organic ferments that Bredig[2] published an extensive investigation on the action of colloidal metals upon hydrogen peroxide under the sensational heading "Inorganic Ferments."

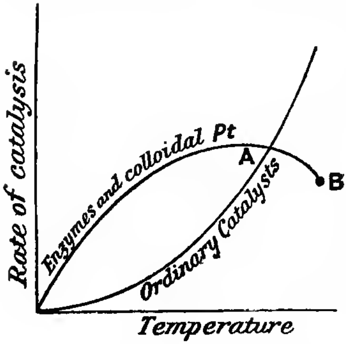

FIG. 24.

1. As indicated in § 104, organic ferments and colloidal platinum act in an analogous manner upon a great number of chemical changes, at least, so far as the result of the change is concernéd.

2. The activity of organic and of inorganic ferments increases with rise of temperature; with both a certain maximum is reached, when further heating diminishes the activity of both

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[1] H. Siedentopf and R. Zsigmondy have produced a microscope with which they claim to have seen colloidal gold (*Ann. der Physik*, 1, 1903; *Zeit. Elektrochem.*, **8**. 684, 1902). See also J. C. M. Garnett, *Proc. Roy. Soc.*, **73**. 443, 1904; *Phil. Trans.*, **203**. 385, 1904, where it is estimated that the particles are 0·000001 cm. in diameter.

[2] G. Bredig and R. Müller von Berneck, *Zeit. phys. Chem.*, **31**. 258, 1899; G. Bredig and K. Ikeda, *ib.*, **37**. 1, 1901; G. Bredig and W. Reinders, *ib.*, **37**. 323, 1901 (gold); G. Bredig, *L. Asher and K. Spiro's Ergebnisse der Physiologie*, Wiesbaden, **1**. i., 134, 1902; with M. Fortner, *Ber.*, **37**. 798, 1904 (palladium).

the ferments; there is a certain *optimum temperature*, above which the activity of the ferment is destroyed altogether. This is shown by the curves in Fig. 24, which are self-explanatory. Each ferment has its own optimum temperature. The effect of heat is to alter the ferment itself. With inorganic ferments, the colloidal platinum is precipitated in the metallic form; with organic ferments, the albumenous matter is coagulated, etc.[1]

3. Schonbein[2] long ago noticed that the presence of very small quantities of certain substances, hydrogen cyanide, hydrogen sulphide, mercuric chloride, etc., inhibit the activity of organic ferments. Bredig has found that the same thing might be said of the inorganic ferments. The inhibitors are sometimes called poisons.

§ 110. Influence of "Poisons" upon Colloidal Platinum.

The decomposition of hydrogen peroxide by colloidal platinum is a unimolecular reaction, so that—

$$\log \frac{a}{a - x} = kt, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is constant, a refers to the amount of hydrogen peroxide present in the solution at the beginning of the reaction, x the amount decomposed at the end of an interval of time, t.

The effects of adding varying amounts of hydrogen cyanide, or of iodine, to hydrogen peroxide decomposing in the presence of colloidal platinum, are shown in the subjoined diagrams (Figs. 25 and 26). The abscissæ represent the times which have elapsed since the commencement of the reaction; the ordinates represent the corresponding values of the left side of equation (1); in other words, the effect of the inhibitor upon the rate of decomposition. The first curve, starting from the ordinate axis in each diagram, represents the course of the

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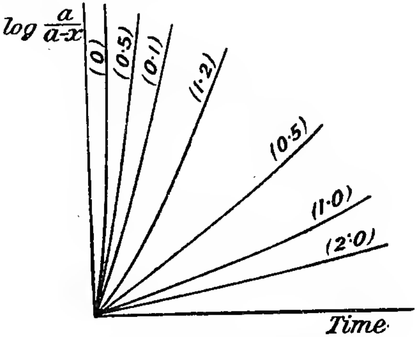
[1] G. Senter, *Zeit. phys. Chem.*, **44**. 257, 1903.

[2] C. F. Schönbein, *Journ. prakt. Chem.* [1], **89**. 340, 1863; [1], **105**. 202, 1868; J. Schlossberger, *Liebig's Ann.*, **51**. 193, 1844.

reaction when no "poison" is present; the following six curves show the effects of adding increasing amounts of the "poison." The numbers in brackets indicate the number of gram-molecules of the inhibitor, multiplied by 10^6, added per litre of solution.

The effect of hydrogen cyanide (Fig. 25).—The second curve shows that the effect of adding one gram-molecule to twenty million litres of water is quite perceptible. It has also been found that the effect of adding one gram-molecule of hydrogen cyanide to twenty million litres of water perceptibly reduces the activity of red-blood corpuscles upon the decomposition of hydrogen peroxide.



(*Hydrogen cyanide*)

FIG. 25.

The curves for the dilute solutions are convex to the abscissa axis. This means that the effects of the poison become less and less as time goes on, in other words, the colloidal solution is *recovering from the effects of the poison.* A similar result has been observed during the action of hydrogen cyanide upon red-blood corpuscles and upon ferments. It is possible that the recovery is due to the oxidation of the hydrogen cyanide in the solution.[1]

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[1] R. W. Raudnitz, *Zeit. phys. Chem.*, **37**. 551, 1901; G. Bredig, *ib.*, **38**. 122, 1901.

With stronger solutions of hydrogen cyanide, the curve is first concave, and then becomes convex after the elapse of a longer time. This means that the effects of the poison at first increase, and then decrease after the elapse of a longer interval of time.

The effect of iodine (Fig. 26).—Here it will be observed that none of the curves are convex to the abscissæ axis. This means that when the iodine is just sufficiently dilute to have an appreciable effect, the platinum cannot recover. The curves show that the iodine inhibits the action of the colloidal metal in a marked manner. Iodine is also known to be an intense blood-poison.

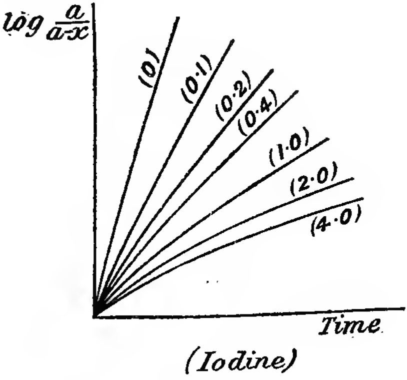

FIG. 26.

The inhibitory action of about thirty substances on colloidal platinum solutions has been studied in this way. The strongest poisons examined were hydrogen cyanide, cyanogen iodide iodine, mercuric chloride, hydrogen sulphide, sodium thiosulphate, carbon monoxide, phosphorus, phosphine, arsine, mercuric cyanide, and carbon disulphide. The metal was able to recover from the effects of some of these. Among the weaker poisons were aniline, hydroxylamine, bromine, hydrogen chloride, oxalic acid, amyl nitrate, arsenious acid, sodium sulphate, ammonium chloride; among the weakest poisons were phosphorous acid, sodium nitrite, nitrous acid, pyrogallol, nitrobenzene, and ammonium fluoride. It was found that potassium chlorate, ethyl alcohol, glycerol, turpentine, and chloroform, were nearly neutral. On the contrary, formic acid, hydrazine, and dilute nitric acid, increase the activity of the colloidal metal (see also p. 262).

These effects are quite parallel with the influence of these substances on blood. There are a few exceptions. For example, aniline strongly accelerates the activity of blood, and yet it retards the activity of colloidal platinum. Notwithstanding this, Bredig has come to the conclusion that the analogies are not accidental. He says, "all these facts point to an unmistakable analogy between the contact actions of the inorganic world and the action of ferments in the organic world. . . . I do not maintain that there is a mysterious identity between the colloidal metals and the enzymes. But without exaggerating the overwhelmingly large number of analogies, we are compelled to regard the colloidal solutions of the metals, in many relations at least, as inorganic models of the organic ferments."

In spite of the seductive nature of the analogy indicated by Bredig, it appears from the work of Kastle and Loevenhart[1] upon the same subject that the analogy is a mere coincidence. Quite a number of substances have been found which "act differently with the two orders of catalysis, that is to say, they inhibit the one and retard the other." Hydrogen cyanide, for example, greatly accelerates the decomposition of hydrogen peroxide by copper, iron, copper sulphide, and iron sulphide; again, while hydroxylamine and the nitrates of potassium, sodium, and ammonium retard the activity of liver catalase, these substances accelerate the activity of finely divided silver, and exert no influence on the activity of platinum. Similarly, while thiourea accelerates the decomposition of liver catalase, it retards the decomposition of hydrogen peroxide in the presence of silver or platinum.

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[1] A. S. Loevenhart and J. H. Kastle, *Amer. Chem. Journ.*, **29**. 397, 563, 1903.

Kastle and Loevenhart conclude that the retardation which many substances exert on the catalytic power of the metals is due to the formation of a thin insoluble film of a compound of the metal over its surface. This compound is formed by the action of the metal on the substance added. For example, only those substances which yield insoluble silver salts inhibit the catalytic action of finely divided silver. Such substances are sodium chloride, ammonium chloride, potassium bromide, hydrogen sulphide, hydrogen cyanide, etc.

It is, however, possible for a salt like potassium iodide to inhibit the activity of the metal, but of itself to accelerate the decomposition of hydrogen peroxide. A substance like ammonium thiocyanate may inhibit for different reasons. It may be oxidized by the hydrogen peroxide, and so act by removing the latter from the solution, or it may produce a substance, like hydrogen cyanide, as a decomposition product, which, in turn, acts as indicated above.[1]

Liebermann[2] also thinks that the mechanism of the decomposition of hydrogen peroxide by colloidal platinum and by "catalases" of animal or vegetable origin is essentially different. In the former case it is inferred that the action takes place by the formation of an intermediate oxide of platinum which is reduced by the hydrogen peroxide, as indicated on p. 268; with ferments, however, the hydrogen peroxide is supposed to form an unstable intermediate "ferment oxide" ("Fermentoxyd" or "Fermentsuperoxyd") by union of the ferment with the hydrogen peroxide.

§ 111. Negative Catalysis.

Since Turner's discovery (1823), § 77, of the diminution in the activity of finely divided platinum upon a mixture of hydrogen and oxygen when certain foreign gases are present, a

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[1] See also J. A. Trillat, *Compt. Rend.*, **137**. 922, 1903; **138**. 94, 274, 1904; *Bull. Soc. Chim.* [3], **31**. 190, 1904, for the paralysis of the catalytic action of manganese salts upon oxidizing enzymes by arsenic acid, hydrogen cyanide, and hydrogen sulphide.

[2] L. Liebermann, *Ber.*, **37**. 1519, 1904.

great number of similar observations have been made. The presence of water vapour, for instance, retards the decomposition of ammonia,[1] and the oxidation of phosphorus;[2] alcohol vapour retards the formation of ammonium carbamate;[3] chlorine retards the formation of ozone;[4] oxygen retards the rate of formation of hydrogen chloride;[5] the vapour of organic compounds retards the oxidation of phosphorus,[6] and of sodium sulphite;[7] the presence of $\frac{1}{800}$ gram-molecule of ammonia reduces the rate of decomposition of an aqueous solution of ammonium nitrite two-thirds.[8]

A number of plausible suggestions have been made to explain the inhibitory action. For example, (1) the destruction of the "positive catalyst" by the retarder; (2) the combination of the negative catalyst with one of the reacting substances.

1. Titoff[9] has investigated the oxidation of aqueous solutions

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[1] K. Than, *Liebig's Ann.*, **131**. 121, 1864.

[2] H. G. van de Stadt, *Zeit. phys. Chem.*, **12**. 329, 1893.

[3] J. H. van't Hoff, *Studien*, Amsterdam, 36, 1896; T. Ewan's trans., 34, 1896.

[4] T. Hautefeuille and J. Chappuis, *Compt. Rend.*, **91**. 762, 1880; W. A. Shenstone and W. A. Evans, *Journ. Chem. Soc.*, **73**. 246, 1898.

[5] R. Bunsen and H. F. Roscoe, *Pogg. Ann.*, **100**. 481, 1857; *Phil. Trans.*, **146**. 355, 601, 1857; M. Wildermann, *ib.*, **199**. 337, 1902; G. Dyson and A. Harden, *Journ. Chem. Soc.*, **83**. 201, 1902.

[6] C. L. Berthollet, *Journ. de l'école polyt.*, **3**. 274, 1795–6; T. Graham, *Quart. Journ. Science*, **6**. 83, 1829; *Schweigger's Journ.*, **57**. 230, 1829; *Pogg. Ann.*, **17**. 375, 1829; J. Davy, *Edin. Phil. Journ.*, **15**. 48, 1833; *Schweigger's Journ.*, **68**. 384, 1833; M. Centnerszwer, *Zeit. phys. Chem.*, **26**. 1, 1898.

[7] S. L. Bigelow, *Zeit. phys. Chem.*, **27**. 585, 1898; S. W. Young, *Journ. Amer. Chem. Soc.*, **23**. 119, 1901; **24**. 297, 1902; A. Berg, *Compt. Rend.*, **138**. 907, 1904.

[8] A. V. Harcourt, *Chem. News*, **18**. 15, 1868; A. Millon, *Ann. Chim. Phys.* [3], **19**. 255, 1847; S. P. L. Sorensen, *Zeit. anorg. Chem.*, **7**. 38, 1894; R. Wegscheider, *Zeit. phys. Chem.*, **36**. 543, 1901; K. Arndt, *ib.*, **39**. 64, 1901; **45**. 571, 1903; A. A. Blanchard, *ib.*, **41**. 680, 1902; A. Angeli and G. Boeris, *Gazz. Chim. Ital.*, **22**. ii., 349, 1892; M. Berthelot, *Bull. Soc. Chim.* [2], **21**. 55, 1874; V. H. Veley, *Journ. Chem. Soc.*, **83**. 736, 1903; **43**. 370, 1883.

[9] A. Titoff, *Zeit. phys. Chem.*, **45**. 641, 1903; R. Knietsch, § 77.

of sodium sulphite which only proceeds with a measureable velocity in the presence of some catalytic agent, say, copper sulphate. Mannite acts as a negative catalyst. The retardation is proportional to the amount of mannite present. There are two influences at work—an acceleration of the main reaction by the copper salt, and the destruction of the positive catalyst by union with the negative catalyst.

2. Turner (1823), Faraday (1834), and W. C. Henry (1836), § 77, have shown that the presence of carbon monoxide does not permanently modify the surface of the platinum employed as catalytic agent to effect the union of hydrogen and oxygen gases; and, further, "that all the gases which have hitherto been observed to exhibit this power are such as are capable of uniting with oxygen; and the non-interfering gases are such as cannot, at least within a considerable range of temperature, be brought to combine with that element . . ." It is also shown that the inhibitory action of carbon monoxide and of olefiant gas is due to the union of these gases with the oxygen, as well as to the fact that the product of the oxidation of hydrogen "at once quits the surface of the metal, while the combustion of carbon monoxide yields a gas which remains for a while adherent to the metallic surface, next to which it is generated, and thereby prevents the access of fresh unaltered gas to the surface of the platinum. . . ."

These facts also suggest an "explanation" of Kühl's[1] observation that the rate of combination of carbon monoxide and oxygen is modified by the order in which the reacting gases are brought into contact with each other. If carbon monoxide is brought in first, the rate of combination is said to be quicker than if the oxygen be introduced first. Gaseous reactions, as we have seen, probably take place close to the surface of the glass. It takes a long time to remove a film of gas from the surface of glass. Hence, for some considerable time the surface film of gas will depend upon the gas first admitted to the vessel in which the reaction takes place.

Speaking of the interaction of the reacting substances with

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[1] H. Kühl, *Zeit. phys. Chem.*, 44. 385, 1903.

the catalytic agent reminds me of the interesting effects obtained by the addition of a soluble chromate or bichromate to a solution of an alkali chloride undergoing electrolysis. Müller[1] has shown that the addition of 0·18 per cent. of potassium chromate to a 30 per cent. solution of sodium chloride raises the efficiency of the current from 32·8 to 69·6 per cent. The mechanism is as follows: When the current is passed through an aqueous solution of sodium chloride, the chlorine evolved at the anode reacts with the sodium hydroxide evolved at the cathode, forming sodium hypochlorite, and ultimately sodium chlorate. When the hypochlorite comes in contact with the cathode it acts as a depolarizer, and is reduced. The consequence is that the yield of chlorate is lowered. In presence of chromates, a deposit or film of an oxy-chromium compound is formed on the surface of the cathode, which prevents the hypochlorite coming into contact with the electrode, and there is therefore very little depolarization. The presence of sulphates and chlorates also facilitates the production of periodates.

§ 112. The Kinetics of Catalytic Reactions.

V. Henri[2] divides catalytic reactions into two divisions, according as (1) the reaction takes place by simple contact, as in the action of acids upon cane sugar; and (2) the reaction takes place with the formation of intermediate compounds.

I. Catalysis by simple contact.—If the catalyst is present all through the reaction in its original state, the "order" of the chemical reaction will not be changed by the catalytic agent. For example, in the hydrolysis of cane sugar by acids, the acidity of the solution, so far as chemical analysis is concerned, has the same value throughout the whole progress of the reaction.

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[1] E. Müller, *Zeit. Elektrochem.*, **8**. 8, 425, 909, 1902; **10**. 49, 1903; with F. Foerster, *ib.*, **8**. 515, 633, 665, 1902; **9**. 171, 195, 1903.

[2] V. Henri's *Lois Générales de l'action des diastases*, Paris, 14, 1903; V. Henri and Larguier des Bancels, *Compt. Rend. Soc. Biol.*, **55**. 864, 1903.

When a reaction can be represented by the equations—

$$\frac{dx}{dt} = k(a - x) ; \ \frac{1}{t} \log \frac{a}{a - x} = k,$$

we can only say that the active mass of one substance is changing concentration. There is nothing to show whether or not the catalyzer takes part in the reaction. This subject has been treated in an earlier chapter.

II. Catalysis by the formation of intermediate compounds.—If a substance, A, undergoing chemical transformation, combines very rapidly—instantaneous in fact—with a catalyzer, C, to form an intermediate compound, M, which decomposes, as soon as it is formed into the products of the reaction B, and regenerates anew the catalyzer C, the latter will instantaneously combine with more of the substance A, and the cycle will be repeated until all of A is transformed into B. There are thus two dependent chemical reactions—

$$\text{(i.) } A + C = M ; \text{ and (ii.) } M = B + C.$$

There are two interesting cases—

1. *If all the catalyzer combines with* A, and the quantity of the catalyst is very small in comparison with A, the velocity of the reaction will be proportional to the amount of catalyzer present in the solution, but the amount of catalyzer actually present is constant, hence—

$$\frac{dx}{dt} = \text{constant} = k ; \text{ or, } x = kt. \quad . \quad . \quad (1)$$

Some interesting reactions of this kind occur during the decomposition of aqueous solutions of many of the "diazo" derivations of naphthylamines, in which an intermediate compound appears to be momentarily formed before the evolution of nitrogen commences. Sodium 8-hydroxy-β-diazonaphthalene-6-sulphonate,[1] for example, furnishes, on decomposition, the following numbers :—

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[1] J. C. Cain and F. Nicoll, *Journ. Chem. Soc.*, **83**. 206, 1903.

t	x	k
7·4	19·6	2·65
9·4	24·7	2·63
11·4	29·9	2·62
13·4	35·4	2·64
15·4	41·2	2·67
17·4	46·9	2·69

Duclaux[1] employs equation (1) to represent the action of diastase upon cane sugar, but in this case the products of the reaction retard the activity of the ferment, and therefore of the whole reaction. It is assumed that this retarding action is proportional to the quantity of invert sugar, x, present at the time t, and inversely as the amount of cane sugar in solution before the reaction commenced. Hence, from the principle of the mutual independence of different reactions—

$$\frac{dx}{dt} = k - k_1\frac{x}{a}; \text{ or, } k_1 = \frac{a}{t}\log\frac{ka}{ka - k_1x}.$$

For some reactions $k=k_1$, and in that case we have the regular equation for the inversion of cane sugar.

When the amount of catalyzer is greater than the amount of substance undergoing transformation, the velocity of the reaction will be proportional to the amount of A present in the solution, and we shall have the usual equations—

$$\frac{dx}{dt} = k(a - x); \text{ or, } \frac{1}{t}\log\frac{a}{a - x} = k.$$

2. *If only part of the catalyzer combines with* A, in other words, if the reaction between A and C is incomplete or reversible—

$$\mathrm{A + C \rightleftharpoons M;\ \ M = B + C.}$$

Such a series of changes would occur in Fischer's theory of ferment action, where the ferment is supposed to unite with the

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[1] E. Duclaux, *Annales de l'Instit. Pasteur*, **12**. 96, 1898; *Microbiologie*, Paris, **2**. 142, 1897–1901.

substance undergoing transformation to form an intermediate compound which decomposes into the original catalytic agent and the product of fermentation.[1] Let c denote the quantity of catalyzer and a the amount of the substance A present at the beginning of the experiment; let x denote the amount of A which has been transformed at the time t; and let y denote the amount of the intermediate compound M present at the time t.

The velocity of formation of the products of the action at any moment will be proportional to the amount of intermediate compound present at that instant, or—

$$\frac{dx}{dt} = k_1 y. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But since $a-x$ denotes the amount of the original substance present at the time t, $c-y$ the amount of the catalyzer which remains uncombined at the time t, we shall have for equilibrium—

$$(a-x)(c-y) = k_2 y; \text{ or, } y = \frac{c(a-x)}{k_2 + a - x}. \quad . \quad (3)$$

Substituting this value of y in the equation (2), we have—

$$\frac{dx}{dt} = \frac{k_1 c(a-x)}{k_2 + a - x}; \text{ or, } k_1 c = \frac{1}{t}\left(x + k_2 \log \frac{a}{a-x}\right). \quad (4)$$

It will now be apparent that the mathematical representation of the course of a reaction assumes a much more complicated form whenever we attempt to compensate the errors introduced by making simplifying assumptions.

We have seen that one great difference between the inversion of cane sugar by dilute acids and by ferments is that with the former the products of the reaction have no influence on the rate of inversion, while with the latter the products of the reaction retard the rate of inversion. Suppose that the diminution of the speed of hydrolysis by the ferment is really due to the union of the ferment with the products of the reaction, and

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[1] See also A. J. Brown, *Journ. Chem. Soc.*, **81**. 373, 1902; A. J. Brown and T. A. Glendinning, *ib.*, **81**. 389, 1902, for combination of cane sugar with invertase, and of starch with diastase.

let us dress up the theory in mathematical symbols. Let u denote the quantity of ferment uncombined, and v the quantity combined with the cane sugar at the time t; let w be the quantity of the ferment which becomes inactive owing to combination with the products of hydrolysis, then the total amount of ferment present in the reacting system will be—

$$c = u + v + w. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

There will be equilibrium between the ferment and the cane sugar when—

$$u(a - x) = K_1 v; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and between the ferment and the invert sugar when—

$$ux = K_2 w, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $a-x$ denotes the amount of cane sugar, x the amount of invert sugar, present in the system; K_1 and K_2 are the usual constants of equilibrium.

Solving this set of equations for v, in the usual manner, we get—

$$v = \frac{K_2 c(a - x)}{K_1 K_2 + K_2(a - x) + K_1 x}. \quad . \quad . \quad . \quad (8)$$

If, now, the intermediate compound of cane sugar and ferment decomposes as indicated above, the velocity of the inversion of the cane sugar will be proportional to the quantity of the intermediate compound present, namely, v, consequently—

$$\frac{dx}{dt} = K_1 v,$$

$$\therefore \frac{dx}{dt} = \frac{K_1 K_2 c(a-x)}{K_1 K_2 + K_2(a-x) + K_1 x} = \frac{K(a-x)}{K_1 K_2 + K_2(a-x) + K_1 x}, \quad (9)$$

where K is a constant proportional to the quantity c of ferment present. By integration—

$$\frac{1}{t}\left\{(K_2 - K_1)x + K_1(a + K_2) \log \frac{a}{a - x}\right\} = K, \quad (10)$$

an expression containing three unknown constants, K_1, K_2, and K. By taking three sets of experimental values of a, t, and x, the constants can be readily determined. The agreement between the observed and calculated values of x led V. Henri[1] to conclude that Fischer's hypothesis is a very fair explanation of the mechanism of the reaction. Note the likeness of (10) to (4).

This is a convenient opportunity to again emphasize the danger of bowing down and worshipping the mathematical fetish. The assumption that the hydrolysis is effected by the *uncombined* catalyzer furnishes a similar expression to that just deduced on the assumption that that part of the ferment which is united with the substance undergoing transformation effects the hydrolysis. Often enough two different theories of a chemical process furnish similar equations, or if there be a difference it is outside the range of experimental verification.

Henri and Larguier[2] propose to distinguish between the two conflicting theories by selecting two reactions produced by the same catalytic agent, and then measuring the velocity of transformation when the catalytic agents are acting (i.) separately and (ii.) conjointly. They call this *la méthode de combinaison.*

1. If the resultant velocity of the reaction with both catalytic agents is a simple additive effect, it is inferred that the catalysis is a simple case of contact action—*catalyse pure.* This occurred with the inversion of cane sugar and the hydrolysis of methyl acetate in presence of an acid.[3]

2. If the velocity of the joint action is *greater* than that calculated on the assumption that the resultant value is the sum of the two, an intermediate compound is formed which decomposes so as to reform the original catalytic agent.

3. If the resultant velocity is equal to or *less* than the sum of the two isolated reactions, it is the free part of the catalytic agent which exercises the catalytic power. *E.g.* the action of trypsin upon gelatine and caseine,[4] and the action of emulsin upon salicine and amygdaline.[5]

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[1] V. Henri's *Lois générales de l'action des diastases*, Paris, 1903; *Zeit. phys. Chem.*, **39.** 194, 1901.

[2] V. Henri and Larguier des Bancels, *Compt. Rend. Soc. Biol.*, **55.** 864, 1903.

[3] V. Henri, *ib.*, **53.** 784, 1901.

[4] V. Henri and Larguier des Bancels *Compt. Rend. Soc. Biol.*, **55.** 868, 1903.

[5] V. Henri and S. Lalou, *Compt. Rend.*, **136.** 1693, 1903; *Compt. Rend. Soc. Biol.*, **55.** 868, 1903.

Tammann[1] has shown that in the hydrolysis of salicine by emulsin, the latter is gradually decomposed, and that the rate of decomposition of the ferment—*i.e.* the rate at which the ferment is rendered inactive—follows the course of a unimolecular reaction. Hence, as in § 12, it is easy to see that even after an infinite time some of the original substance must remain undecomposed, a conclusion which agrees with the work of Tammann.

Suppose, now, that the formation of the intermediate compound occupies a measurable time, the velocity of formation of the products of the action will be proportional to the amount of intermediate compound present in the solution at the time t. The velocity of formation of M will be proportional to the amounts of A and of C present in the solution. Hence, with the same symbols as before, $a-x-y$ denotes the amount of the original substance present at the time t, and $c-y$ the amount of catalyzer present at the same time. Hence—

$$\frac{dy}{dt} = k_1(a - x - y)(c - y)\,;\ \frac{dx}{dt} = k_2 y. \quad . \quad (11)$$

By integration in series—

$$x = At^2 + Bt^3 + Ct^4 \quad . \,., \quad . \quad . \quad . \quad . \quad (12)$$

where A, B, C, . . . are constants.

The velocity constant of a catalyzed reaction.—Let the velocity of a reaction be represented by the expression—

$$-\frac{dC}{dt} = kf(C),$$

where $f'(C)$ is employed to represent the relation between the velocity and the concentration of the reacting substances, when we do not wish to commit ourselves to such a definite statement as is implied by the law of mass action, or when the disturbing influences are so great that we do not know what else to write on the left side of the above equation. By integration—

$$f(C_1 - C_2) = k(t_2 - t_1). \quad . \quad . \quad . \quad . \quad . \quad (13)$$

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[1] G. Tammann, *Zeit. phys. Chem.*, **16**. 285, 1892; **18**. 426, 1895.

If the reaction now takes place in the presence of a catalytic agent, and the value of k changes to k', while the form of the function $f(C_1 - C_2)$ remains the same, we have—

$$f(C_1' - C_2') = k'(t_2' - t_1'). \quad . \quad . \quad . \quad . \quad (14)$$

If we let the two reactions run on until the same amount of substance is transformed in each case, we get, from (13) and (14)—

$$f(C_1 - C_2) = f(C_1' - C_2'); \ \frac{k}{k'} = \frac{t_2' - t_1'}{t_2 - t_1}. \quad . \quad (15)$$

That is to say, the intervals of time required for the transformation of the same amount of substance in a catalyzed and in a non-catalyzed reaction is inversely as the velocity constants of the two reactions.[1]

Hence it is possible to determine the change, κ, effected by the catalytic agent upon the velocity constant of the normal reaction, even when the velocity equation is not known. We assume that the catalytic agent does not alter the actual form of $f'(C)$. If the catalyzed reaction goes *viâ* an intermediate compound not formed with the simple reaction, (15) no longer holds good.

By a suitable transformation of the above equations, making $k(t_2 - t_1)$ unity—

$$\kappa = k' - k = \frac{1}{t_2' - t_1'} - \frac{1}{t_2 - t_1}. \quad . \quad . \quad . \quad (16)$$

This means that the increase which takes place in the velocity of a reaction in presence of a catalytic agent can be determined from the time required for the transformation of a certain amount of the substance in presence and in the absence of the catalytic agent.[2]

If the time $t_2 - t_1$ required for the transformation of the substance in the absence of the catalytic agent is very great in

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[1] W. Ostwald, *Zeit. phys. Chem.*, **2**. 134, 1888.

[2] W. Ostwald, *l.c.;* T. S. Price, *Zeit. phys. Chem.*, **27**. 474, 1898; J. Brode, *ib.*, **37**. 257, 1901.

comparison with $t'_2 - t'_1$, the second term of (16) vanishes, k is very small in comparison with k', and we get—

$$\kappa = k' = \frac{1}{t'_2 - t'_1}.$$

This equation applies to the inversion of cane sugar, and it is only necessary to find how the constant k' changes with the quantity of the catalytic agent in different experiments.

As a rule, *the acceleration is proportional to the amount of catalytic agent present.* It is then possible to determine the amount of catalytic agent from the velocity of the reaction. Trevor and Palmaer[1] have found that the rate of inversion of cane sugar is proportional to the concentration of the catalyzing acid, as the following numbers show:—

$$\begin{aligned} C_{\text{acid}} &= 0{\cdot}00995, \quad 0{\cdot}00704, \quad 0{\cdot}00500, \quad 0{\cdot}00206, \ldots; \\ k' &= 0{\cdot}00183, \quad 0{\cdot}00130, \quad 0{\cdot}00093, \quad 0{\cdot}00038, \ldots; \\ C_{\text{acid}}/k' &= 0{\cdot}186, \quad 0{\cdot}186, \quad 0{\cdot}186, \quad 0{\cdot}184. \end{aligned}$$

Price also noticed that the catalytic action of ferrous sulphate in the reaction between potassium persulphate and potassium iodide is proportional to its concentration. If—

$$\frac{dx}{dt} = k(a - x)(b - x)$$

denotes the velocity of the reaction in presence of the catalyst, then—

$$\frac{dx}{dt} = kc(a - x)(b - x)$$

will be the velocity of the reaction in presence of c gram-molecules of the catalytic agent. The rule, however, is by no means general.

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[1] J. E. Trevor, *Zeit. phys. Chem.*, **10**. 330, 1892; W. Palmaer, *ib.*, **22**. 504, 1897; H. Goldschmidt with H. Larsen for the catalytic action of metallic chlorides in the chlorination of nitrobenzene—*Zeit. phys. Chem.*, **48**. 424, 1904; with K. Ingelbrechten, *ib.*, **48**. 435, 1904; T. S. Price, *ib.*, **27**. 474, 1898.

CHAPTER XII

INFLUENCE OF TEMPERATURE ON CHEMICAL REACTIONS

§ 113. Influence of Temperature on Chemical Reactions.

The influence of temperature on chemical reactions is so very marked that this has been universally recognized as one of the most important factors in the study of chemical changes. Although many interesting facts have been brought to light by a happy combination of theory and experiment, this subject still forms, as Ostwald has said, "one of the darkest chapters in chemical mechanics." The subject, too, is vested with a certain amount of technical interest, since the manufacturer must know the best temperature to keep unstable solutions, such as the "azo-colours" of the dye-house, in order to have a minimum loss by decomposition.[1]

The velocities of all chemical reactions, with few exceptions,[2] increase rapidly with rise of temperature. For example, barium formate decomposes twice as rapidly at 330° as it

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[1] G. Bredig's *Ueber die Chemie der extremen Temperaturen*, Leipzig, 1901.

[2] We have a few reactions in which the rate is diminished by raising the temperature. For example, the rate of liberation of iodine from a mixture of potassium iodide, ferrous sulphate, and chromic acid is less at 30° than at 0° C. (C. C. Benson, *Journ. Phys. Chem.*, **8.** 116, 1904); the rate of reduction of ferric sulphate by iron in acid solution "appears" to decrease with increase of temperature (T. E. Thorpe, *Journ. Chem. Soc.*, **41.** 287, 1882); and those reactions in which a colloidal catalyst is involved. Like negative catalyses, the explanation, when found, will possibly turn on the presence of disturbing secondary reactions.

does at 260°;[1] the inversion of cane sugar proceeds five times as fast at 55° as it does at 25°;[2] the conversion of solid ammonium cyanate into urea is fifty times as rapid at 57° as it is at 33°;[3] the transformation of dibromosuccinic acid into bromomaleïc acid goes three thousand times as rapidly at 101° as at 15°; and although the reaction between hydrogen and oxygen is so slow at 155° that no sign of combination can be detected after many months, yet, at about 600° the combination takes place with explosive violence.[5] Dewar, too,[6] has shown that at the temperature of liquid air (– 183°) photographic action is 20 per cent., and at the temperature of liquid hydrogen (–250°), it is but 10 per cent. of its value at ordinary temperatures. The rapid increase in the velocity of the esterification of alcohol as the temperature rises from 8° to 100° is shown graphically in Fig. 27; the ordinates represent the amount of ethyl acetate transformed, the abscissæ the time. It must be particularly noticed that the abscissæ for the lower curve represent time in days, for the upper, time in hours. The influence of temperature is brought out very clearly. At 200° the velocity of esterification is 22,000 times as great as it is at 8°.[7]

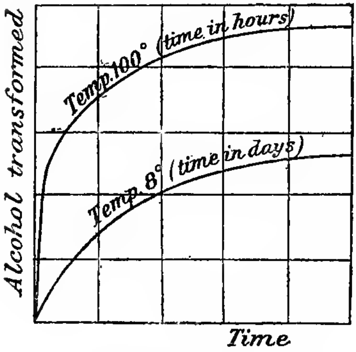

FIG. 27.—Velocity curves.

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[1] M. Berthelot, *Compt. Rend.*, **59**. 616, 817, 861, 901, 1864; *Ann Chim. Phys.* [4], **18**. 146, 1869.

[2] J. Spohr, *Zeit. phys. Chem.*, **2**. 195, 1888.

[3] J. Walker and J. K. Wood, *Journ. Chem. Soc.*, **79**. 21, 1900.

[4] J. H. van't Hoff, *Études*, 112, 1884; T. Ewan's trans., 127, 1896.

[5] V. Meyer and W. Raum, *Ber.*, **28**. 2804, 1895.

[6] J. Dewar, *Chem. News*, **84**. 281, 293, 1901.

[7] M. Berthelot, *Essai de Mécanique Chimique fondée sur la Thermochemie*, Paris, **2**. 93, 1879.

According to the law of mass action the velocity of a chemical reaction, at any moment, is proportional to the amount x of substance actually undergoing transformation at the time t. That is to say—

$$\frac{dx}{dt} = kx\text{; or, } \frac{1}{t}\log\frac{x_0}{x} = k, \quad . \quad . \quad . \quad . \quad (1)$$

where k is the specific velocity of the reaction, constant, provided we keep the temperature constant. If the temperature changes during the reaction, k is no longer constant, but increases proportionally with the temperature. Thus Harcourt and Esson[1] found that in the reaction—

$$H_2O_2 + 2HI = I_2 + 2H_2O,$$

k varied with the temperature, as indicated by the following numbers:—

When $T =$	0,	10,	20,	30,	40,	50° C.;
$k =$	1·00,	2·08,	4·32,	8·38,	16·19,	30·95.

The problem now presented is to find a mathematical expression which will enable k to be calculated when T is known, or enable T to be calculated when k is known. In other words, we want to find what function k is of the temperature. We may put provisionally—

$$k = f'(T),$$

meaning that k is equal to some mathematical expression which will enable k to be calculated when T is known, or *vice versâ*. Hence—

$$\frac{dx}{dt} = xf'(T)\text{; or, } \log\frac{x_0}{x} = f(T),$$

when $f(T)$ is independent of x.

Wilhelmy[2] was probably the first to attempt to express the relation between the temperature and the velocity of a chemical reaction in mathematical symbols. Since that time

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[1] A. V. Harcourt and W. Esson, *Phil. Trans.*, **167.** 117, 1867.

[2] L. Wilhelmy, *Pogg. Ann.*, **81.** 422, 499, 1850; W. Ostwald's *Klassiker*, No. 29.

various formulæ have been proposed by Berthelot, Harcourt and Esson, Warder, Urech, Hood, van't Hoff, and Arrhenius.

Warder[1] employed the empirical formula—

$$(7·5 + k)(62·5 - T) = 521·4,$$

for the rate of hydrolysis of ethyl acetate by sodium hydroxide—

$$CH_3.COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

A comparison of values of k calculated by means of the above formula with the values of k actually observed at different temperatures prove fairly satisfactory.

By multiplying out Warder's formula, dividing, and collecting together the constants under the proper symbols, we get—

$$k = A + BT^2,$$

showing that by accepting the above empirical formula we accept the statement that the specific velocity of the reaction is proportional to the square of the absolute temperature. Warder's formula also agrees with Reicher's[2] experiments.

§ 114. Influence of Temperature on Chemical Equilibria.

If two different reacting substances, A and B, are in equilibrium so that—

$$A \rightleftharpoons B,$$

the quantity of B formed in unit time is equal to the amount of A reformed from B in the same time. The quantity of A transformed in unit time will be represented by k_1C_A, where C_A denotes the concentration of the substance A; the quantity of B transformed in the same time will be k_2C_B, where k_1 and k_2 respectively denote the velocity of transformation of unit mass of A to B, and of B to A. For equilibrium, the velocities of the opposing reactions are the same, or—

$$k_1C_A = k_2C_B; \quad \therefore K = \frac{k_1}{k_2} = \frac{C_B}{C_A}. \quad . \quad . \quad . \quad (3)$$

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[1] R. B. Warder, *Amer. Chem. Journ.*, **3**. 203, 1881; *Ber.*, **14**. 1365, 1881; F. Urech, *Ber.*, **16**. 762, 1883; **17**. 2165, 1884; **20**. 1836, 1887.

[2] L. T. Reicher, *Liebig's Ann.*, **228**. 257, 1885; **232**. 103, 1886.

Since this relation holds good only when the temperature is constant, Nernst proposes to call K the "reaction isotherm."

In his work, *Études de dynamique Chemie*,[1] van't Hoff has deduced the expression—

$$\frac{d \log k_1}{dT} - \frac{d \log k_2}{dT} = \frac{q}{2T^2}, \quad . \quad . \quad . \quad . \quad (4)$$

from the mechanical theory of heat for the relation between k_1 and k_2, and the quantity (q) of heat set free when one gram molecule of A is transformed into B at the absolute temperature,[2] T. "Although this equation," says van't Hoff, "does not directly express the relation between the velocity constants of the two inverse reactions and the temperature, yet it does show that this relation must have the form—

$$\frac{d \log K}{dT} = \frac{P}{T^2} + Q, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where P and Q are constants." The differential coefficient on the left side of (5) refers to the variation of the value of K with temperature. This law of chemical equilibrium, it will be observed, deals only with the end state of a reaction, and it has nothing to say about the time in which that end state will be attained. Although thermodynamics gives us a relation between the state of equilibrium and the thermal value of a reaction, the time factor finds no place in that expression. P is not necessarily constant because the quantity of heat (q) absorbed or evolved in any reaction changes with the temperature. This change, however, is usually so small that we may often assume that P is really constant throughout a small interval of temperature; but the thermal value of some reactions varies considerably with temperature. For example, the thermal value of the reaction—

$$H_2 + I_2 = 2HI,$$

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[1] 126, 1884. A. Dupre has a similar expression in his *Théorie mécanique de la Chaleur*, Paris, 97, 1869.

[2] Instead of the absolute temperature T we may write, $273 + \theta$, where θ denotes ° C.

at 10° is -6100 cal., at 180° $+1883$ cal., and at 520° $+4444$ cal.[1]

Since P is really a function of the temperature, van't Hoff's solution of the problem is still indefinite, owing to the lack of any information as to the form of the function—

$$q = f(T). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Whenever we are in a predicament of this kind, it is customary to write—

$$f(T) = A + BT + CT^2 + DT^3 + \ldots, \quad . \quad (7)$$

where $A, B, C, \ldots$ are constants, because we know that whenever a physical change is represented by such an expression we can generally approximate as close as ever we please to the numerical value of q by increasing the number of terms included in the calculation. The smaller the value of B relative to A, of C relative to B, etc., the less will be the number of terms to be included in the calculation. The numerical values of the constants $A, B, C, \ldots$ are determined from the measurements themselves.[2]

I change the constants $A, B, C, \ldots$ into $a, b, c, \ldots$ after integration so as to avoid the use of numerical coefficients and of negative signs which might enter during integration.

It is interesting to notice that nearly all the empirical formulæ which have been proposed by different investigators to represent the unknown relation between the temperature and the velocity of a chemical reaction can be referred to the formula—

$$\frac{d \log K}{dT} = \frac{A + BT + CT^2 + \ldots}{T^2}; \quad . \quad . \quad (8)$$

which on integration assumes the form—

$$\log K = \frac{a}{T} + b \log T + cT + \ldots + \text{constant}, \quad . \quad (9)$$

where $a, b, c, \ldots$ are constants.

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[1] V. Meyer and M. Bodenstein, *Ber.*, **26.** 1146, 1893; M. Bodenstein, *Zeit. phys. Chem.*, **13.** 56, 1894.

[2] This subject is fully discussed in J. W. Mellor's *Higher Mathematics*.

It may be necessary to again emphasize the fact that equation (7)—and consequently equations (8) and (9)—is only a mathematical fiction, useful, because it renders calculations easy, but it does not necessarily correspond with anything in reality.

We may now apply equations (8) and (9) to particular reactions.

O. Hahn employed the first three terms of the series (7) to represent the influence of temperature upon the reaction between hydrogen and carbon dioxide at high temperatures; and M. Bodenstein[1] to represent the influence of temperature on K in the reaction—

$$H_2 + I_2 \rightleftharpoons 2HI.$$

I here select five measurements to show the result of applying equation (9). The numerical values of the constants were found to be $a = 90{\cdot}48$; $b = -1{\cdot}5959$; $c = 0{\cdot}0055454$; constant $= 2{\cdot}6881$. By introducing these numbers in equation (9), we get an expression which permits us to calculate corresponding values of T and K.

When $T^\circ = 793$, 753, 693, 613, 553°;
K (obs.) = 0·00436, 0·00609, 0·00990, 0·00018, 0·00028;
K (calc.) = 0·00436, 0·00609, 0·00990, 0·00018, 0·00028.

D. M. Kooij[2] omitted all terms succeeding the second, and thus obtained the expressions—

$$\frac{d\log K}{dT} = \frac{A + BT}{T^2}; \text{ or, } \log K = \frac{a}{T} + b\log T + \text{constant}, \quad (10)$$

for the influence of temperature on the decomposition of phosphine and arsine.

Arrhenius[3] only retained the first term of the series (7) and employed the equations—

$$\frac{d\log K}{dT} = \frac{A}{T^2}; \text{ or, } \log k_1 - \log k_0 = a\left(\frac{1}{T_1} - \frac{1}{T_0}\right), \quad (11)$$

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[1] M. Bodenstein, *Zeit. phys. Chem.*, **13**. 56, 1894; **29**. 298, 1899; O. Hahn, *Zeit. phys. Chem.*, **42**. 703, 1903; **44**. 513, 1903; **48**. 735, 1904.

[2] D. M. Kooij, *Zeit. phys. Chem.*, **12**. 155, 1893.

[3] S. Arrhenius, *Zeit. phys. Chem.*, **4**. 226, 1889.

i.e.—

$$k = k_0 e^{-\left(\frac{T_0 - T_1}{T_1 T_0}\right)}. \quad . \quad . \quad . \quad . \quad (12)$$

This equation has given very satisfactory results with a large number of the measurements to which it has been applied. Arrhenius himself compared it with measurements by Hood, Warder, Schwab, and Hecht and Conrad, as well as with the experiments of Urech and of Spohr on the inversion of cane sugar. Price[1] employed it in his work on the hydrolysis of the esters; I. Remsen and E. E. Reid[2] for the hydrolysis of nitrobenzamide by the bases; J. H. Kastle and A. S. Loevenhart[3] for the oxidation of formaldehyde by hydrogen peroxide; Goldschmidt and Reinders[4] for the conversion of diazoamido- into amidoazo-compounds; Ley[5] also obtained very fair results with the transformation of anisynaldoxime acetate into the corresponding nitrile, and for the intramolecular transformation of the acetates of anisynaldoxime, *p*-chlorbenzsynaldoxime, and thiophensynaldoxime.

Harcourt and Esson,[6] in their study of the reaction—

$$H_2O_2 + 2HI = I_2 + 2H_2O,$$

sought the form of the function $f(T)$. They showed that if temperatures be reckoned on the absolute scale, and k_0 be the value of k at T_0, and k the value of the velocity at some other temperature, T, then—

$$\frac{k}{k_0} = \left(\frac{T}{T_0}\right)^B, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where B is a constant to be evaluated from the experimental data. With the subjoined measurements B was found to be 20·38, and, since $k = 0·00433$, when $T = 273$, the values of k

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[1] T. S. Price, *Ofvers. Kongl. Vet.-Ak. Forhand.*, 921, 1899; *Journ. Chem. Soc.*, **79**. 303, 1901.

[2] I. Remsen and E. E. Reid, *Amer. Chem. Journ.*, **21**. 281, 1899.

[3] J. H. Kastle and A. S. Loevenhart, *Amer. Chem. Journ.*, **26**. 539, 1901.

[4] H. Goldschmidt and R. V. Reinders, *Ber.*, **29**. 1369, 1899, 1896.

[5] H. Ley, *Zeit. phys. Chem.*, **18**. 376, 1895.

[6] A. V. Harcourt and W. Esson, *Phil. Trans.*, **157**. 117, 1867.

corresponding with the different values of T can be calculated from the formula—

$$k = 0{\cdot}00433\left(\frac{T}{273}\right)^{20{\cdot}38}$$

The results were as follows :—

When $T =$ 0,	10,	20,	30,	40,	50°;
k (obs.) = 1·00,	2·08,	4·32,	8·38,	16·19,	30·95;
k (calc.) = 1·00,	2·08,	4·21,	8·36,	16·20,	30·80.

The apparent agreement between the observed and calculated values of k is pretty close.

The equation proposed by Harcourt and Esson is a special case of our fundamental equation, obtained by omitting the third and first terms of the series. We thus get—

$$\frac{d \log K}{dT} = \frac{B}{T}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which, on integration, assumes the form indicated in (13).

Van't Hoff's equation [1]—

$$\frac{d \log K}{dT} = \frac{A}{T^2} + C, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or, integrated—

$$\log K = \frac{a}{T} + cT + \text{constant}, \quad . \quad . \quad . \quad (16)$$

is obviously a special case of the fundamental equation obtained by putting $B = 0$. Schwab [2] applied this equation to the transformation of dibromosuccinic acid into bromomaleïc acid; and to the reaction between sodium monochloroacetate and sodium hydroxide; R. Wegscheider [3] to the decomposition of the hydrochloride of methyl ether; J. Spohr [4] to the inversion of cane sugar; and G. Buchböck used it to represent his

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[1] J. H. van't Hoff, *Études*, 112, 1884.

[2] L. C. Schwab, *Inaug. Diss.*, Amsterdam, 1883; J. H. van't Hoff's *Études*, 113, 1884.

[3] R. Wegscheider, *Sitz. d. Wien. Akad.*, **108**. ii*a*, 119, 1899.

[4] J. Spohr, *Zeit. phys. Chem.*, **2**. 194, 1888.

results on the influence of temperature on the decomposition of carbonyl sulphide by water.[1]

Once more returning to the original equation, if we neglect the first two terms of the series, we get—

$$\frac{d \log K}{dT} = C, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which on integration becomes—

$$\log K = cT + \text{constant.}$$

If we take natural logarithms, this may be written—

$$k = k_0 e^{cT}, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

a formula employed by Pendlebury and Seward[2] in their study of the interaction of hydrogen iodide and hydrogen chlorate in the presence of potassium iodide; by Tammann[3] to represent the velocity of crystallization at different temperatures; by Reid[4] to represent the hydrolysis of nitrobenzamides; and by Veley[5] for the reaction between nitric acid and copper.

If common logarithms be employed, expression (18) becomes—

$$k = k_0 \times 10^{cT}, \quad . \quad . \quad . \quad . \quad (19)$$

which was used by Bugarszky[6] to represent the influence of temperature on the reaction between bromine and ethyl alcohol; and by Hecht and Conrad[7] in their work on the action of alkyl iodides on sodium alkylates.

If we take logarithms to some other base, say a, we get—

$$k = k_0 a^{cT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The equation proposed by Berthelot[8] in 1862, for the action

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[1] G. Buchböck, *Zeit. phys. Chem.*, **23**. 123, 1897.

[2] W. H. Pendlebury and M. Seward, *Proc. Roy. Soc.*, **45**, 396, 1889.

[3] G. Tammann, *Wied. Ann.*, **62**. 292, 1897; S. Arrhenius, *Zeit. phys. Chem.*, **28**. 317, 1899.

[4] I. Remsen and E. E. Reid, *Amer. Chem. Journ.*, **21**. 281, 1899.

[5] V. H. Veley, *Journ. Chem. Soc.*, **54**. 200, 361, 1889.

[6] S. Bugarszky, *Zeit. phys. Chem.*, **42**. 545, 1903.

[7] W. Hecht and M. Conrad, *Zeit. phys. Chem.*, **3**. 450, 1889.

[8] M. Berthelot, *Ann. Chim. Phys.* [3], **66**. 110, 1862.

of acetic acid upon ethyl alcohol; by Spring[1] for the dissolution of marble in mineral acids; and by Hood[2] for the rate of oxidation of ferrous sulphate by potassium chlorate, are modifications of (20). In this latter case it was found that—

$$k = k_0(1{\cdot}093)^T,$$

agreed fairly well with the experimental work.

These expressions are but a few out of the infinite number of equally effective formulæ which might be proposed. Those mentioned above are temporary substitutes applicable to special cases. We shall only be satisfied when the formula selected can be logically deduced from known laws of chemical phenomena. The generalization or law connecting the thermal value of a reaction with the temperature has yet to be discovered. In the absence of any better guide, we have sought an expression which would serve, for the time being, to represent the numerical relation between T and K and involve the least trouble in calculation. Even supposing that we were able to formulate the theoretical relation between the velocity of a chemical reaction and the temperature, that would not always be sufficient to give a satisfactory agreement with experimental results because many other influences materially affect any measurement we might make of the relations between temperature and the velocity of a channel reaction. There may be, for example, a variation of the viscosity of the solution with temperature, and disturbing effects due to secondary reactions inappreciable at lower temperatures.

§ 115. Arrhenius' Views.[3]

Attempts have been made to deduce the velocity of a reaction from the number of collisions which take place between the reacting molecules on the assumption that the molecules of a liquid or gas are always in a state of active motion. Now,

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[1] W. Spring, *Zeit. phys. Chem.*, **1**. 209, 1887.

[2] J. J. Hood, *Phil. Mag.* [5], **20**. 323, 1885.

[3] S. Arrhenius, *Zeit. phys. Chem.*, **4**. 226, 1889; **28**. 317, 1899.

the velocity of inversion of cane sugar increases 15 per cent. per degree rise of temperature. This increase is not likely to be due to the increased number of collisions between the molecules of cane sugar and the catalyzing acid because the increase in the number of collisions of the molecules of a gas is less than 1 per cent. per degree rise of temperature,[1] and we can safely assume that the frequency of collision of the molecules in a solution will be of the same order of magnitude.

Nor will the decrease in the viscosity of the solution with rising temperature explain the great change of velocity with temperature because the viscosity of the solution only increases by 2 per cent. per degree.

The increase of the velocity of inversion per degree rise of temperature is less at high than it is at low temperature. For example, the reaction velocity is twice as great at 6° as it is at 0°, 2^2 times as great at 12° as it is at 0°, and about 2^5 times as great at 30° as it is at 0°.

An exponential increase of any physical property with rise of temperature is very rare. The increase of the vapour pressure of a liquid with rise of temperature is an exception, and, in consequence, Arrhenius concludes that the increase of the velocity of a chemical reaction with temperature cannot be explained by any change in the physical property of the solution with temperature, and he puts forward the hypothesis that cane sugar contains two kinds of molecules—active and passive. The former can alone be hydrolyzed by the acid, while the latter are not susceptible to attack. The amount of "active" cane sugar in solution is supposed to be very small in comparison with the "inactive" sugar. In order to explain the influence of temperature on the rate of inversion, Arrhenius still further assumes that the quantity of "active cane sugar" must increase very rapidly—about 12 per cent. per degree rise of temperature—and this at the cost of the inactive sugar. The transformation of active into inactive sugar is said to be

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[1] O. E. Meyer's *Kinetische Theorie der Gase*, Breslau, 1877; R. E. Baynes' trans., 168, 1899; R. B. Warder, *Proc. Amer. Assoc. Adv. Science*, **30**. 1, 1881.

due either to a rearrangement of the atoms or to the introduction of water into the molecule of inactive cane sugar.

A state of equilibrium between the active and the inactive molecules of cane sugar will be attained when the respective concentrations C_a and C_i are—

$$C_a = KC_i\,;$$

and from van't Hoff's equation (4)—

$$\frac{d\log K}{dT} = \frac{q}{2T^2}\,;\ K_1 = K_0 e^{\frac{q}{2}\left(\frac{T_1-T_0}{T_1T_0}\right)},$$

where q denotes the thermal value of the transformation inactive into active cane sugar, and K_1 and K_0 are the equilibrium constants at the two different temperatures. If the velocities of the reactions at the two temperatures be v_1 and v_0, then it is supposed that—

$$v_1 = v_0 e^{\frac{q}{2}\left(\frac{T_1-T_0}{T_1T_0}\right)}\,;$$

or q is about 25,600 calories per gram molecule of inactive sugar. Arrhenius also thinks that Ericson-Aúren's[1] experiments on the rate of dissolution of zinc in dilute acids prove that the heat of transformation of inactive into active molecule is zero because the velocity of reaction is not affected by changes of temperature.

§ 116. Relation between Equilibrium Constant and the Thermal Value of a Reaction.

Let us now return to van't Hoff's equation, (4) p. 387, and again apply it to some reaction in which the products of the reaction (B) interact with one another to form the original substance (A). That is to say, $A \rightleftharpoons B$. When a state of equilibrium is reached—

$$k_1C_A = k_2C_B\,;\ \text{or, } K = \frac{k_1}{k_2} = \frac{C_B}{C_A},$$

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[1] T. Ericson-Aúren, *Zeit. anorg. Chem.*, **18**. 83, 1898; **27**. 209, 1901; T. Ericson-Aúren and W. Palmaer, *Zeit. phys. Chem.*, **39**. 1, 1901.

as we have seen before. q, be it remembered, denotes the heat of formation of the system A at constant volume.

A very small change of temperature will cause a small change in the numerical value of the coefficient K. Consequently there will be a change in the relative composition of the substances taking part in the reaction. Either B will react to form more of A, or A will react to form more of B. The magnitude of the numerical coefficient K indicates how much faster the reaction proceeds from left to right (formation of B) than from right to left (formation of A).

Let K_1 and K_2 represent the equilibrium coefficients of the reaction at the respective temperatures T_1 and T_2. Let T_2 be the greater. Although we do not know accurately the relation between the thermal value (q) of the reaction and the temperature (T), yet we do know that if T_1 and T_2 are sufficiently close together, q may be regarded as a constant. In that case we get, by integration of van't Hoff's equation—

$$\log K_2 - \log K_1 = \frac{q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \quad . \quad . \quad (21)$$

Consequently, if values of K are known for two temperatures, T_1 and T_2, the heat of formation of A at constant volume[1] may be readily calculated.

For the sake of illustration take an old example, the dissociation of solid ammonium hydrosulphide into equal volumes of hydrogen sulphide and ammonia gases under the influence of heat—

$$NH_4HS \rightleftharpoons H_2S + NH_3.$$

The two gases on the right have always the same concentration, C. Hence—

$$K_1 = C_1^2; \text{ and } K_2 = C_2^2. \quad . \quad . \quad . \quad . \quad (22)$$

The partial pressures of the two gases will also be the same. If p denotes the total pressure of the mixed gases, the partial pressure of each gas will be $\frac{1}{2}p$. Since the volume of any

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[1] That is the same number, but opposite sign, as the heat of formation of B.

mass of a gas is inversely as the concentration, it follows, from the well-known gas equation—

$$pv = RT; \ \frac{p}{C} = R'T; \ \therefore C_1 = \frac{p_1}{R'T_1}; \text{ and } C_2 = \frac{p_2}{R'T_2},$$

where R' is a constant.

$$\therefore \frac{C_1}{C_2} = \frac{p_1T_2}{p_2T_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

By substituting the results of (22) and (23) in (21), we get—

$$2 \log \frac{p_1T_2}{p_2T_1} = \frac{q}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \quad . \quad . \quad . \quad (24)$$

Hence q can be calculated when p_1, p_2, and T_1, T_2 are known. Isambert[1] found that at 9·5° C., $p_1 = 175$ mm.; and at 25·1° C., $p_2 = 501$. Hence—

$$q = 4 \log \frac{175 \times 298{\cdot}1}{501 \times 282{\cdot}5} \times \frac{298{\cdot}1 \times 282{\cdot}5}{282{\cdot}5 - 298{\cdot}1} = -21550 \text{ cal.}$$

The heat of sublimation (dissociation) of a gram-molecule, as recorded by different observers, varies between 22,620 and 22,990 calories under constant pressure (that is, variable volume).[2] But since NH_4HS is a solid, and the products of its dissociation are gases, part of the heat of dissociation must be consumed in the work of expansion. From § 7 we can see that the work of expansion of the gases is—

$$W = p_1v_1 + p_2v_2 = RT_1 + RT_2 = 2(282{\cdot}5 + 298{\cdot}1);$$
$$\therefore W = 2 \times 580{\cdot}6 = 1161{\cdot}2 \text{ cal.}$$
$$\therefore q = -21550 + 1161 = -21639 \text{ cal.}$$

The agreement between the observed (21,550) and the theoretical (21,639) values is thus satisfactory.

From equation (21) it is easy to see that the sign of ($\log K_2 - \log K_1$) depends on the sign q, because, if the temperature T_2 is greater than T_1, the term in brackets will always be positive. Hence, if q is positive, ($\log K_2 - \log K_1$) will

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[1] F. Isambert, *Compt. Rend.*, **92**. 919, 1881. Do not forget that $T° = 273 + \theta°$ C.

[2] A. Horstmann, *Ber.*, **14**. 1242, 1881.

always be positive; if q is negative, ($\log K_2 - \log K_1$) will be negative; and if q be zero, ($\log K_2 - \log K_1$) will be zero.

Case I.—If q be positive, the formation of A will be attended with an evolution of heat, and therefore the formation of B will be attended by an absorption of heat. If a reaction is endothermal in one direction, it is exothermal in the opposite direction.[1] In the reactions—

$$CaO + CO_2 \rightleftharpoons CaCO_3 + 42{,}500 \text{ cal.};$$
$$2NO_2 \rightleftharpoons N_2O_4 + 2500 \text{ cal.};$$
$$2HI \rightleftharpoons I_2 + H_2 + 6100 \text{ cal.},$$

q is positive because the formation of calcium carbonate and N_2O_4, and the decomposition of hydrogen iodide, are attended by an evolution of heat.

When q is positive, K_2 will be greater than K_1. In other words, with rising temperature, the products on the left side of the equation will increase. In particular, the heat of formation of N_2O_4 is positive. Hence, with rising temperature, NO_2 will be formed at the expense of N_2O_4; so also hydrogen iodide will be formed at the expense of the elementary constituents iodine and hydrogen.

Hence the law: *If the passage from* A *to* B *is accompanied by an evolution of heat, a rise of temperature will cause an increase in the quantity of* A. — i.e. a, [illegible] of

This law, it may be added, is true for physical as well as for chemical changes. For example, the condensation of water—

$$H_2O \text{ (gas)} \rightleftharpoons H_2O \text{ (liquid)} + 526 \text{ cal.}$$

is attended by an evolution of heat. Hence an increase of temperature causes an increase in the quantity of steam.

Case II.—If q be negative, the formation of A will be attended by an absorption of heat, and the formation of B by an evolution of heat. When q is negative, K_2 will be less than K_1. Such reactions are—

$$CaCO_3 \rightleftharpoons CaO + CO_2 - 42{,}500 \text{ cal.};$$
$$N_2O_4 \rightleftharpoons 2NO_2 - 2500 \text{ cal.};$$
$$I_2 + H_2 \rightleftharpoons 2HI - 6100 \text{ cal.}$$

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[1] "Endothermal" and "exothermal" are two terms introduced by Berthelot, respectively denoting the absorption and evolution of heat.

Consequently the products on the right side of the equation will increase with rising temperature.

It must be remembered that the system is supposed to be in a state of equilibrium before the influence of temperature is investigated. Of course, if we start with the elements hydrogen and oxygen, the effect of a gradual increase of temperature will be to set up a state of equilibrium where the rate of decomposition of steam is equal to the rate of combination of hydrogen and oxygen gases. When equilibrium is once attained, a further rise of temperature will increase the amount of hydrogen and oxygen at the expense of the water vapour.

Hence the law: *If the passage of* A *to* B *is accompanied by an absorption of heat, a rise of temperature will cause decrease in the quantity of* A.

The transformation of sugar into starch is an endothermal process. Hence a rise of temperature will favour the conversion of sugar into starch, and a reduction of temperature will favour the regeneration of sugar from starch. Overton[1] found that starch of potatoes passes into sugar below 5°, while above this temperature the sugar is transformed into starch. Sugar is more prevalent in the leaves of an evergreen plant out in the cold than when the plant has been in a warm room for a short time. Autumn leaves also contain more sugar than in summer, when the temperature is higher.

Case III.—If q be zero, neither the formation of A nor of B will be accompanied by any thermal change. Hence, $\log K_2 - \log K_1$ will be zero, or K_1 will be equal to K_2. So long as $q = 0$, a rise of temperature will not alter the relative amounts of A and B in the system. Berthelot[2] found that the condition of equilibrium—

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O,$$

is not accompanied by any perceptible thermal change. This is in harmony with the fact that a change of temperature has

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[1] E. Overton, *Jahrb. wiss. Bot.*, **33**. 171, 1899.

[2] M. Berthelot and Péan de St. Gilles, *Ann. Chim. Phys.* [5], **14**. 437, 1878; M. Berthelot, *Bull. Soc. Chim.* [2], **31**. 352, 1879.

practically no influence upon the value of K. Thus, Berthelot and Gilles obtained the following results :—

Temp. ° C.	Ethyl acetate formed, per cent.	Time of heating.
10	65·2	16 years.
100	65·6	A very long time.
170	66·5	42 hours.
200	67·3	24 hours.
220	66·5	38 hours.

A rise of temperature, within the limits named, has no influence upon the condition of equilibrium. The hydrolysis of urea hydrochloride, and the transformation of urea into ammonium cyanate, are not influenced by variations of temperature between 25° and 40°.[1]

We are here discussing the state of equilibrium. The velocity of the opposing reactions may be accelerated by a rise of temperature, but if both are affected to the same extent the equilibrium will still remain unaffected.

Equilibrium is attained with optically active isomers when the inactive mixture is formed. If one isomer be present in larger quantity than the other, the one will always be converted into the other until equal quantities of each isomer have been formed. The state of equilibrium, once attained, will not be affected by variations of temperature. A mixture of optical isomers which is inactive at ordinary temperatures will remain inactive at all other temperatures.[2] This has been verified in the case of anti- and syn-benzaldoximes, and of anti- and syn- para-anisaldoximes.[3]

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[1] J. Walker and J. K. Wood, *Journ. Chem. Soc.*, **83**. 484, 1903; J. Walker and F. J. Hambly, *ib.*, **67**. 746, 1895; C. E. Fawsitt, *Zeit. phys. Chem.*, **41**. 601, 1902; J. Walker, *ib.*, **42**. 207, 1902.

[2] J. H. van't Hoft's *Die Lagerung der Atome in Raume*, Braunschweig, 33, 1894; A. Eiolart's trans., 49, 1898.

[3] F. E. Cameron, *Journ. Phys. Chem.*, **2**. 409, 1898; H. R. Carveth, *ib.*, **3**. 437, 1899.

Hence the law: *If a reaction takes place without any thermal change, a rise of temperature will have no influence on the relative proportions of* A *and* B.

Collecting these three deductions into one generalization, *any change of the temperature of a system in a state of equilibrium is followed by a reverse thermal change within the system;* introduced into chemistry by van't Hoff,[1] in 1884, as **the principle of mobile equilibrium.**

§ 117. The Principle of Maximum Work.

We see that change of temperature will disturb the state of equilibrium of a system and induce a transformation whose thermal sign is opposed to the change of temperature. Cooling favours a reaction accompanied by an evolution of heat; and, conversely, heating favours a reaction accompanied by an absorption of heat. We should therefore expect substances like calcium carbonate, water, and hydrogen chloride, which are formed with an evolution of heat, to predominate at ordinary temperatures which are only about 300° above absolute zero. Consequently, we infer that the majority of substances which exist at the relatively low temperature of our atmosphere have been formed with an evolution of heat. Hence those chemical changes which take place at ordinary temperatures will, in general, be accompanied by an evolution of heat; and, conversely, reactions which take place at high temperatures will generally be accompanied by an absorption of heat. At ordinary temperatures the exothermal reaction—

$$2H_2 + O_2 = 2H_2O + 22000 \text{ cal.},$$

is practically complete; but the reverse endothermal change—

$$H_2O = 2H_2 + O_2 - 22000 \text{ cal.},$$

obtains above 1000°.

It is therefore easy to understand how one of the pioneer

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[1] J. H. van't Hoff, *Études*, 161, 1884.

investigators in thermal chemistry, J. Thomsen,[1] was led to consider that "every chemical change is accompanied by an evolution of heat," and M. Berthelot[2] to infer that "every chemical change which takes place without the aid of external energy tends to the production of that which is accompanied by the development of the maximum amount of heat"—the so-called "principle of maximum work," or the "theorem of the necessity of reactions."

In order to reconcile these statements with reactions which are known to be accompanied by the absorption of heat, Thomsen and Berthelot were compelled to introduce assumptions of the most unsatisfactory kind. The principle of maximum work is not in agreement with transformations which take place in two opposing directions, such as the reaction investigated, strangely enough, by Berthelot himself, namely, the formation of esters by the action of acids on alcohol. Heat is absorbed by the change in one direction, and heat is evolved by the reverse change. According to Berthelot's principle, the reaction ought to go completely to an end, and a state of mobile equilibrium between the original and the final products of the reaction should be impossible. Thomsen, too, has shown that in aqueous solution both the reactions—

$$\tfrac{1}{2}Na_2SO_4 + HNO_3 = \tfrac{1}{2}NaHSO_4 + NaNO_3 - 1{\cdot}752 \text{ cal.};$$
$$NaNO_3 + \tfrac{1}{2}H_2SO_4 = \tfrac{1}{2}NaHSO_4 + HNO_3 + 0{\cdot}288 \text{ cal.},$$

take place, and that although the one reaction is endothermal, and the other exothermal, the same final equilibrium is attained whether we start with the first or with the second system.

Notwithstanding the fact that Berthelot himself[3] has now

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[1] J. Thomsen, *Pogg. Ann.*, **88**. 349, 1853; **90**. 261, 1853; **91**. 83, 1854; **92**. 34, 1854; *Ber.*, **6**. 423, 1873; *Thermochemische Untersuchungen*, Leipzig, **1**. 12, 1880.

[2] M. Berthelot, *Ann. Chim. Phys.* [4], **18**. 103, 1869; *Compt. Rend.*, **71**. 303, 1870; *Bull. Soc. Chim.* [2], **19**. 485, 1873; *Essai de Mécanique Chimique*, Paris, **1**. xxviii., and **2**. 422, 1869.

[3] M. Berthelot, *Compt. Rend.*, **118**. 1378, 1894; P. Duhem, *Thermochemie à propos d'un livre recent de M. Marcelin Berthelot*, Paris, 1897.

repudiated the general accuracy of the principle of maximum work, this generalization, in spite of its imperfections, is undoubtedly in conformity with the majority of chemical reactions at ordinary temperatures.

Van't Hoff's relation between the equilibrium coefficient and the thermal value of a reaction is a necessary consequence of the laws of mass action and of the mechanical theories of heat. It is therefore as unimpeachable and as general as the laws upon which it is founded. In order to find under what conditions the Thomsen-Berthelot principle may be true, it is necessary to find under what conditions (i.) all reactions will be complete, and (ii.) only those reactions will occur which are attended by an evolution of heat.

Let the formation of one substance, say A, be attended by the evolution of heat, and let us find what conditions must be satisfied in order that the heat of formation of B may be zero. Since—

$$K = \frac{C_B}{C_A}; \quad \frac{d \log K}{dT} = \frac{q}{2T^2}; \quad \log K = -\frac{q}{2T} + \text{constant}; \quad (25)$$

if B is zero, the concentration $C_B = 0$, hence $K = 0$. When $K = 0$, T must also be zero, because $\log K = -\infty$. This means that the generalization of Thomsen and Berthelot can only be true at absolute zero. Hence the necessary emendation: *At absolute zero every chemical change will be accompanied by an evolution of heat.*

Only those chemical systems which have been formed with an evolution of heat will be in equilibrium at absolute zero, and only those physical states of a substance which have been formed with an evolution of heat will be in stable equilibrium at absolute zero.

§ 118. Change of the Thermal Sign of a Reaction with Temperature.

If we adopt an expression like—

$$q = a + bT + cT^2, \quad . \quad . \quad . \quad . \quad (26)$$

for the relation between the thermal value of a reaction and the temperature, we can easily find what values of T will make q zero.[1] When $q = 0$—

$$T = \frac{-b + \sqrt{b^2 - 4ac}}{2c}; \text{ or, } T = \frac{-b - \sqrt{b^2 - 4ac}}{2c}. \quad (27)$$

The thermal value of the reaction—

$$CO_2 + H_2 = CO + H_2O - q,$$

is given by the expression—

$$q = -10232 + 0{\cdot}1685T + 0{\cdot}00101T^2,$$

whence from (27), $T = 3100°$; or 2827° C. At 15° C., Berthelot found that $q = -10100$ cal. From Horstmann's[2] experiments, at about 2700° C., $q = 0$. Hence it follows that the thermal value of this reaction gradually increases with rising temperature until q becomes zero, after that q assumes a negative value.

What will be the effect on the constant K? When the system A = B is in equilibrium—

$$K = \frac{k_2}{k_1} = \frac{C_A}{C_B} = \frac{C_{CO_2}C_{H_2O}}{C_{CO_4}C_{H_2}}.$$

The greater the value of K the greater the amount of A relative to B. Of two values of K, say K_1 and K_2, for the respective temperatures T_1 and T_2, that will be the greater for which A preponderates. It has also been shown that—

if q is positive, $K_2 > K_1$;
if q is zero, $K_2 = K_1$;
if q is negative, $K_2 < K_1$.

As the temperature rises q decreases in value; when q decreases, K_2, which determines how much faster the reaction proceeds from B to A than from A to B, also decreases. When $q = 0$, the accumulation of A in the system ceases, and when q assumes a negative value, B begins to accumulate in the system.

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[1] J. W. Mellor's *Higher Mathematics*, § 156.

[2] A. Horstmann, *Liebig's Ann.*, **190**. 228, 1878.

Horstmann found that the value of K when $q = 0$ was about 6·25. Substituting the above value of q in equation (4), and integrating, we get[1]—

$$\log K = \frac{5116}{T} + 0{\cdot}08425 \log T + 0{\cdot}000505 - 2{\cdot}1275.$$

By plotting corresponding values of K and T we get the curve shown in Fig. 28. The interpretation follows directly from § 104. We are dealing with Case I. on one part of the curve, and with Case II. on another part of the curve. Up to 2825° the amount of CO is increasing, attains a maximum at 2825°, and then begins to diminish. The dotted points represent the results of Horstmann's experiments.

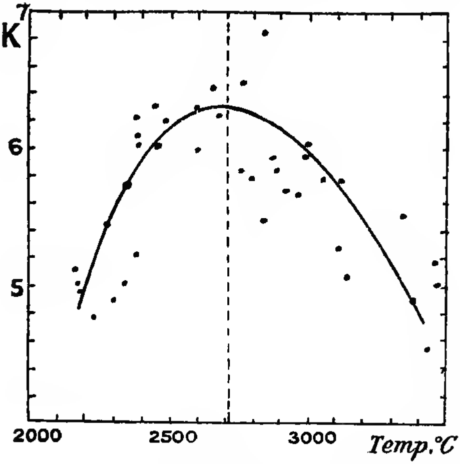

FIG. 28.

We can now distinguish two types of chemical changes.

I. The reaction is endothermal at a low temperature, and exothermal at a higher temperature. According to Bodenstein

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[1] The integration constant is evaluated by putting $K = 6{\cdot}25$ when $T = 3100$.

and Meyer,[1] the heat of formation of hydrogen iodide is −6100 cal. at 18° C., and −400 cal. at 186°. Rise of temperature therefore favours the production of hydrogen iodide. This is found to continue until the temperature 320° is attained. Above that temperature the amount of hydrogen iodide decreases. Here are a few of Bodenstein's measurements made in the vicinity of the point of maximum amount of hydrogen iodide—

When θ° = 290, 310, 320, 340, 350, 394, 448;
% of HI = 83·6, (83·3), 84·0, 82·9, 82·4, 80·5, 78·6.

The number for 310° is a bit doubtful. The plotting of these two variables gives a curve resembling that in Fig. 28. This result is in harmony with the preceding observation as to the influence of temperature on the thermal value of the reaction.

Hydrogen combines with selenium at temperatures between 150° and 520°. Combination increases with rising temperature up to 520°, beyond that temperature hydrogen sulphide begins to dissociate.[2]

Hydrogen combines with sulphur at temperatures between 200° and 358°, the amount of hydrogen sulphide steadily increasing as the temperature rises. At 358° combination is complete. At higher temperatures the gas dissociates, and the higher the temperature the greater the dissociation.[3]

Hydrogen peroxide is also endothermal, and in consequence it should become more stable at higher temperatures.[4] The transformation of α- into β- benzil-*o*-carboxylic acid[5] presents similar phenomena. The yellow variety becomes more

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[1] M. Bodenstein and V. Meyer, *Ber.*, **26**. 1146, 1893; M. Bodenstein, *Zeit. phys. Chem.*, **29**. 295, 1899.

[2] A. Ditte, *Compt. Rend.*, **74**. 980, 1872; *Annales de l'Ecole normale superieure* [2], **1**. 293, 1872; C. Fabre, *Ann. Chim. Phys.* [6], **10**. 482, 1887; H. Pélabon, *Zeit. phys. Chem.*, **26**. 657, 1898; M. Bodenstein, *ib.*, **29**. 429, 1899.

[3] H. Pélabon, *Mem. de la Soc. des Sciences phys. et nat. de Bordeaux* [5], **3**. 257, 1898; M. Bodenstein, *Zeit. phys. Chem.*, **29**. 315, 1899.

[4] W. Nernst, *Zeit. phys. Chem.*, **46**. 720, 1903; *Boltzmann's Festschrift*, 904, 1904.

[5] C. A. Soch, *Journ Phys. Chem.*, **2**. 364, 1898.

stable above 65°, but above 132° the white modification predominates. Silver oxide Ag_2O, though unstable below 100°, is in a state of false equilibrium; above 100° decomposition takes place. But then silver oxide is formed when silver is heated in the oxyhydrogen flame above the temperature of volatilization of silver.[1]

Klein has shown that the reaction—

$$PbI_2 + K_2SO_4 \rightleftharpoons PbSO_4 + 2KI,$$

below 8°, is an endothermal process, while above this temperature the reaction takes place with an evolution of heat.[2] Similarly, Knüpffer[3] has shown that the thermal value of the reaction—

$$TlCl + KCNS \rightleftharpoons TlSCN + KCl,$$

has a maximum at 32°.

II. The reaction is exothermal at a low temperature and endothermal at a higher temperature. Silicon hexachloride, Si_2Cl_9 is a colourless volatile liquid, which boils without decomposition at 146°. Troost and Hautefeuille[4] prepared the compound by passing the vapour of silicon tetrachloride over metallic silicon heated to whiteness in a porcelain tube. It was found that silicon[5] was deposited on the cooler part of the tube, although the temperature was not sufficient to volatilize the silicon itself; the deposit must therefore have been formed by the decomposition of the hexachloride. Vapour density determinations subsequently showed that the gas is stable at temperatures below 350° and above 1000°, but dissociation

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[1] H. St. Claire Deville and H. Debray, *Ann. Chim. Phys.* [3], **56.** 413, 1859.

[2] A. Klein, *Zeit. phys. Chem.*, **36.** 360, 1901.

[3] C. Knüpffer, *Zeit. phys. Chem.*, **26.** 255, 1898; G. Bredig, *Zeit. Elektrochem.*, **4.** 544, 1898.

[4] L. Troost and P. Hautefeuille, *Compt. Rend.*, **73.** 443, 1871; **84.** 946, 1877; *Ann. Chim. Phys.* [5], **9.** 70, 1876.

[5] For the volatilization of oxides and sulphides of zinc and cadmium, in presence of their respective metals, see H. St. Claire Deville, *Ann. Chim. Phys.* [3], **43.** 7, 477, 1855; with L. Troost, *ib.* [4], **5.** 118, 1865; A. N. Morse and J. White, jr., *Amer. Chem. Journ.*, **11.** 258, 348, 1889.

begins at 350°, and attains a maximum at 800°, when it is completely dissociated into $SiCl_4$ and Si. If the temperature be quickly raised beyond 1000°, the dissociation at the intermediate temperature does not become apparent. Silicon hexafluoride behaves in a similar manner.

It is easy to interpret these observations in the light of what precedes. The curves *AB* and *CD* (Fig. 29) show the relation between the temperature and the percentage amount of silicon hexachloride actually present when equilibrium is attained. As the temperature rises to 800° the compound dissociates, because the heat of formation of silicon hexachloride is exothermal; above 1000° the raising of the temperature brings about a combination of silicon hexachloride, because the heat of formation is endothermal.

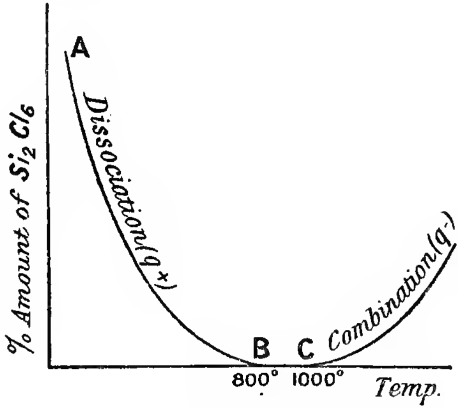

FIG. 29.

A chemical compound may appear to be stable at a high and at a low temperature; at intermediate temperatures it may appear to be unstable. Thus Dewar[1] inferred that ozone

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[1] L. Troost and P. Hautefeuille, *Compt. Rend.*, **84**. 946, 1877; J. Dewar, *Year-book of the Royal Inst.*, 559, 1887-89; W. N. Warren, *Chem. News*, **77**. 192, 1898; O. Brunck, *Ber.*, **26**. 1790, 1893; C. Zengelis, *Zeit. phys. Chem.*, **46**. 287, 1903. It must be added that J. K. Clement's experiments (*Drude's Ann.*, **14**. 334, 1904) lead him to the conclusion that

has "two centres of stability," one above the melting point of platinum, and the other at ordinary temperatures. Between 200° and 1000° ozone is decomposed; below and above these limits ozone appears to be relatively stable. Ruthenium tetroxide,[1] also, is stable at ordinary temperatures, and above a white heat: it is unstable at intermediate temperatures. Similarly, Meyer and Langer[2] have stated that chlorine rapidly attacks platinum at temperatures below 300° and above 1300°, and that in the interval there is no visible action showing the instability of the platinum chloride between these temperatures.[3]

Thus it would appear that the higher temperature to which an exothermal compound is heated, the more unstable it becomes, because the absorption of heat is necessary for its dissociation; conversely, if endothermal compounds are heated, the more stable they become, because the absorption of heat is necessary for their combination.

"It is generally believed that at a high temperature, such as that which exists in the electric arc, and in the sun's atmosphere, all compounds must be dissociated into their elements. This view is certainly not justified. On the contrary, what we actually know about the stability of compounds is that *all compounds which are formed with an absorption of heat become more stable with rising temperature, and vice versâ.* Owing to the fact that the majority of compounds known to us are formed from their elements with the evolution of heat, and, in consequence, become more unstable as the temperature rises, it has been concluded that this is generally the case.

"most of the recorded observations of the formation of ozone at high temperatures are in reality due to the formation of small quantities of nitrogen oxides."

[1] H. Debray and A. Joly, *Compt. Rend.*, **106**. 100, 1888; H. St. Claire Deville and H. Debray, *Ann. Chim. Phys.* [5], **4**. 537, 1875.

[2] V. Meyer and C. Langer, *Ber.*, **15**. 2769, 1882.

[3] T. Curtius and H. Schulz, *Journ. prakt. Chem.* [2], **42**. 521, 1890, obtained values for the vapour density of hydrazine hydrate which seemed to show that the hydrate is unstable below 183°, and stable above this temperature; but A. Scott—*Journ. Chem. Soc.*, **85**. 913, 1904—has shown that the alleged recombination of the products of the dissociation of the hydrate does not occur at higher temperatures.

But if we remember that cyanogen and acetylene—two compounds formed with the absorption of energy—are readily formed in quantity at the high temperatures of the blast furnace, and in the arc light, we see the possibility that spectra occurring at high temperatures may belong to compounds which exist only at elevated temperatures."[1]

Since all reactions are exothermal at absolute zero, and some, endothermal at atmospheric temperatures, become exothermal at more elevated temperatures, it has been suggested that endo- and exo- thermality runs in cycles[2]—

$$\text{Exo-} \rightarrow \text{endo-} \rightarrow \text{exo-} \rightarrow \text{endo-} \rightarrow \ldots \text{thermality.}$$

The distinction between endo- and exo- thermal reactions, though convenient, is arbitrary. It is all a question of temperature. A combination may be exothermal at one temperature, and endothermal at another. If the prevailing temperature had been a few thousand degrees higher than what it is, Thomsen's empirical law might have been reversed so as to read, "every chemical change is accompanied by the absorption of heat," and Berthelot's principle of maximum work would have been transposed in a corresponding manner.

§ 119. Passive Resistance.

As a general rule, the velocity of any reaction increases continually with the rise of temperature. If we plot the experimental results of a number of different reactions, or draw graphs for van't Hoff's equation, we shall get a series of curves all of which apparently converge towards a zero velocity at absolute zero, as shown in Fig. 30. It is therefore inferred that a reaction need not absolutely cease at any temperature short of absolute zero. If a reaction goes on at one temperature, it will go at any other temperature, but with a different velocity.

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[1] From W. Ostwald's address, "Fortschritte der physikalischen Chemie in den letzten Jahren," at the annual meeting of the German Association of Science, at Halle, Sept. 24, 1891; W. Ostwald's *Abhandlungen und Vorträge*, Leipzig, 41, 1904.

[2] G. Martin, *Chem. News*, **81**. 301, 1900.

According to Pélabon, hydrogen does not act upon selenium at temperatures below 250°;[1] sulphuric acid, according to Pictet,[2] does not act upon sodium hydroxide at −125°, but as the temperature rises to −80°, reaction sets in; sulphuric acid does not react with potassium hydroxide below −90°; concentrated ammonia and sulphuric acid are inert below −65°; at −120° neither hydrochloric nor sulphuric acid acts upon blue litmus, but hydrochloric acid does begin to act at −110°, and sulphuric acid at −105°.

We are not to conclude that chemical action absolutely ceases at these temperatures. The reaction may be going very slowly. According to Gore,[3] liquid carbon dioxide only acts very slowly upon metallic potassium or sodium, and Besson and Dorn and Völlmer [4] find that a solution of hydrogen chloride

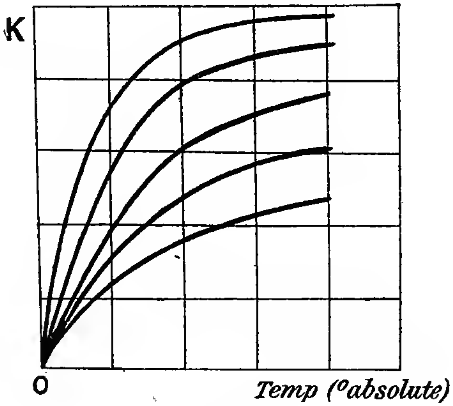

FIG. 30.

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[1] H. Pélabon, *Mem. Soc. Sciences Phys. et Nat. de Bordeaux* [5], **3.** 141, 1898.

[2] R. Pictet, *Compt. Rend.*, **115.** 814, 1892.

[3] G. Gore, *Phil. Trans.*, **151.** 83, 1861; *Journ. Chem. Soc.*, **15.** 103, 1862.

[4] A. Besson, *Compt. Rend.*, **124.** 763, 1897; E. Dorn and B. Völlmer, *Wied. Ann.* [2], **60.** 468, 1897.

in contact with sodium at − 80° does really contain some sodium. This shows that chemical action has not altogether stopped at these low temperatures, and further, although phosphorus does not appear to react with liquid oxygen (−180°), yet Moissan and Dewar[1] state that solid fluorine and liquid hydrogen, at −252°, *i.e.* within 21° of the absolute zero, combine with explosive violence. At −187° liquid fluorine also combines readily with sulphur, selenium, phosphorus, arsenic, potassium (explosive), calcium oxide, and anthracene (explosive); and Linde[2] states that the combustion of a mixture of "blasting gelatine" in petroleum and liquid air is more rapid than of any known liquid or solid substance, in spite of the fact that its temperature is below −180°.

On the other hand, hydrogen and oxygen can be kept in a vessel confined over mercury, at ordinary temperatures, an indefinite time without any apparent change. Indeed, some chemists hold that "the mixture of gases obtained by the electrolysis of water must reach a certain minimum temperature . . . in order that union shall take place;" and L. Meyer[3] proposes to call the lowest or minimum temperature at which a given reaction will take place, the **temperature of the reaction**—"le point de réaction" of Salet.[4] According to one school of chemists, "this only means that the reaction between hydrogen and oxygen is immeasurably slow at ordinary temperatures." Gautier and Hélier were able to detect signs of combination at 180°;[5] but V. Meyer and Raum[6] could not detect the formation of water on heating a mixture of

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[1] H. Moissan and J. Dewar, *Compt. Rend.*, **136**. 641, 785, 1903.

[2] F. Linde, *Sitzber. Münchener. Akad. Wiss.*, 65, 1899.

[3] L. Meyer, *Dynamik der Atome*, Breslau, 417, 1883; R. Bunsen, *Gasometrischen Methoden*, Braunschweig, 336, 1877.

[4] G. Salet, in *Wurtz's Dict. de Chim.*, Paris, **1**. 79, 1874.

[5] A. Gautier and H. Hélier, *Compt. Rend.*, **122**. 566, 1896; **124**. 1269, 1897; H. Hélier, *Ann. Chim. Phys.* [7], **10**. 521, 1897; H. Hélier, *Recherches sur les combinaisons Gazeuses*, Paris, 1896.

[6] J. H. van't Hoff's *Études*, 60, 1884; H. B. Dixon, *Nature*, **32**. 535, 1885; V. Meyer and G. Krause, *Liebig's Ann.*, **264**. 85, 1891; V. Meyer and P. Askenasy, *ib.*, **269**. 49, 1892; V. Meyer and W. Raum, *Ber.*, **28**. 2804, 1895.

hydrogen and oxygen for ten days at 300°; after 65 days' exposure to this temperature, the formation of water was distinctly evident; and no sign of change could be detected after heating for 218 days at 100°. Similarly, a mixture of carbon monoxide and steam shows no sign of chemical action at 580°; a little above this temperature chemical action begins, and at 950° about 10 per cent. of the carbon monoxide is oxidized to carbon dioxide.[1]

These observations show that when the temperature is low enough, the velocity of the reaction may be so slow that no sign of chemical change can be detected in the time at our disposal. When we remember the enormous influence which a few degrees rise of temperature has upon the velocity of many changes, there is nothing remarkable in the fact that a reaction may be so slow that, at ordinary atmospheric temperatures, the amount of change in a number of years is less than that produced in a few moments when the temperature is elevated a few degrees more.

Although van't Hoff's principle of mobile equilibrium furnishes a general criterion for predicting whether a reaction is, or is not possible, it *does not tell us whether a reaction which is possible will really take place.* The principle, so far as it goes, is in perfect harmony with our experience. No chemical transformation—combination or dissociation—has ever been observed to take place in opposition to the theory. If a transformation be theoretically impossible, it is never realized in practice. We must recognize that the two laws of thermodynamics, however important they may be in dealing with states of chemical equilibria, leave us altogether in the lurch when we have to deal with the *velocity* of a chemical change. Time does not enter into the thermodynamics of the present decade.

While many reactions begin immediately the different components are brought together, other changes which, according to theory, "ought" to take place, do not do so. Oxide of silver ought to decompose at ordinary temperatures, a molten

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[1] A. Naumann and C. Pistor, *Ber.*, **18**. 2894, 1885.

solid cooled down below its freezing point ought to solidify, and a supersaturated solution ought to precipitate the dissolved salt.

In some cases it does seem as if some initial impulse, supply of energy, or "travail preliminaire" (Berthelot) must be performed to overcome this passive resistance. Every explosive substance is in a metastable condition waiting for a suitable impulse to set the process of energy transformation in motion. With gunpowder this preliminary impulse may take the form of heat; with a mixture of hydrogen and chlorine, a flash of light is sufficient; with fulminate of mercury, or nitroglycerine, a sudden shock will start the reaction; in some cases the presence of a catalytic agent may suffice to start the flow of energy from a high to a lower potential.

Just as a pile of bricks needs some initial impulse to set it toppling over; or a stone placed on top of a hill requires a preliminary shake to send it rolling down the hill, or the throttle valve of a steam engine must be moved before the latter can start on its journey, so conditions may be at work which prevent a system taking up a state of greater stability. J. Willard Gibbs, as early as 1876, designated these conditions **passive resistances.** The study of the mode of action of passive resistances is of the greatest importance, and yet the field is practically unexplored.

The union of hydrogen and chlorine is a promising reaction to investigate in this connection. If the chlorine be exposed to the action of light,[1] to a silent electric discharge,[2] or to an elevated temperature,[3] before it is mixed with hydrogen, the period of induction, described on page 115, is shortened.

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[1] Discovered by J. W. Draper, *B. A. Reports*, ii., 9, 1843; *Phil. Mag.* [3], **25.** 1, 1844; denied by R. Bunsen and H. E. Roscoe, *Phil. Trans.*, **146.** 398, 1857. The experiment of the latter was accepted by J. W. Mellor, *Journ. Chem. Soc.*, **81.** 1280, 1902; but P. V. Bevan, *Phil. Trans.*, **202.** 71, 1903, showed the presence of an unsuspected error in Bunsen and Roscoe's experiment; verified by Mellor, *Proc. Chem. Soc.*, **20.** 53, 140, 1904; and by C. H. Burgess and D. L. Chapman, *ib.*, **20.** 52, 164, 1904.

[2] Mellor, *l.c.*

[3] Burgess and Chapman, *l.c.*

I have found the numbers recorded in the following table; these may be regarded as proportional to the speed of the reaction. The asterisk denotes that the period of induction was ended :—

Time, minutes.	Ordinary chlorine.	Exposed to acetylene light.	Exposed to silent discharge.	Exposed to heat of Bunsen flame.
1	0·1	2·5	1·8	0·7
2	0·1	4·2 *	4·4 *	1·3
3	0·4	—	—	2·5
4	1·5	—	—	4·2 *
5	3·0	—	—	—
6	4·0 *	—	—	—

We do not know how these different forms of energy—actinic, thermal, and electric—are able to overcome the "passive resistance" of chlorine to react with hydrogen in this remarkable manner. Budde[1] thought that light loosened the bonds joining the atoms in the molecule.[2] This view does not explain what part water plays in the reaction except by the aid of another obvious assumption. Bevan (*l.c.*) thinks that chlorine unites with water to form $n\mathrm{H_2O}.m\mathrm{Cl_2}$, before forming the $x\mathrm{Cl_2}.y\mathrm{H_2O}.z\mathrm{H_2}$ of page 118. This conclusion is in agreement with the fact that if chlorine be well dried before it is exposed to light and admixed with moist hydrogen, it is not so reactive as if moist chlorine were similarly treated. Burgess and Chapman (*l.c.*) seem to think that their experiments on the velocity of the reaction render this conclusion "absurd." But we are fast losing faith in the infallibility of velocity measurements as a key to the mechanism of chemical

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[1] See page 117. E. Budde, *Journ. prakt. Chem.* [2], **4**. 431, 1871; **7** 376, 1873.

[2] It is interesting to observe that HI decomposes in single molecules in light according to the unimolecular law; but in darkness, under the influence of heat, the molecules seem to break up in pairs according to the bimolecular law. M. Bodenstein, *Zeit. phys. Chem.*, **13**. 116, 1894; **22**. 123, 1897; Inaug. Diss., *Über die Zersetzung des Jodwasserstoffgases in der Hitze*, Leipzig, 1894; see also A. Slator, *Journ. Chem. Soc.*, **81**. 729, 1903, for the action of chlorine on benzene in light.

reactions. Here, then, the problem stands inviting fresh investigators. The decomposition of chlorine water in light presents similar phenomena.[1]

Were it not for the passive resistance, the velocity of a chemical reaction would no doubt be proportional to the amount of available energy, E. If we regard passive resistance as an obstruction which entails the expenditure of a certain amount of the available energy, we may write the velocity of the reaction—

$$\frac{dx}{dt} = \frac{E}{R},$$

where R denotes the magnitude of the passive resistance. There is a formal analogy between this expression and Ohm's well-known formula. R may be called the *chemical resistance*. The velocity of the reaction is the product of two factors: (i.) the free energy, and (ii.) the reciprocal of the chemical resistance.

(i.) *Available energy.*—Consider the reversible reaction—

$$2H_2 + O_2 \rightleftharpoons 2H_2O,$$

in a state of equilibrium at a temperature T_1, when the mixture contains a per cent. of H_2O. If the temperature falls to T_2, hydrogen and oxygen will unite to form more H_2O. Skrabal[2] has pointed out that $T_1 - T_2$ may be regarded as a measure of the available energy of the system. The free energy of the system diminishes as the difference $T_1 - T_2$ becomes less and less, and when $E = 0$, the reaction will be at a stand-still. If the reaction takes place at a constant temperature, R will be constant. The velocity of the reaction will then be greatest at the beginning, and gradually slow down as the amount of available energy diminishes.

(ii.) *Passive resistance.*—Since the resistance R diminishes with rising temperature, the reciprocal of R will increase. At absolute zero, E will have its greatest value, and $1/R$ its least

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[1] J. W. Draper, *Phil. Mag.* [3], **27**. 327, 1845; see also Burgess and Chapman, *l.c.*

[2] A. Skrabal, *Oesterreichische Chem. Ztg.* [2], **6**. 533, 1903.

value; as the temperature rises, $1/R$ becomes very great, and E very small. By plotting the subjoined (imaginary) values of E, $1/R$, and dx/dt, in turn, as ordinates, with T as abscissa, we get a velocity curve which increases from zero to a maximum value, and then diminishes:—

T	E	$\frac{1}{R}$	$\frac{dx}{dt}$
1	10·0	0·3	3·0
50	7·0	0·7	4·9
100	5·0	1·0	5·0
150	0·8	4·0	3·2
200	0·1	8·0	0·8

The temperature at which the product E/R has its maximum value is called the **optimum temperature.** The optimum temperature for the conversion of a mixture of martensite with 0·85 per cent. of carbon into pearlite is 600°; for a mixture of sulphur dioxide and oxygen in contact with platinum asbestos, 400°; in contact with ferric oxide, 550°; and in contact with fragments of pumice, 600°. Since sulphur trioxide begins to dissociate above 450°, it is obvious that platinum asbestos is the best catalytic agent to use for the oxidation of sulphur dioxide.

§ 120. False Equilibrium—Temperature.

When oxygen is brought into contact with ordinary phosphorus the oxidation is attended with "phosphorescence." There is, however, a criticial temperature for any given pressure, at which the oxidation is attended with luminescence. Below this temperature phosphorescence does not take place, while above this temperature phosphorescence readily occurs. This temperature is proportional to the pressure of the gas. According to Ewan,[1] the pressure at which oxidation begins is identical

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[1] T. Ewan, *Zeit. phys. Chem.*, **16.** 315, 1895; *Phil. Mag.* [5], **38.** 505, 1894.

with that at which the phosphorus becomes luminous. Joubert[1] measured the pressure at which phosphorescence begins at different temperatures. The results are shown in the following table, and graphically in Fig. 31 :—

When $\theta = 1·4$, $3·0$, $5·0$, $6·0$, $8·9$, $9·3$, $11·5, \ldots$;
$p = 355$, 387, 428, 460, 519, 538, 580 mm.

The curve divides the plane of the paper into two regions. At any point above the boundary line oxidation occurs, below that line no oxidation occurs, and the mixture of phosphorus and oxygen remains in a passive state. Hence Joubert was led to enunciate the law that every temperature corresponds with a certain critical pressure, p, such that if the pressure of a mixture of oxygen and phosphorus is above this, oxidation begins; while if the pressure is below the critical pressure, no oxidation occurs, and the mixture is apparently in a state of equilibrium. An abrupt—*per saltum*—change is said to occur as soon as the line of oxidation is crossed. The slope and curvature of the line is modified by the presence of "foreign" gases.[2]

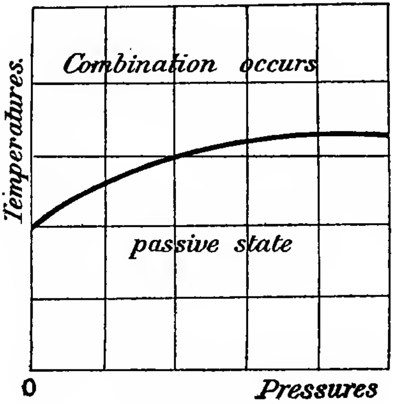

FIG. 31.

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[1] J. Joubert, *Ann. de l'Ecole normale superieure* [2], **3**. 209, 1874; *Sur le phosphorescence du phosphor*, Paris, 1874.

[2] M. Centnerszwer, *Zeit. phys. Chem.*, **26**. 1, 1898.

Instead of the transformation of a mixture of hydrogen and oxygen (2 : 1) at temperatures below 1000°, Gautier and Hélier[1] believe that metastable states of "false equilibrium" occur at a temperature of 200° when 0·12 per cent. has combined; at 416° when 35·7 per cent. has combined; and at 620° when 84·52 per cent. has entered into combination.

In these states of apparent equilibrium, it is claimed that chemical action ceases before the reaction in one direction is balanced, so to speak, by the reverse change. Such states of equilibria are quite distinct from the true equilibria set up when the velocities of the two opposing reactions, being equal, neutralize one another. According to Duhem[2] "all those states of equilibrium which are actually in the condition required by theory are in a state of real equilibrium—état d'équilibre véritable; while those states which are not in the condition required by theory are in a state of apparent or false equilibrium—état de faux équilibre."

It is true enough that all systems strive to attain a state of stable equilibrium. If we know the conditions of equilibrium, we are in a position to predict whether a system can pass into a condition of greater stability, but we cannot yet predict whether a particular transformation which is possible will really take place. We know, well enough, that phosphorus can combine with iodine, and that hydrogen will combine with oxygen, yet could never have predicted that phosphorus and iodine would combine as they do when placed in contact, or that hydrogen and oxygen gases would combine, if at all, with infinite slowness at ordinary temperatures.

Let us now turn to a mechanical illustration of false equilibrium. Imagine a cylinder of unit sectional area fitted with a tightly fitting piston which will move up or down the cylinder without friction (Fig. 32). Let p_0 and v_0 respectively

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[1] A. Gautier and H. Hélier, *l.c.*; M. Berthelot, *Compt. Rend.*, **124**. 1273, 1897; A. Gautier, *ib.*, **124**. 1276, 1897.

[2] P. Duhem, *Introduction a le Mécanique Chimique*, Paris, 159, 1893; M. Wildermann, *Phil. Mag.* [6], **4**. 468, 1902.

denote the initial pressure and volume of the gas, and let p_1 and v_1 be the corresponding pressure and volume of the gas when an additional pressure is put on the piston. From Boyle's law, the condition of equilibrium is—

$$p_0v_0 = p_1v_1\,;\ \text{or, } p_1 = \frac{v_0}{p_1}p_0, \quad . \quad . \quad . \quad . \quad (1)$$

provided there be no friction between the piston and the cylinder.

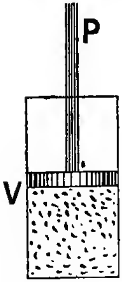

FIG. 32.

Now suppose that the free motion of the piston up and down the cylinder is opposed by friction. Let x be the extra pressure necessary to overcome the friction. Then, when the piston is descending, the condition for equilibrium is, by Boyle's law—

$$p_0v_0 = (p_1 + x)v_1\,;\ \text{or, } p_1 + x = \frac{v_0}{v_1}p_0\,;\ \text{or, } p_1 = \frac{v_0}{v_1}p_0 - x. \quad (2)$$

Although the system will only be in a state of true equilibrium when equation (1) is satisfied, yet the system will *appear* to be in equilibrium for all values of p which fall between $p_1 + x$, and p_1.

Similarly, if the piston be rising owing to a diminution of pressure p_0, the condition for equilibrium will be—

$$p_0v_0 = (p_1 - x)v_1\,;\ \text{or, } p_1 - x = \frac{v_0}{v_1}p_0\,;\ \text{or, } p_1 = \frac{v_0}{v_1}p_0 + x, \quad (3)$$

and the system will appear to be in equilibrium for all values of p lying between p_1 and $p_1 - x$. Consequently, the system will appear to be in equilibrium for all values of p lying between $p_1 + x$ and $p_1 - x$.

For the sake of convenience, let v_0p_0 have some arbitrary value, say unity. It is then easy to plot the pv-curve of true equilibrium from equation (1). This graph is shown by the thickened line in Fig. 33. Similarly, by assigning some arbitrary value to x, say unity, we get from equations (2) and (3) the two lightly drawn curves in Fig. 33.

Take the gas at any volume v. If its pressure falls anywhere between the line of true equilibrium and the upper

$p + x$ line, the pressure will not be sufficient to overcome the friction of the piston against the sides of the cylinder, and consequently the piston will remain stationary; and if p falls anywhere between the line for true equilibrium and the lower $p - x$ line, the pressure will still be insufficient to move the piston, and the volume of the gas will remain stationary in spite of the fact that one part of the system is in a condition of instability. The equilibrium is apparent, not real. All pressures lying between the points $p + x$ and $p - x$ form a region of apparent or false equilibrium. In the limiting case, when $x = 0$, one single line—the pv-curve of our text-books—alone remains.

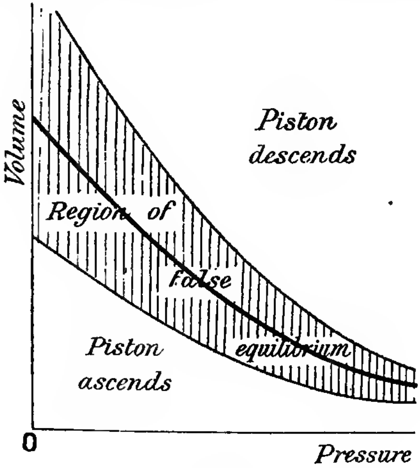

FIG. 33.

Pélabon and Duhem[1] maintain that this analogy can be extended to chemical transformations. Just as a mechanical system may exist in a state of apparent equilibrium under conditions which would, in the absence of friction, be impossible,

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[1] P. Duhem, *Traité Élémentaire Mécanique Chimique fondée sur la Thermodynamique*, Paris, 1897–99; *Théorie Thermodynamique de la Viscosité, du Frottement et des Faux Équilibres Chimiques*, Paris, 1896; *Thermodynamique et Chimie*, Paris, 1902; G. K. Burgess' trans., New York, 1904.

so may states of false equilibrium be realized under conditions which would be impossible in the absence of some force retarding the progress of chemical change. "All chemical changes," says Duhem, "may present states of false equilibria, but in a great many cases the region of false equilibrium lies so close to the curve of true equilibrium that the one state cannot be distinguished from the other, and a state of true equilibrium alone appears to be realized."

We need not take this seductive analogy too seriously. It is just as easy to imagine a kind of "viscous friction" which delays but does not actually prevent motion. A system may appear to be in a state of unstable equilibrium and yet be slowly progressing towards a state of true equilibrium, just as a penny placed on a block of ice will slowly pass through to the other side. The question, "Very slow chemical change or false equilibrium?" must be settled by an appeal to experiment.

A. Jouniaux[1] has measured the course of the reaction in

$$2AgCl + H_2 \rightleftharpoons 2HCl + Ag,$$

vessels containing silver chloride and hydrogen at 380 mm. pressure, and in vessels containing hydrogen chloride and metallic silver at 760 mm. pressure. The results are shown in the following table:—

Initial mixture:		Initial mixture:	
$H_2 + 2AgCl$.		$HCl + Ag$.	
Time (days).	Per cent. of HCl.	Time (days).	Per cent. of HCl.
7	71·09	8	95·98
24	82·57	24	93·92
36	82·46	36	92·02
70	88·66	70	91·53
408	88·88	408	91·67
504	88·42	504	91·55

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[1] A. Jouniaux, *Compt. Rend.*, **129**. 883, 1899; **132**. 1270, 1901; **133**. 228, 1901 (HBr); *Actions des hydracides halogénés sur l'argent et réactions inverses*, Lille, 1901.

The experimental results are plotted in Fig. 34. If the equilibrium attained in each case were real, the two curves should meet and continue in one line as indicated in Fig. 8, p. 81. Here, however, the system may be in equilibrium when the percentage amount of hydrogen chloride in the mixture varies between 88·88 and 91·55 per cent.

In another series of experiments, Jouniaux studied the states of equilibrium obtained at different temperatures. The results are tabulated below:—

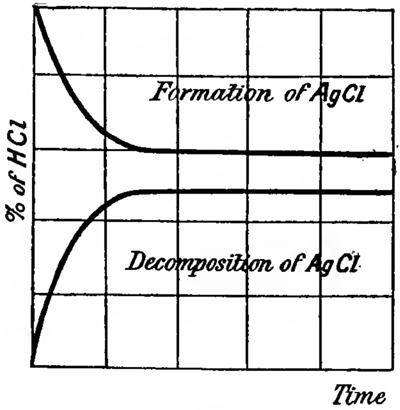

FIG. 34.

Temp.	Initial system:	
	$H_2 + 2AgCl$.	$2HCl + 2Ag$.
200	—	1·0000
250	0·0500	1·0000
350	0·7588	0·9500
448	0·8881	0·9155
490	0·9036	0·9094

On plotting these results, the plane of the paper is divided into the two regions shown in Fig. 35.

Engel[1] obtained similar results in his study of the decomposition of the double carbonate of potassium and magnesium, $MgCO_3.KHCO_3.4H_2O$, by water. Pélabon[2] has also investigated the action of hydrogen on silver sulphide; and the formation of hydrogen selenide in the reaction—

$$H_2Se \text{ (gas)} \rightleftharpoons Se \text{ (solid)} + H_2 \text{ (gas)}.$$

$$\therefore k_1 C_{H_2Se} = k_2 C_{H_2} C_{Se}; \text{ or, } K = \frac{C_{H_2}}{C_{H_2Se}} = \frac{p_1}{p_2},$$

since C_S is constant, and p, the pressure, is proportional to the concentration of the reacting gases. Pélabon employed equation (10) of § 114 to represent the relation between K and temperature—

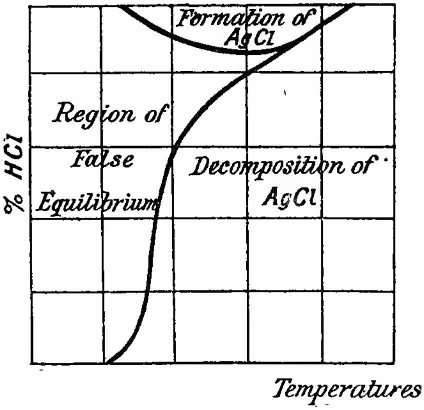

FIG. 35.

$$\therefore \frac{d \log K}{dT} = \frac{A + BT}{T^2}; \text{ or, } \log K = \frac{a}{T} + b \log T + c, \quad (4)$$

where a, b, and c are constants whose numerical values were

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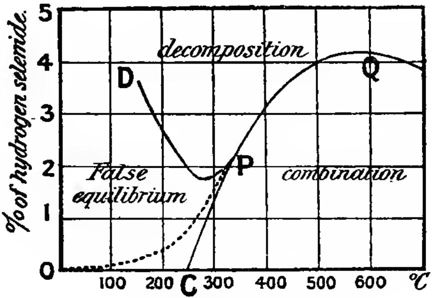
[1] M. Engel, *Compt. Rend.*, **101**. 749, 1885.

[2] H. Pélabon, *Mem. de la Soc. des Sciences Phys. et Nat. de Bordeaux* [5], **3**. 141, 257, 1898; *Compt. Rend.*, **124**. 35, 360, 686, 1897; *Zeit. phys. Chem.*, **26**. 659, 1898; *Ann. Chim. Phys.* [7], **25**. 365, 1902 (for the action of H on S and Se); *Compt. Rend.*, **126**. 1864, 1898 (for H on Ag_2S).

obtained from the experimental data. By plotting, Pélabon obtained the curve *OPQ*, shown in Fig. 36. Pélabon found that the formation and decomposition of hydrogen selenide always led to the same final state of equilibrium, provided that the temperature be over 350°; but below 325° the final state of equilibrium attained depends upon whether the initial mixture be hydrogen selenide or a mixture of selenium and hydrogen. If a mixture of hydrogen and selenium be employed, at 270°, equilibrium occurs when the system contains 4·8 per cent. of hydrogen selenide; while if hydrogen selenide be employed at the start, equilibrium sets in when 16 per cent. of hydrogen selenide remains. The calculated amount of hydrogen selenide is 10 per cent. Hence, if at 270° the amount of hydrogen selenide be less than 4·8 per cent., hydrogen combines with selenium to form hydrogen selenide; if the amount of the latter gas present in the system be greater than 16 per cent., the hydrogen selenide will be decomposed; while if the amount of hydrogen selenide lies between 4·8 per cent. and 16 per cent., a state of equilibrium ensues. In other words, the system will be in equilibrium when—



Pelabon's curves

FIG. 36.

$$\text{Per cent. of } H_2Se \leqq 4{\cdot}87 \leqq 16 \text{ per cent.}$$

Hence if we have 10 per cent. of hydrogen selenide, the system will be in equilibrium. Similar experiments conducted at other temperatures yielded the results shown in the following table:—

Temp.	Time of heating.	Per cent. of H_2Se formed when original mixture was	
		$H_2 + Se$.	H_2Se.
300	212	12·4	17·2
300	322	12·7	17·0
315	196	16·4	18·5
325	175	18·7	19·3
325	230	18·82	19·2

By plotting these results the plane of the paper is divided into three regions. Pélabon traced the curve *PD* experimentally to 150°; the *PC* curve cut the abscissa axis at 250°. If a point falls within the area *DPQ*, it means that the H_2Se is in a state of dissociation; if a point falls in the region *CPQ*, H_2Se will be produced; when the point falls on the curve *OPQ*, there will be a state of true equilibrium; and when the point falls in the region *DRC*, there will be a state of false equilibrium, because the system will be in a passive condition, no matter whether the state of the system is described by a point falling on the line of true equilibrium or not. Note that the region of false equilibrium converges about the line of true equilibrium as the temperature approaches 350°, so that beyond the point *P* the two states cannot be distinguished. Pélabon has obtained similar results with the reaction–

$$H_2S \rightleftharpoons H_2 + S.$$

So far the evidence is clear. Bodenstein[1] has tried to repeat Pélabon's work, but without success. He always obtained a state of true equilibrium no matter whether he started with selenium and hydrogen, or with hydrogen selenide. The experimental results of both investigators are plotted on one

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[1] M. Bodenstein, *Zeit. phys. Chem.*, **29**. 147, 295, 315, 429, 665, 1899; **30**. 113, 569, 1899; D. Konowalow, *Journ. Russ. Phys. Chem. Soc.* [4], **30**. 371, 1898; Abstract, *Chem. Central*, ii., 657, 1898; H. Kühl, *Zeit. phys. Chem.*, **44**. 385, 1903.

diagram in Fig. 37. Bodenstein has also failed to verify Hélier and Gautier's observation on the existence of a state of false equilibrium during the combination of hydrogen and oxygen; nor did D. Konowalow detect any signs of a state of false equilibrium during the decomposition of hydrogen sulphide.

Bodenstein believes that Pélabon did not heat his mixture long enough to obtain the "true and only state of equilibrium," and adds that "there is no experimental basis for the hypothesis of false equilibrium." Duhem[1] then pointed out that this view is not legitimate; Pélabon always proved that his tubes were heated long enough by showing that a more prolonged heating always gave the same results (Table, p. 426). Duhem has also suggested that Bodenstein's "states of equilibrium" with hydrogen sulphide, etc., were modified by "the presence of a great excess of sulphur which, without doubt, obscured the point at issue."

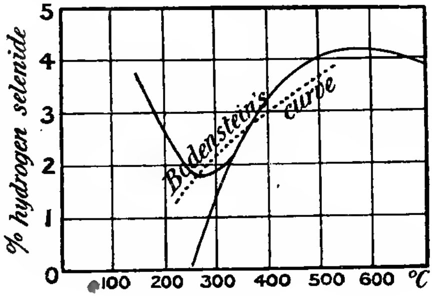

FIG. 37.

I have now laid the experimental evidence *pro et con* before the reader in order that he may form his own opinion upon the two questions involved—

1. Does the reaction between, say, hydrogen and oxygen, take place at low temperatures?

2. Are there two states of equilibrium with a reversible

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[1] P. Duhem, *Zeit. phys. Chem.*, **29**. 711, 1899; and M. Bodenstein's reply, *ib.*, **30**. 567, 1899.

chemical reaction, say, $H_2Se \rightleftharpoons H_2 + Se$, according as the end state is approached from different sides of the equation?

Of course the reader is not called upon to believe anything. The capacity to believe is largely a question of psychology. It is well, however, to draw attention to the fact that the experimental work has all been performed under adverse conditions. Gautier and Hélier's experiments, for example, were performed in glazed porcelain tubes packed with "baguettes" of glazed porcelain so as to present "an enormous surface to the action of the reacting gases." It is always a difficult matter to measure the speed of chemical reactions between gases in glass vessels at high temperatures, and we have nothing to show that the disturbing effects of the walls of the vessel mentioned on page 58 were eliminated. These troubles are, no doubt, accentuated when one of the reacting components is in a different state of aggregation from the rest of the system.

Granting the validity of the experimental work, the theory of false equilibrium is not the only hypothesis available. Just as Pélabon[1] himself found that the apparent state of false equilibrium, produced during the action of hydrogen sulphide upon metallic bismuth, was due to the formation of a protective film of bismuth sulphide on the surface of the metal, so might we assume that, in all the cases of false equilibrium so far observed in heterogeneous systems, films of some kind are produced on the surface separating the reacting components. "Phosphorus," says E. J. Russell,[2] "is extremely sensitive to surface contamination, which either greatly retards oxidation or altogether stops it," and it is suggested that the cessation of phosphorescence observed by Joubert at high pressures, is due to the formation of a surface film of moisture, or of an oxide of phosphorus. There is no sign of "false equilibrium" when the oxygen is dry.

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[1] H. Pélabon, *Compt. Rend.*, **132**. 78, 1901.

[2] E. J. Russell, *Journ. Chem. Soc.*, **83**. 1263, 1903.

CHAPTER XIII

THE INFLUENCE OF PRESSURE ON CHEMICAL REACTIONS

§ 121. The Work done by Chemical Affinity.

THE influence of pressure on the velocity of chemical reactions has long been recognized, although exact measurements of the relation between the two are comparatively rare. As early as 1805, Biot[1] found that detonating gas combined under pressure in an iron tube with explosive violence. The heat of compression may, however, have raised the temperature of the gas to the ignition point, for De la Roche[2] observed no combination when the gases were *gradually* subjected to a pressure of 50 atm., nor did Degen[3] observe any sign of a re-combination of the gases obtained by the electrolysis of dilute sulphuric acid, at a pressure of 150 atm. In a similar experiment, Warren[4] did get combination, with the production of flame, at 180 atm. pressure.

According to Beketoff,[5] hydrogen gas at a high pressure will precipitate the respective metals from silver sulphate, platinum chloride, and palladium chloride. For example, no

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[1] J. B. Biot, *Gehlen's Journ.*, **5**. 95, 1805; *Gilbert's Ann.*, **20**. 99, 1805.

[2] De la Roche, *Schweigger's Journ.*, **1**. 172, 1811.

[3] A. F. E. Degen, *Pogg. Ann.*, **38**. 454, 1836.

[4] H. N. Warren, *Chem. News*, **67**. 195, 1893.

[5] N. N. Beketoff, *Compt. Rend.*, **48**. 442, 1859; *Bull. Soc. Chim.* [2], **2**. 44, 1864; *Zeit. Chem.* [2], **1**. 376, 1865; *Phil. Mag.* [4], **31**. 306, 1866; *Inaug. Dissert.*, Charkow, 1865; C. Brunner, *Pogg. Ann.*, **122**. 153, 1864; P. A. Favre, *Compt. Rend.*, **51**. 1027, 1860; J. Babinet and P. A. Favre, *ib.*, **51**. 1029, 1860; A. Colson, *Compt. Rend.*, **127**. 961, 1898.

action could be observed after exposing a solution of silver sulphate in 350 parts of water to a pressure of 4·75 atm. for several days; with 6 atm., a slight action could be observed; while violet-colored silver separated after a day's exposure to a pressure of 14 atm.

Cailletet[1] has shown that the evolution of hydrogen by the action of sulphuric acid upon zinc or sodium amalgam can be made to stop by the application of a sufficiently high pressure, and this appears to have suggested to Tammann and Nernst[2] the determination of the maximum pressure of the liberation of hydrogen from acid solutions by sodium, magnesium, aluminium, zinc, cadmium, iron, and nickel. To quote one example, it was found that a pressure of 18 atm. was necessary to stop the further evolution of hydrogen from a 0·13 N-solution of sulphuric acid containing 1·3 N-zinc sulphate in contact with zinc. A higher pressure appeared to cause the precipitation of zinc.

This raises the interesting question: When a reaction is accompanied by an increase in volume, can the work done by chemical affinity be expressed in terms of the pressure required to just stop the reaction? In the reaction under consideration, it is not exactly the *mechanical* pressure of the hydrogen which opposes the reaction, because an equal pressure of another gas will not do this. What does oppose the reaction is a certain concentration of the hydrogen gas, and on this account, the reaction is not very well adapted for the purpose of measurement. But where a mechanical pressure p just stops a reversible reaction, say $A \rightleftharpoons B$, measured from either end, the work dW done by affinity during the process of transformation is given by the expression—

$$dW = v.dp = q\frac{dT}{T},$$

where q denotes the heat absorbed in the change of A into B;

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[1] L. P. Cailletet, *Compt. Rend.*, **68.** 395, 1869; M. Berthelot, *ib.*, **68.** 536, 780, 810, 1869; F. Pfaff, *Neues Jahrbuch für Mineralogie*, 834, 1871 (action of nitric acid on calcspar); G. de Laire and C. Girard, *Compt. Rend.*, **68.** 825, 1869; *Bull. Soc. Chim.* [2], **12.** 345, 1869 (formation diphenylamine).

[2] W. Nernst and G. Tammann, *Zeit. phys. Chem.*, **9.** 1, 1892.

v is the increase in volume; T the transition temperature; and dp represents the pressure which will just stop the transformation of A to B at a temperature dT degrees higher than the transition temperature. This relation has been verified by the work of Reicher[1] on the transition of rhombic into monoclinic sulphur at 95·6° C.; by Mallard and Le Chatelier[2] on the conversion of silver iodide from the hexagonal to the regular form at 146°; and by Roozeboom[3] for the decomposition of the hydrate of hydrogen bromide, $HBr.2H_2O$, at $-11{\cdot}3°$.

§ 122. Influence of Pressure on the Velocity of Gaseous Reactions.

A theoretical relation between the pressure and the velocity of a chemical reaction is easy to determine, because a change of pressure produces a change in the concentration of the reacting compounds, which is determined by Boyle's law. The reaction proceeds according to the law of mass action. Let us consider the reaction $nA = B$, and let C denote the number of gram-molecules of A per litre. The rate of transformation of A into B will be—

$$-\frac{dC}{dt} = kC^n,$$

where n denotes the number of molecules of A taking part in the reaction. Since the concentration of the gas is directly proportional to the pressure, we shall have, corresponding with the pressures p_1 and p_2—

$$\left(-\frac{dC}{dt}\right)_{p_1} : \left(-\frac{dC}{dt}\right)_{p_2} = \left(\frac{p_1}{p_2}\right)^n;$$

and if S denotes the number of gram-molecules of A in v litres—

$$\frac{dC}{dt} : \frac{dS}{dt} = 1 : v; \text{ or, } \frac{dS}{dt} = v\frac{dC}{dt}.$$

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[1] L. T. Reicher, *Rec. Travs. Pays-Bas* [2], **2**. 46, 1883.

[2] E. Mallard and H. le Chatelier, *Compt. Rend.*, **99**. 157, 1884.

[3] H. W. B. Roozeboom, *Zeit. phys. Chem.*, **2**. 455, 1888.

If now v_1 and v_2 respectively denote the volumes of the system corresponding with the pressures p_1 and p_2, we shall have, in consequence—

$$\left(-\frac{dS}{dt}\right)_{p_1} : \left(-\frac{dS}{dt}\right)_{p_2} = v_1\left(-\frac{dC}{dt}\right)_{p_1} : v_2\left(-\frac{dC}{dt}\right)_{p_2}$$

$$= \frac{v_1}{v_2}\left(\frac{p_1}{p_2}\right)^n = \frac{p_2}{p_1}\left(\frac{p_1}{p_2}\right)^n = \left(\frac{p_1}{p_2}\right)^{n-1},$$

since the volume of a gas varies inversely as the pressure (Boyle's law). Hence, the influence of pressure on the velocity may be written—

$$\frac{dS}{dt} = kp^{n-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant. This equation means that when n molecules take part in a reaction, the amount transformed will be proportional to the $(n - 1)$th power of the pressure.

For unimolecular reactions, $n = 1$, hence the fraction of the total quantity transformed in unit time will be independent of the pressure. This is in harmony with the experiments of Kooij on the rate of decomposition of arsine;[1] of Bone and Wheeler on the union of hydrogen and oxygen, and the oxidation of carbon monoxide;[2] or of Pélabon[3] on the decomposition of selenium hydride. From Bone and Wheeler's measurements of the rate of combination of dry hydrogen and oxygen ($2H_2 + O_2$), kept at constant volume in contact with porous porcelain at 450° (unit of time = 12 hrs.)—

$p=$	465·6,	324·0,	228·6,	163·9,	116·1,	84·6,	60·7,	42·9, ...;
$\Delta p/p=$	—	0·304,	0·294,	0·283,	0·292,	0·271,	0·282,	0·293.

For bimolecular reactions, $n = 2$, here the fraction of the total quantity transformed in unit time will be directly proportional to the pressure. This is supported by the experiments of Bodenstein,[4] where the rate of decomposition of hydrogen

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[1] J. H. van't Hoff, *Études*, 83, 1884; see also p. 57.

[2] W. A. Bone and R. V. Wheeler. Private communication. See also M. Bodenstein, *Zeit. phys. Chem.*, **46**. 725, 1903.

[3] H. Pélabon, *Compt. Rend.*, **119**. 73, 1894.

[4] M. Bodenstein, *Zeit. phys. Chem.*, **13**. 116, 1894.

iodide is approximately proportional to the pressure of the gas. Thus, at 518°—

When p = 0·5, 1·0, 1·5, 2·0 atm.;
Specific velocity = 0·00366, 0·00503, 0·00800, 0·01143.

For termolecular reactions, $n = 3$, and the velocity of transformation will be proportional to the square of the pressure.

§ 123. Influence of Pressure on the Velocity of Reactions in Liquids.

Unlike gases, the volume of a liquid is but slightly influenced by variations of pressure, and consequently the influence of pressure on the velocity of the reaction will be very much less than is the case with gases. Berthelot and Gilles[1] could find no difference in the rate of esterification of an alcohol at pressures up to 50 atm.; van't Hoff[2] found that the rate of transformation of dibromosuccinic acid at 100° was not affected by pressures up to 6 atm.; Röntgen[3] studied the effect of pressures as high as 500 atm. on the rate of inversion of cane sugar in the presence of hydrogen chloride. He suspected that the rate of inversion was diminished by pressure, but the deviations observed fell within the limits of experimental error.[4] According to V. Rothmund,[5] at a pressure of 250 – 500 atm., the rate of inversion of a 20 per cent. solution of cane sugar by normal hydrochloric acid was diminished by about 1 per cent. per 100 atm., the number previously surmised by Röntgen. Thus—

Temp.	p atm.	k
16	1	0·001664
16	250	0·001702
15	1	0·001337
15	500	0·001416

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[1] M. Berthelot and L. Péan de St. Gilles, *Ann. Chim. Phys.* [3], **66** 45, 1862.

[2] J. H. van't Hoff, *Études*, 14, 1884.

[3] W. C. Röntgen, *Wied. Ann.*, **45**. 98, 1892.

[4] G. Tammann, *Zeit. phys. Chem.*, **14**. 444, 1894.

[5] V. Rothmund, *Zeit. phys. Chem.*, **20**. 168, 1896.

Rothmund ascribed the retardation to the diminution of the ionization of the acid with pressure; but the corresponding change does not occur in the hydrolysis of the esters in the presence of the same acid. On the contrary, the velocity of hydrolysis of the esters increases with increasing pressure. Thus, while a pressure of 500 atm. diminishes the rate of inversion of cane sugar some 5 per cent., there is a rise of 20 per cent. during the hydrolysis of methyl acetate. At 14°, with a 5 per cent. solution of methyl acetate, and a N-solution of hydrochloric acid, Rothmund found—

When $p = 1$,	100,	200,	300,	400,	500 atm.;
$10^4 \times k = 10·73$,	11·09,	11·44,	11·97,	12·6,	12·94.

Similar results were obtained by Stern[1] with a solution of methyl acetate and acetic acid.

The presence of potassium chloride, or variations in the strength of the acid or of the ester do not perceptibly alter the influence of the pressure. These facts do not appear to be in harmony with the hypothesis that the variations of pressure change the speed of catalytic reactions by changing the degree of ionization of the acid.[2] Nor will the change of the viscosity of a liquid with variations of pressure explain the facts, because the influence of pressure on the viscosity of a liquid is very small.[3]

"Every individual reaction," says Dammar's Handbuch,[4] "appears to be specifically influenced by variations of pressure," this means that the relation has not yet been observed between the velocity of a reaction and the magnitude of the pressure to which the system is subjected.

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[1] O. Stern, *Wied. Ann.*, **59**. 652, 1896.

[2] G. Tammann, *Zeit. phys. Chem.*, **17**. 725, 1895; A. Bogojawlensky and G. Tammann, *ib.*, **17**. 725, 1895; **23**. 13, 1897; **27**. 457, 1898; G. Foussereau, *Compt. Rend.*, **104**. 1161, 1887.

[3] L. Hauser, *Inaug. Dissert.*, Tübingen, 1900; *Drude's Ann.*, **5**. 597, 1901; W. C. Röntgen, *Wied. Ann.*, **22**. 510, 1884; E. Warburg and J. Sachs, *ib.*, **22**. 518, 1884.

[4] O. Dammar's "*Handbuch der Anorganische Chemie*," Stuttgart, **4**. 72, 1902.

§ 124. Influence of Pressure on Chemical Equilibria.

The deduction of the principle which relates to the influence of temperature on chemical equilibria is one of the most important contributions of thermodynamics to chemistry. A similar relation has been established for the influence of pressure. In 1879, for example, G. Robin,[1] following the method of Moutier,[2] was led to enunciate the law: "For constant temperatures, there is one definite pressure for which a system will be in equilibrium. On raising the pressure, the reaction will take place in that direction which is produced with a decrease in volume; while if the pressure is reduced, the reaction will proceed in that direction which has the greater volume." Thus, as Braun[3] has shown, the solubility of a salt will increase with pressure if the solution occupies a less volume than the resultant volume of the constituents; while the solubility will diminish if the solution occupies a greater volume than the total volume of the constituents.

This calls to mind the mechanical principle of least action foreshadowed, in a vague sort of way, by Maupertius, in 1747. According to this, *all natural changes take place in such a way that the existing state of things will suffer the least possible change.* This principle appears in various guises in mechanics, optics, thermodynamics, electricity, and magnetism. In chemistry, too, we recognize the principle underlying van't Hoff's law of mobile equilibrium, and the relation obtained by Robin is but a particular case of the same generalization. In 1888, Le Chatelier[4] enunciated this same idea as "the principle of the opposition of a reaction to further change:" "when any system is in a state of physical or chemical equilibrium, a change in one of the factors of equilibrium will cause a reverse change within the

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[1] G. Robin, *Bull. de la Soc. Philomath.* [7], **4.** 24, 1879.

[2] J. Moutier, *Societe Philomath.* [3], **39.** 96, 1877; J. W. Gibbs, *Trans. Connect. Acad.*, **3.** 232, 1876.

[3] F. Braun, *Wied. Ann.*, **30.** 250, 1887; **33.** 337, 1888; *Zeit. phys. Chem.*, **1.** 259, 1887.

[4] H. le Chatelier's *Recherches Expérimentales et Théoriques sur les Équilibres Chimiques*, Paris, 48, 1888; *Compt. Rend.*, **99.** 786, 1884.

system."[1] The factors of equilibrium are: "temperature, pressure, and electromotive force, corresponding to the three forms of energy—heat, electricity, and mechanical energy." To these might be added actinic energy.

For example, the addition of heat will cause an increase in those products which are formed with an absorption of heat; the decomposition of a compound by electrolysis "tends" to produce a current of electricity in the opposite direction to that which induces the decomposition. This fact is employed in the construction of accumulators.

Planck[2] has deduced the following relation between the equilibrium constant and the pressure—

$$\frac{d \log K}{dp} = \frac{v}{2T},$$

which holds for dilute solutions when v denotes the change of volume in cubic metres which occurs when a kilogram-molecule is transformed from one state to another; p is reckoned in kilograms per square metre. When the reaction is in a state of stable equilibrium—

$$k_1 C = k_2 C; \quad K = \frac{k_2}{k_1} = \frac{C_A}{C_B}.$$

$$\therefore \frac{d \log k_2}{dp} - \frac{d \log k_1}{dp} = \frac{v}{2T},$$

which bears a formal resemblance to van't Hoff's well-known equation. This result is in harmony with the experiments of V. Rothmund, previously mentioned. As in the analogous relation between the equilibrium constant and temperature, we have three important cases.

Case I.—If v be positive, a decrease of pressure will favour the formation of the second system, and an increase of pressure will favour the first system. With the reaction—

$$2H_2O + Cl_2 \rightleftharpoons 4HCl + O_2,$$

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[1] F. Riedel, *Zeit. angew. Chem.*, **16**. 493, 1903; G. Bredig and F. Haber, *ib.*, **16**. 557, 1903; A. Skrabel, *ib.*, **16**. 621, 1903.

[2] M. Planck, *Wied. Ann.*, **32**. 495, 1893; *Vorlesungen über Thermodynamik*, Leipzig, 218, 1897; A. Ogg's trans., London, 1904; J. J. van Laar, *Die Thermodynamik in der Chemie*, Leipzig, 106, 1893.

the total volume of the products on the left is but two-thirds of the total volume of the products on the right. An increase of pressure will displace the equilibrium in favour of the components indicated on the left of the equation, while a reduction of pressure will favour the formation of the compounds indicated on the right.

W. Spring has shown that hydrated arsenic sulphides, $As_2S_36H_2O$, is transformed into the anhydrous sulphide and water at a pressure of 6000 – 7000 atm. This agrees with the fact that the specific volume of As_2S_3 is 53,174 at 256°, while $As_2S_3.6H_2O$ has a specific volume of 50,626 at the same temperature.

Case II.—If v be negative, a decrease of pressure will favour the formation of the first system. Thus, hydrogen and oxygen combine to form water according to the equation—

$$2H_2 + O_2 \rightleftharpoons 2H_2O.$$

The volume of the products of the reaction from right to left is but two-thirds of that of the components on the left. In agreement with theory, it has been observed that an increase of pressure favours the formation of steam. Similarly, dry silver chloride is decomposed by a pressure of "100,000 lb. per sq. in."[1] Reicher[2] has also shown that the transformation of copper calcium acetate into a mixture of calcium and of copper acetates is accompanied by a contraction in volume, and Spring and van't Hoff have shown that under a pressure of about 6000 atm. the hydrate is converted into the single salts according to the equation—

$$CuCa(C_2H_3O_2)_4.6H_2O = Cu(C_2H_3O_2)_2.H_2O$$
$$+ Ca(C_2H_3O_2)_2.H_2O + 4H_2O.$$

These two relations might be expressed in the following words: *An increase of pressure favours the system formed with a decrease in volume, while a reduction of pressure favours the system formed with an increase in volume.*

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[1] M. Carey Lea, *Phil. Mag.* [5], **31.** 323, 1891.

[2] T. L. Reicher, *Zeit. phys. Chem.*, **1.** 221, 1887; W. Spring and J. H. van't Hoff, *ib.*, **1.** 227, 1887.

W. Spring has verified the preceding law by his experiments upon the influence of pressure upon chemical reactions. He says, "every substance, at a certain temperature, assumes that state which is forced upon it," and he shows that by great pressures substances may be transformed into their allotropic forms, mixtures may be transformed into compounds, provided that the final products occupy a smaller volume than the original components.

Case III.—If v be zero, a variation of pressure will have no influence on the equilibrium. A mixture of hydrogen and iodine combine to form hydrogen iodide without change of volume—

$$H_2 + I_2 = 2HI.$$

The equilibrium should not therefore be altered by variations of pressure. Lemoine[1] found the following relations between the pressure and the equilibrium constant at a temperature of 440°.

Press. =	4·4,	2·3,	1·0,	0·2 atm.;
K =	0·24,	0·26,	0·26,	0·29.

Bodenstein observed a slight decomposition with increased pressures, and attributed the small rise of the dissociation constant to the existence of some secondary reaction at the temperature of the experiment.

§ 125. Combined Influence of Pressure and Temperature on Chemical Equilibria.

To illustrate the combined influence of pressure and temperature on chemical equilibria, let us take the reaction—

$$2AgCl + H_2 \rightleftharpoons 2HCl + 2Ag,$$

where the condition of equilibrium is—

$$K = \frac{C_{H}}{C_{HCl}^2} = \frac{p_1}{p_2^2}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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[1] G. Lemoine, *Ann. Chim. Phys.* [5], **12**. 145, 1877.

Case I. above. From van't Hoff's well-known equation (p. 387)—

$$\frac{d \log K}{dT} = \frac{A + BT}{T^2}; \therefore \log \frac{p_1}{p_2^2} = \frac{a}{T} + b \log T + c. \quad (2)$$

If v_1 and v_2 respectively denote the volumes of hydrogen and of hydrogen chloride, these volumes will be proportional to the corresponding partial pressures p_1 and p_2, or—

$$\frac{v_1}{v_2} = \frac{p_1}{p_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let p_0 denote the pressure of the hydrogen at the beginning of the experiment when the apparatus is completely filled with this gas at the absolute temperature T_0; let p_1 denote the partial pressure of the hydrogen, and p_2 the partial pressure of the hydrogen chloride at the temperature T (abs.). The total pressure of the mixed gases at the temperature T will be $p_1 + \frac{1}{2}p_2$. If the volume be kept constant, we get, from the ordinary gas equation—

$$\frac{p_0}{T_0} = \frac{p_1 + \frac{1}{2}p_2}{T}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Divide by p_1, and by p_2, then substitute the two results in (3) and (4); we get—

$$p_1 = \frac{T}{T_0} \cdot \frac{2p_0v_1}{2v_1 + v_2}; \; p_2 = \frac{T}{T_0} \cdot \frac{2p_0v_1}{2v_1 + v_2}. \quad . \quad . \quad (5)$$

Let x denote the fraction of hydrogen chloride per unit volume of the mixed gases, then—

$$x = \frac{v_2}{v_1 + v_2}; \; \therefore v_2 = \frac{v_1x}{1 - x}. \quad . \quad . \quad . \quad (6)$$

Substitute (5) and (6), in (2), and—

$$\log \frac{(2 - x)(1 - x)}{x^2} = \frac{a}{T} + (b - 1) \log T + \log \frac{2p_0}{T_0} + c. \quad (7)$$

Where the constants a, b, and c are to be evaluated from the experimental data in the usual way. It is now possible to calculate the value of x in terms of T, T_0, and p_0 as Jouniaux[1]

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[1] A. Jouniaux, *Journ. Chim. Phys.*, **1**. 608, 1903–4; *Compt. Rend.*, **136**. 1003, 1903.

has done for the action of hydrogen on the metallic haloids. The following numbers show that measurements made on this reaction are in harmony with theory.

p_0 mm. of mercury.	Temp. ° C.	$100x$, *i.e.* per cent. of HCl.	
		Obs.	Calc.
760	600	9·4	8·0
380	600	10·7	10·5
760	655	11·8	11·8
380	655	13·4	12·3
760	705	14·1	15·0
380	705	15·7	16·3

Very little quantitative work has been done in connection with the influence of other forms of energy upon chemical reactions. Light will be discussed in Baly's "Spectroscopy." The effect of magnetism upon chemical action is inappreciably small; and we know little more than that some chemical reactions may be induced when certain substances are exposed to the influence of Röntgen rays; radium, and other forms of radiant and "radio-active" energy.

§ 126. False Equilibrium—Pressure.

As with temperature, some observers state that a discontinuity occurs in the relation between the concentration of a reacting substance and the velocity of the reaction. In some cases the oxidation of phosphorus compounds is more rapid the less the concentration of the oxygen. In 1798, van Marum[1] observed that phosphorus glows more brightly in air under diminished pressure than under normal pressure, and Fourcroy,[2] ten years earlier, noticed that phosphorus does not

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[1] Van Marum, *Verhandelingen uitgegeven door Teylers Genootschap.*, 10, 1798. See J. H. van't Hoff's *Études*, 50, 1884.

[2] A. F. de Fourcroy, *Mem. de l'Acad. des Sciences*, 365, 1788.

oxidize so readily in pure oxygen as in air (that is, oxygen diluted with nitrogen). Joubert, Ikeda, Ewan, and Russell[1] have closely investigated the phenomenon under various conditions. Ewan proved that the velocity of oxidation of moist phosphorus is proportional to the pressure of the oxygen up to 520 mm., and after that, the velocity rapidly decreases, until, at 700 mm., the velocity was zero. The experimental numbers correspond with the curve shown in Fig. 38. The measurements of the rate in dry oxygen were somewhat irregular, as indicated in § 95. Ewan found that the rate of oxidation of acetaldehyde gradually increased with increasing pressure up to a maximum about 450 mm., and after that the rate of oxidation diminished with increasing pressure, becoming zero at 530 mm. The maximum rate of oxidation of sulphur was not attained at a pressure of 800 mm., and "whether a maximum velocity really exists at higher pressures . . . must be decided by future experiments."

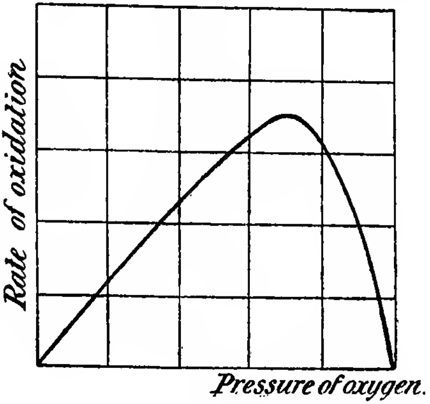

FIG. 38.

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[1] K. Ikeda, *Journ. Coll. Sci. Imperial Univ. Japan*, **6**. 43, 1893; T. Ewan, *Zeit. phys. Chem.*, **16**. 315, 1895; *Phil. Mag.* [5], **38**. 505, 1894; E. J. Russell, *Journ. Chem. Soc.*, **83**. 1263, 1903.

Like phosphorus, arsenic, sulphur (Joubert), silicon hydride,[1] nickel carbonyl,[2] and aldehyde (Ewan) oxidize more readily at low than at high pressures, and detonating gas is more inflammable at low than it is at high pressures. Thus, the ignition point falls from 620° at 760 mm., to 540° at 360 mm. pressure.[3] It is also interesting to notice that chemical reactions intimately associated with the respiration of animals and plants are influenced in the same way by pressure. Compressed oxygen appears to hinder the growth of animals and plants,[4] while rarefied oxygen has a stimulating effect upon certain organisms.[5]

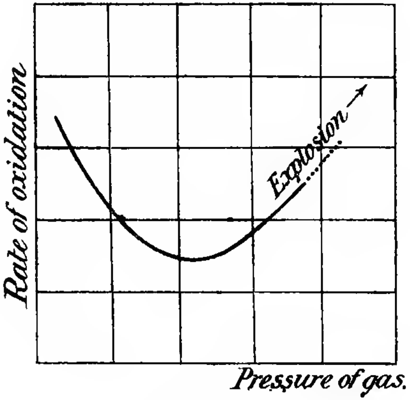

FIG. 39.

On the other hand, pyrogallol and ferrous sulphate are more readily oxidized by compressed oxygen.[6]

While engaged in the study of the chemical behaviour of

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[1] C. Friedel and A. Ladenburg, *Ann. Chim. Phys.* [4], **23**. 430, 1871.

[2] M. Berthelot, *Compt. Rend.*, **112**. 1343, 1891; *Ann. Chim. Phys.* [4], **26**. 561, 1892.

[3] A. Mitscherlich, *Ber.*, **26**. 163, 1893.

[4] P. Bert and O. Lehmann in W. Pfeffer's *Pflanzenphysiologie*, Leipzig, **1**. 548, 1897; **2**. 132, 1901; A. J. Ewart's trans., 1903.

[5] T. W. Engelmann, *Botanische Zeit.*, 320, 1882.

[6] O. Lehmann, *Pflüger's Archiv.*, **33**. 178, 1884.

phosphine, Houton de Labillardierre[1] noticed that when phosphine is mixed with half its own volume of oxygen, and placed in a suitable vessel, oxidation occurs at a certain stage of the rarefaction with explosive violence. Van de Stadt's[2] measurements of the relation between the pressure and the velocity of oxidation are shown graphically in the subjoined diagram (Fig. 39). The ordinates denote the rate of oxidation of the phosphine at the pressures indicated along the abscissa axis. Jorissen[3] obtained similar results for the oxidation of triethylphosphine, and Thorpe and Rodger[4] for the oxidation of thiophosphoryl fluoride.

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[1] Houton de Labillardierre, *Ann. Chim. Phys.* [2], **6**. 304, 1817.

[2] H. G. van de Stadt, *Zeit. phys. Chem.*, **12**. 322, 1898.

[3] W. P. Jorissen, *Zeit. phys. Chem.*, **21**. 304, 1896.

[4] T. E. Thorpe and J. W. Rodger, *Journ. Chem. Soc.*, **55**. 306, 1889.

CHAPTER XIV

EXPLOSIONS

§ 127. Ignition or Kindling Temperature.

ALTHOUGH the velocity of a chemical reaction is, in general, very sensitive to changes of temperature, yet, with the majority of chemical changes so far investigated, the quantity of heat developed during the reaction is either too small to have any appreciable effect on the velocity of the reaction; or the heat developed is dissipated by radiation or conduction before any marked rise of temperature occurs. The conduction and radiation of heat obviously depend on the nature of the walls of the vessel; on the nature and amount of foreign gases present; on the specific heat, diffusivity, and thermal conductivity of the substances taking part in the reaction, as well as on the temperature of the surroundings.

I. Explosive reactions.—The heat developed during the combination of oxygen and hydrogen gases at temperatures below 500° is dissipated too quickly to affect, very materially, the velocity of the reaction. Above this temperature heat is developed more rapidly than it can be conducted away. In consequence, there is a marked rise of temperature. This accelerates the velocity of the reaction. The increased velocity causes the development of a greater amount of heat. This, in turn, still further accelerates the rate of chemical transformation. The acceleration continues until finally the reaction goes on with explosive violence. We may therefore define an **explosion or detonation** *to be a reaction which goes on with an increasing velocity, and is accompanied by a rise of temperature.*

The minimum temperature which will enable combustion or explosion to take place is called the *ignition or kindling temperature, the flash point, or the temperature of explosion.* Thus, the ignition point of phosphorus in air is (about) 60°. Below its own ignition temperature phosphorus will not combine with oxygen fast enough to cause inflammation; at and above this temperature the oxidation is attended by combustion. Many gases spontaneously inflame at ordinary temperatures. Such are, for example, phosphorus dihydride, boron and silicon hydrides, thiophosphoryl fluoride, cacodyl, zinc ethyl. This means that the ignition temperature of these gases is at or below ordinary atmospheric temperatures.

It is not always necessary to heat the whole system to the temperature of ignition. The heat may be applied locally. A lighted match applied at one point will ignite a barrel of gunpowder; and a small electric spark is sufficient to ignite a vessel of detonating gas. . . . We must not confuse the "temperature of reaction" with the "temperature of ignition." The ignition temperature is no more the temperature at which the gases *begin* to combine than the boiling point of a liquid is the temperature at which vaporization begins.

II. Distinction between isothermal and adiabatic reactions.—When the temperature at any point in a mixture of gases is raised to the temperature of reaction, the heat developed may be sufficiently great to raise the temperature of the surrounding gas to such an extent that the reaction spreads throughout the system with great rapidity, or, the heat developed by the reaction may be conducted away so quickly that the temperature of the reacting gases never reaches the ignition point. In this case, the velocity of the reaction will gradually slow down to its normal value at the prevailing temperature.

For instance, if a bulb containing a mixture of equal volumes of hydrogen and chlorine gases be momentarily exposed to a flash of light, combination occurs and heat is evolved. The gases quickly expand, and as quickly contract, by cooling, to their former volume. If the gases had been exposed to the light for the fraction of a second more, the whole mixture would have entered into combination with explosive violence. Here, although the reaction has actually started, the heat evolved is conducted away so quickly that the temperature is at once reduced below the "temperature of reaction," and chemical action ceases. Again, Emich[1] has shown that under normal conditions of temperature and pressure, sparks less than 0·22 mm. in length will not ignite an explosive mixture of hydrogen and oxygen gases. In this case, so little of the gas enters into combination under the stimulus of the small spark that the surrounding gas is able to conduct away the correspondingly small amount of heat evolved during the reaction; thus the temperature of the gas is kept below the ignition point. The nitrogen and oxygen of atmospheric air can be made to burn with a flame producing nitric and nitrous acids,[2] but the evolution of heat is not sufficiently great to raise the temperature of the gas up to its ignition point; were it otherwise, the flame would quickly spread through the atmosphere "and deluge the world with a sea of nitric and nitrous acids."

If an endothermal reaction be started at one point, heat will be absorbed from the immediate neighbourhood; the temperature at the seat of the reaction will be reduced, and the velocity of the reaction will, in consequence, gradually slow down. It is therefore necessary that the temperature required to bring about the union of the gases be maintained, for, if the temperature be reduced below this point, the reaction will gradually come to a stand-still. In illustration, a candle flame may be extinguished by placing a helix of cold copper wire about the flame; if the helix be first heated, the flame will not be extinguished. The Hemming safety-jet for the oxy-

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[1] F. Emich, *Sitzber. Wiener Akad. Wiss.*, **16.** 10, 1897; *Natur. Rundsch.*, **12.** 575, 1897; *Monatshefte Chem.*, **18.** 6, 1897; **19.** 299, 1898; **21.** 1061, 1900. Emich noticed, by chance, that a mixture of hydrogen and oxygen exploded when a stream of mercury was run into the vessel. This was traced to the formation of small sparks which can be seen when the mercury strikes against the bottom of the vessel in darkness. For the difference between ignition by electric sparks and by an incandescent wire, see A. von Hemptinne, *Bull. Acad. Roy. Belg.*, **11.** 761, 1902.

[2] W. Crookes, *Chem. News*, **65.** 201, 1892.

hydrogen blow-pipe and the Davy safety-lamp are also applications of this principle.

It is therefore necessary to distinguish between isothermal and adiabatic reactions.

1. *Isothermal reactions.*—If the temperature of a reacting system be kept constant, and the volume and pressure remain constant, the velocity of the reaction will slow down more or less rapidly. The velocity of a reaction which proceeds isothermally must diminish from instant to instant.

2. *Adiabatic reactions.*—When the heat of an exothermal reaction is not conducted away from the seat of the reaction to the surrounding bodies, the resultant elevation of temperature may heat the mixture to the temperature of explosion.

III. Variable ignition temperatures.—H. Davy[1] appears to have been the first to investigate the ignition temperature of gases; the subject was also taken up by Bunsen in 1867, and by V. Meyer and pupils in 1890.[2] The ignition temperature is not only conditioned by the temperature and pressure of the gas, but it also depends upon the conduction of heat away from the seat of the reaction. This explains why the results given by different investigators vary considerably. Thus, numbers varying from 500° to 845°[3] have been published for the ignition temperature of hydrogen and oxygen gases mixed in the

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[1] H. Davy, *Phil. Trans.*, **105**. 225, 1816; **106**. 447, 1817.

[2] A. Gautier, *Bull. Soc. Chim.* [2], **13**. 1, 1869; V. Meyer with G. Krause, *Liebig's Ann.*, **264**. 85, 1890; with P. Askenasy, *ib.*, **269**. 49, 1892; with F. Freyer, *Ber.*, **25**. 622, 1892; *Zeit. phys. Chem.*, **11**. 28, 1893; with A. Münch, *Ber.*, **26**. 2421, 1893; *Nature*, **49**. 138, 1893; with M. von Recklinghausen, *Ber.*, **29**. 2549, 1896. For the ignition temperature of organic substances, see F. Ganther, *Chem. Zeit. Rep.*, **11**. 65, 1887; P. N. Raikow, *Chem. Zeit.*, **23**. 145, 1899.

[3] 500°–600°, E. Mallard and H. le Chatelier, *Annales des Mines* [8], **4**. 274, 1883; *Recherches expérimentales et théoriques sur la combustion des mélanges explosifs*, Paris, 7, 1883; 620°–710°, A. Mitscherlich, *Ber.*, **26**. 163, 400, 1893; *Compt. Rend.*, **122**. 566, 1896; *Zeit. analyt. Chem.*, **16**. 67, 1877; 845°, H. Hélier, *Ann. Chim. Phys.* [7], **10**. 521, 1897; A. Gautier and H. Hélier, *Compt. Rend.*, **122**. 566, 1896. For the reaction between carbon monoxide and oxygen, see V. Meyer and A. Münch, *Ber.*, **26**. 2429, 1893; for carbon disulphide, H. B. Dixon and E. J. Russell, *Journ. Chem. Soc.*, **75**. 600, 1899.

proportions to form water. The higher temperature—845°—was obtained by heating the mixed gases in contact with fragments of porcelain. These conducted away the heat so very quickly that the reaction almost lost its explosive character.

A current of gas passing through a hot tube can conduct away more heat than a gas confined in a closed tube at the same temperature. Hence the temperature of ignition appears to be higher in the former case than in the latter.[1] Freyer and Meyer (*l.c.*) found that—

Gas mixed with an equivalent of oxygen.	Temperature of ignition (explosion).	
	Current of gas.	Gas in closed tubes.
Hydrogen	650–730	530–606
Methane, CH_4	650–730	606–650
Ethane, C_2H_6	606–650	530–606
Ethylene, C_2H_4	606–650	530–606
Carbon monoxide	650–730	650–730
Hydrogen sulphide	315–320	250–270
Mixture: $H_2 + Cl_2$	430–440	240–270

Emich (*l.c.*) found that by increasing the pressure of electrolytic gas the inflammability was augmented, while an increase of the temperature diminished the inflammability of the gas.

IV. The presence of an indifferent gas, or of an excess of one of the reacting gases.—Combustion may be prevented by mixing the inflammable gases either with an indifferent gas, or with an excess of one of the reacting gases; the retardation is probably due to the absorption of heat by the added gases. For example, if a spark be passed through a mixture of air and ordinary "undried" hydrogen containing less than 5 per cent., or more than 72 per cent. of hydrogen, no explosion occurs. The gases only combine in the immediate neighbourhood of the spark. All mixtures of air and hydrogen

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[1] The temperature of the tube through which the gas was passing was not necessarily the temperature of the gas.

between these limits will explode. The following measurements[1] refer to mixtures of the gases named with air:—

Gas.	Per cent. of gas mixed with air.	
	Lower limit.	Upper limit.
Hydrogen	5	72
Methane	5	13
Carbon monoxide . .	13	75
Ethene	4	22
Acetylene	3	82
Water gas	9	55
Coal gas	6	29

According to Emich (*l.c.*), gases like hydrogen, nitrogen, and carbon dioxide act as diluents, and reduce the inflammability of electrolytic gas by reducing the partial pressure of the electrolytic gas. The first additions of oxygen appear to increase the inflammability, but further additions diminish it.

§ 128. Rate of Propagation of Flame through a Gaseous Mixture.

In the course of his celebrated investigation "On the Propagation of Flame through Small Tubes and Orifices," at the beginning of the nineteenth century, the attention of Humphry Davy[2] was drawn to the rate at which an explosion

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[1] F. Clowes, *Trans. Federated Inst. Mining Engineers*, **9.** 373, 382, 1898; *Journ. Soc. Chem. Ind.*, **14.** 1024, 1895; *Proc. Chem. Soc.*, **11.** 201, 1895; see also H. le Chatelier, *Annales des Mines* [8], **19.** 396, 1891; [9], **3.** 496, 1892; H. Bunte, *Ber.*, **31.** 19, 1898; P. Roszokowski, *Zeit. phys. Chem.*, **7.** 485, 1891; R. Bunsen's *Gasometrische Methoden*, Braunschweig, 48, 1877; H. E. Roscoe's trans., 1857; W. Hempel's *Gasanalytische Methoden*, Braunschweig, 113, 1900; L. M. Dennis' trans., 96, 1892; S. Tanater, *Zeit. phys. Chem.*, **35.** 340, 1900; H. le Chatelier and O. Boudouard, *Compt. Rend.*, **126.** 1344, 1510, 1898; H. B. Dixon, *Proc. Roy. Soc.*, **37.** 56, 1884; *Journ. Chem. Soc.*, **69.** 774, 1896; D. Clerk, *On the Theory of the Gas Engine*, London, 1882.

[2] H. Davy, *Phil. Trans.*, **105.** 225, 1816; **106.** 447, 1817; *Collected Works*, London, **6.** 26, 73, 1839–40.

passes along a tube, but the first careful measurements of the rate of an explosion were made by Bunsen[1] in 1867. An explosive mixture of gases was sent through a small orifice at the end of a tube, and the jet was ignited. In the Bunsen burner, it will be remembered, the flame is only steady when the mixture of gases travels along the tube faster than the flame can travel through the combustible gases. If otherwise, the flame "strikes back." Now, Bunsen measured the least speed which would prevent the flame "striking back" into the reservoir. In this way Bunsen found that a mixture of two volumes of hydrogen and one volume of oxygen burns at the rate of about 34 metres per second, while most other gases burn at the rate of about a metre per second. Bunsen obtained the following velocities in metres per second with various mixtures of carbon monoxide and oxygen:—

Vol. of CO = 25, 35, 45, 55, 65, 75, 85, 95 per cent.
Velocity = 0·30, 0·49, 0·66, 0·80, 0·88, 0·91, 0·70, 0·20 metres per sec.

Bunsen assumed that when the velocity of efflux of the gas is equal to the velocity of propagation of explosion the flame will not run back. This assumption cannot be allowed, because the flame would be cooled as it nears the jet owing to the conductivity of the metal around the orifice. Mallard and Le Chatelier[2] have shown that the velocity of efflux is smaller if an excess of one of the reacting gases is present. The results obtained were also found to depend upon the mode of ignition of the jet of gas.

Fourteen years after Bunsen's work on the velocity of explosion, Berthelot and Vieille,[3] and Mallard and Le Chatelier,[4] independently and simultaneously observed that

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[1] R. Bunsen, *Pogg. Ann.*, **131.** 161, 1867; *Phil. Mag.* [4], **34.** 489, 1867; W. Michelson, *Zeit. phys. Chem.*, **3.** 493, 1889.

[2] E. Mallard and H. le Chatelier, *Recherches*, Paris, 52, 1883.

[3] M. Berthelot and P. Vieille, *Compt. Rend.*, **93.** 18, 1881; **94.** 101, 149, 822, 1882; **95.** 151, 199, 1882.

[4] E. Mallard and H. le Chatelier, *Compt. Rend.*, **95.** 599, 1352, 1882; *Ann. Chim. Phys.* [5], **28.** 289, 1883.

an explosion may travel through a gaseous mixture with a far greater velocity than Bunsen supposed.[1] Berthelot and Vieille, moreover, made the important discovery that the rate of explosion increases rapidly from its point of origin until it reaches a maximum velocity, and subsequently travels with a uniform velocity, however long the column of gas may be. The velocity at which the explosion travels through the gas is seven or eight times that of a sound in the same gas, as will be seen from the second and third columns of the subjoined table. There is for every mixture of gases a specific value for the rate at which this rapid combustion spreads throughout the whole body of the gas when once it is started at any point. Berthelot and Vieille call this constant *l'onde explosive*, which may be rendered **explosion or detonation wave.** The rate of propagation of the explosion wave in various gases has been measured with great accuracy by M. Berthelot and by H. B. Dixon. A few of Berthelot's measurements are recorded in the second column of the following table:—

Mixture of gases.	Velocity in metres per second.	
	Explosion wave.	Sound wave.
$2H_2 + O_2$ . . .	2810	514
$2CO + O_2$. . .	1089	328
$CH_4 + 2O_2$ . .	2287	345
$C_2H_4 + 3O_2$ . .	2209	320
$2C_2H_2 + 5O_2$ . .	2482	323
$C_2H_2 + 2O_2$ . .	2195	286

It is perhaps necessary to point out that a "wave" in physics is simply a general word to represent the process by which energy is transmitted from one point of an elastic medium to another. There is no actual transfer of matter. in an explosion wave a certain *state* of matter is transmitted throughout the gaseous mass.

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[1] The fact, however, appears to have been suspected some time before. H. B. Dixon, *Phil. Trans.*, **184**. 97, 1893.

§ 129. The Explosion or Detonation Wave.

We have seen that explosive reactions may be propagated in two ways—

1. *A relatively slow combustion*, whose rate of progression was measured by Bunsen, and by Mallard and Le Chatelier, as indicated above.

2. *A rapid explosion wave*, whose rate of propagation was measured by Berthelot and Vieille, and by Dixon.

Some idea of the method employed by H. B. Dixon to measure the rate of explosion of gases in closed tubes may be obtained from the subjoined diagrams.[1] The apparatus is shown diagrammatically in Fig. 40. *AC* and *EF* are two steel tubes, between which is inserted a coil of lead pipe, *D*, of any desired length. Thin strips of silver foil are soldered across the tubes at *C* and *E* so as to form two "bridges." The whole is then completely filled with gas by means of the stopcocks *A* and *F*. A heavy pendulum carrying a plate of smoked glass (Fig. 41) is allowed to fall from a certain height. Two adjustable switches are arranged side by side so that the fall of the pendulum acts upon both at the same instant. Each of these switches, in a preliminary experiment, is in electrical connection with two electro-magnetic styles, which press against the blackened plate. When the switches are struck both

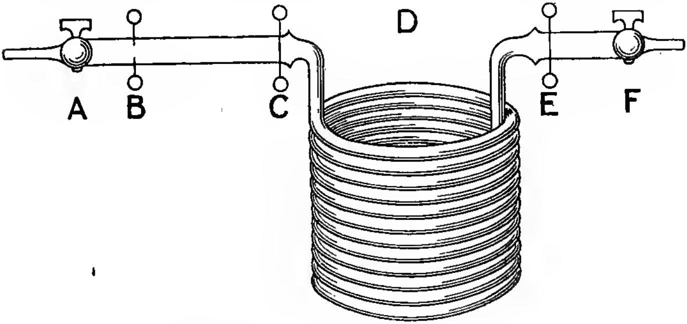

FIG. 40.—Dixon's app. (diagrammatic).

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[1] H. B. Dixon, *Phil. Trans.*, **184.** 97, 1893.

styles are released, and record their motion on the moving plate. The position of the marks so recorded, b_1 and b_2, are affected by a certain "retardation" of the electro-magnets. The pendulum is replaced at its former height, one style is connected with the silver bridge *C*, and the other with the bridge *E*, and one of the switches is connected with a coil and the sparking wires *B*. Within a minute of the preliminary experiment, the pendulum is again let fall and fire the mixture of gases at *B*. The explosion, starting at *B*, acquires its maximum velocity before it reaches the first silver bridge. When the flame reaches *C*, the bridge is broken and the first style is released, recording its mark on the moving plate c_1. This mark will of course be affected by the same retardation as its former mark, b_1. The explosion travels through the coil and breaks the bridge *E*, releasing the second style, which records its mark, c_2. The distance between the marks b_2 and c_2 gives the time between

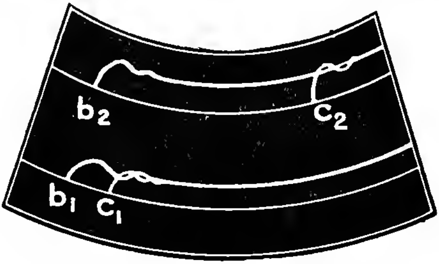

FIG. 41.—Style marks on smoked-glass plate.

the breaking of the second bridge independently of any retardation of the second electro-magnet. The distance between the marks b_1 and c_1 gives the time between the breaking of the spark-circuit and the breaking of the first bridge independently of any retardation of the first electro-magnet. Therefore, by subtracting a short interval (b_1 to c_1) from the longer interval (b_2 to c_2) we get the time of the passage of the explosion between the two bridges—cutting out the errors of the electro-magnets. In a subsequent experiment the styles and switches were reversed; the mean of two such experiments being taken as one determination.

To quote one experiment, Dixon found that the length of the tube from *C* to *E* was 75·35 metres; distance between the firing mark b_1 and the second bridge mark on the smoked glass *e* was 70·3 mm.; distance between the firing mark b_2 and the first bridge mark *c* was 4·7 mm. Hence the distance between the first and second bridge marks was (70·3 – 4·7 =) 65·8 mm. It was found, by means of a tuning-fork, that the plate moved 24·62 mm. per $\frac{1}{100}$ sec. Hence the time required by the wave to traverse 75·35 metres was—

$$\frac{65·8 \times 0·01}{24·62} = 0·0267 \text{ second};$$

$$\therefore \text{ Rate of explosion} = \frac{75·35}{0·0267} = 2820 \text{ metres per second.}$$

§ 130. Theoretical Rate of Explosion in Gaseous Mixtures.

After fairly accurate measurements of the rate of propagation of Berthelot and Vieille's "explosion wave" through various mixtures of gases had been made, attention was directed to the relation between the velocity of propagation of the explosion and the composition of the gaseous mixture. In the absence of any knowledge as to the mode of propagation of the disturbance, attempts have been made to find this relation from the study of particular cases. The different attempts may be grouped under two heads:—

I. The explosion wave is an ordinary physical (sound) wave in an homogeneous medium, and under such conditions that the normal velocity of translatory motion of the molecules is accelerated by the heat of the chemical reaction—Berthelot, Dixon.

II. The explosion wave is propagated like a physical wave in a medium which is discontinuous in the vicinity of the wave—Riemann, Hugoniot, Duhem.

I. According to the first hypothesis the phenomenon is supposed to be due to the passage of a physical wave of compression adiabatically through the gas. The layer of burning gas exerts a pressure on the layer of unburnt gas just in front. This causes a rise of temperature.[1] When the temperature of each succeeding layer is raised by adiabatic compression to its temperature of ignition, the explosion will be propagated through the gases. From this point of view, the wave of detonating gas is preceded by a wave of compressed gas.

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[1] E. Mallard and H. le Chatelier, *Recherches*, **88**. 1883.

Chemical action takes place in a layer of compressed gas at an elevated temperature.

The pressure necessary to raise a mixture of hydrogen and oxygen to the ignition point can be readily calculated from the well-known formula—

$$\left(\frac{T}{T_0}\right)^\gamma = \left(\frac{p}{p_0}\right)^{\gamma-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the ratio of the specific heats of the gas at constant pressure and at constant volume, *i.e.* 1·41; T_0 is the initial temperature of the gas corresponding with the pressure p_0; similarly, T is the absolute temperature of the gas corresponding with the pressure p. If, when $T_0 = 237°$ (*i.e.* 0° C.), $p_0 = 1$ atmosphere—

$$T = 273p^{0·29}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the temperature of ignition of a mixture of two volumes of hydrogen and one volume of oxygen be 600° C., the corresponding value of p will be 40 atm. (nearly).

Assuming the truth of the kinetic theory of gases, we can calculate the mean velocity U with which the molecules must be moving when we know the absolute temperature T, and the density ρ of the gas, for Clausius[1] has shown that—

$$U = 29·354\sqrt{\frac{T}{\rho}} \text{ metres per second.} \quad . \quad . \quad (3)$$

If all the heat Q which is evolved when the mixed gases—say, hydrogen and oxygen—combine is spent in warming up the products of combustion—water vapour—then the maximum temperature T, attained by the products of the reaction during the explosion, is given by the expression—

$$Q = CT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C denotes the specific heat of the gaseous steam under the conditions of the experiment.

Berthelot (*l.c.*) thinks that the specific heat of the products of the reaction is the ordinary specific heat of the gas at constant pressure; C is therefore written C_p. But he has some

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[1] R. Clausius, *Pogg. Ann.*, **110**. 375, 1857; *Phil. Mag.* [4], **14**. 108, 1857; O. E. Meyer's *Kinetische Theorie der Gase*, Breslau, 1877; R. E. Baynes' trans., London, 29, 1899.

misgivings, for he adds, "this method of arriving at the temperature is open to some doubt because of dissociation, and of the uncertainty of our knowledge of the specific heats of a gas at high temperatures." But granting the premises, Berthelot arrives at the expression—

$$V = 29{\cdot}354\sqrt{\frac{Q}{\rho C_p}}, \text{ (BERTHELOT'S FORMULA)} \quad . \quad (5)$$

from (3) and (4), for the velocity V of propagation of the explosion wave. This formula agrees fairly well with the measured rates of explosion of about twenty different mixtures.

In consequence of this agreement between the velocity of explosion and the mean velocity of translation of the gaseous molecules, Berthelot concludes that in the act of explosion a certain number of molecules in the wave dart in front with a velocity corresponding with the maximum temperature developed by the chemical combination. The impact of the products of combustion of one layer upon the unburnt gases of the next layer ignites the gases in that layer, and this goes on from layer to layer until the reaction is at an end. *The maximum rate of propagation of the explosion wave is therefore the mean velocity of the translatory motion of the products of combustion at the maximum temperature of the explosion.*

Dixon (*l.c.*) has measured the velocity of the explosion wave in many mixtures, and found that the rate is largely in excess of the rates given by Berthelot's formula. For instance, the velocity of the explosion (i.) of cyanogen with its own volume of oxygen; (ii.) of equal volumes of hydrogen and chlorine; and (iii.) of electrolytic gas diluted with either hydrogen or oxygen, is far above the theoretical rate:—

Mixture of gases.	Rate found by experiment.	Rate calculated by Berthelot's formula.
$C_2N_2 + O_2$	2728	2361
$H_2 + Cl_2$	1729	1571
$2H_2 + O_2 + 6H_2$ . .	3532	3028
$2H_2 + O_2 + 5O_2$ . .	1701	1476

Berthelot insists that his formula gives the *maximum* velocity which may be reached, but not surpassed, by the explosion wave. It will be evident from these examples that the formula requires correction. In consequence, Dixon has introduced the following additional assumptions into Berthelot's formula :—

i. *The gases are heated at a constant volume.* Berthelot's C_p must, in consequence, be replaced by C_v.

ii. *The temperature of the gas propagating the wave is double that due to chemical action alone.* Suppose that the molecules A_2 and B_2 combine to form two molecules of AB in the explosion wave. The hot 2AB molecules will collide with the cold molecules A_2 or B_2 just in front and warm them up. The A or B molecules so heated will collide with cold B_2 or A_2 molecules to form two new molecules of AB. The second lot of AB molecules will be warmer than the lot first formed. The heat of the hot molecules is thus shared with the cold molecules, and this, plus the heat of combination of the reacting gas, ultimately raises the temperature of the layer of gas in the explosion wave to *twice* that due to the chemical combination of the cold molecules A_2 and B_2.[1] If T is the initial temperature of the gas above absolute zero, we get the term $2(Q/C_v + T)$ in place of Berthelot's Q/C_p.

iii. *The temperature of the gas is increased when the volume of the products of the reaction is greater, and diminished when the volume of the products of the reaction is less, than the volume of the original mixture.* When a gas like $2H_2 + O_2$ explodes, the volume of the water vapour or steam is less than that of the reacting gases, and conversely, when the mixture $C_2N_2 + O_2$ explodes, the volume of the product $2CO + N_2$ is greater than

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[1] This Dixon illustrates by the following analogy: If a kilo of water at 0° falls *in vacuo* through 425 metres into a vessel containing another kilo of water at 0°, its motion is stopped, and an equal volume of water is displaced. The heat developed would raise the temperature of the fallen water 1°, but this heat is probably shared by the displaced water, which has now a temperature of 0·5°. If this falls another 425 metres into another kilo of water at 0°, the temperature of the displaced water will constantly approach, but never rise beyond 1°.

the volume of the initial mixture. The combination in the explosion wave is so quick that the gases have no time to assume their normal volumes, but are cooler or hotter (as the case might be) by the heat which would be lost or gained by their adiabatic expansion or contraction. Consequently the temperatures calculated for normal volume have to be corrected by means of the familiar relation—

$$\frac{T}{T_0} = \left(\frac{v}{v_0}\right)^{\gamma - 1},$$

where γ is the ratio of the ratio of the specific heats of the gas at constant pressure and at constant volume. The numerical value of the ratio γ, for air, is 1·41; T_0 and T are the temperatures corresponding with the volumes v and v_0, or v is the volume of the products of the reaction, and v_0 is the volume of the initial mixture of the gases.

iv. *The velocity of the molecular motion in the direction of the wave is less than the mean velocity of molecular motion in the body of the gas in the ratio* 0·7 : 1. Since the wave is propagated from layer to layer by the motions of the molecules of the gas, the velocity of the wave must be just as great as that with which the particles move to and fro in the direction of propagation of the wave. But the mean velocity of motion of the molecules is not in the direction of propagation of the wave, and therefore the speed of propagation of the wave is less than the mean speed of molecular motion in this gas. The measured velocity of sound is found to be 332 metres per second, the calculated velocity of the mean speed of the molecules is 485 metres per second, or as 0·68 : 1.[1] Hence, Dixon writes—

$$\text{Velocity of molecular motion} = 29{\cdot}354\sqrt{\frac{2\left(\frac{Q}{C_v} + T\right)\left(\frac{v_2}{v_1}\right)^{\gamma - 1}}{\rho}}. \quad (6)$$

Since the velocity of sound is 0·7 of this (including Laplace's correction), we have, by analogy—

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[1] See O. E. Meyer's *The Kinetic Theory of Gases* (*l.c.*), p. 74.

$$V = 0{\cdot}7 \, . \, 29{\cdot}354 \sqrt{\frac{2\left(\frac{Q}{C_v} + T\right)\left(\frac{v_2}{v_1}\right)^{\gamma - 1}}{\rho}} \quad \text{(Dixon's formula).} \quad (7)$$

A comparison of rate of transmission of the explosion wave calculated by means of this formula with the observed values is given in the next table.

Dixon's formula does not agree with the velocity of the explosion wave in pure mixtures of carbon compounds with oxygen sufficient for complete combustion; it does not agree with the velocity of the explosion wave in cyanogen mixtures burning to carbon *monoxide*, and in electrolytic gas unless largely diluted.

In the following table the rates of explosion of different proportions of hydrogen and oxygen are compared with the theoretical rates calculated according to the formulæ of Berthelot and of Dixon:—

Mixture.	Observed.	Calculated.	
		Berthelot.	Dixon.
$8H_2 + O_2$ . .	3532	3028	3516
$6H_2 + O_2$ . .	3527	3061	3571
$4H_2 + O_2$ . .	3268	3055	3585
$2H_2 + O_2$ . .	2821	2900	3416
$2H_2 + 2O_2$ . .	2328	2252	2650
$2H_2 + 4O_2$ . .	1927	1730	2024
$2H_2 + 6O_2$ . .	1707	1476	1718

It is suggested by Dixon that in the explosion of pure electrolytic gas the combination is limited by dissociation, and therefore the observed rate falls below that calculated for complete combustion. As the temperature is lowered by the addition of inert gases, more and more of the electrolytic gas is able to combine in the wave-front, and the temperature comes nearer to that calculated. In a similar manner in the explosion of carbon compounds, the formation of carbon dioxide in the wave-front is almost entirely prevented, the carbon burns directly to carbon monoxide, which gradually unites with any excess of oxygen *behind* the wave-front.

II. We now pass to the second class of explanations. Newton and Laplace's theory[1] of the propagation of a sound wave—

$$\text{Maximum velocity of sound} = \sqrt{\gamma\frac{p}{\rho}}, \quad . \quad . \quad (8)$$

rests upon the assumption that the gaseous medium is inert and homogeneous in front of the wave. This assumption will not explain how the velocity of propagation of a disturbance might exceed that of sound. Riemann[2] and Hugoniot,[3] however, have shown that when a compression wave has travelled a certain distance, a discontinuity may be set up in the medium just in front of the actual wave. This discontinuity enables the wave to travel with a far greater velocity than the simple theory of sound permits. The medium takes on a new elasticity in the path of the wave—*l'élasticité adiabatic dynamique* of Hugoniot. This hypothesis leads to the expression—

$$\text{Velocity} = \sqrt{\frac{p_0}{\rho_0}\left(\gamma + \frac{\gamma + 1}{2} \cdot \frac{p_1 - p_0}{p_0}\right)}, \quad . \quad . \quad (9)$$

for the rate of propagation of the disturbance. Here p_0 and ρ_0 respectively denote the initial pressure and density of the medium; p_1 the pressure at any point in the wave.

Vieille[4] has found that this expression is in harmony with his measurements of the velocity of transit of compression waves generated by the explosion of a mercury fulminate cartridge, and by the rupture of a diaphragm at one end of a cylindrical tube filled with an inert gas. In illustration, Vieille found that when $p_0 = 10,333$; and $p_1 = 38,000$—

Velocity = 600 (calc.) = 601·8 (obs.) metres per second.

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[1] See any textbook on "Sound." In what follows we cannot spare space to go into mathematical details. The reader must therefore refer to the memoirs quoted for fuller details.

[2] B. Riemann, *Göttingen Abhandlungen*, **8.** 43, 1858–59; Lord Rayleigh's *The Theory of Sound*, London, **2.** 41, 1894–6; W. J. M. Rankine, *Phil. Trans.*, **160.** 277, 1870.

[3] H. Hugoniot, *Journ. Maths. pures app.* [4], **3.** 477, 1887; **4.** 153, 1888.

[4] P. Vieille, *Mémorial des poudres et salpêtres*, **10.** 1, 1899–90.

Jouguet[1] has extended Hugoniot's theory to the explosion wave, and, with the aid of certain assumptions as to the specific heats of the reacting gases, has set up a formula which fits in with a number of observed velocities.

Riemann expresses the relation between the velocity of propagation of an abrupt variation of pressure and density in an inert gas by the formula—

$$\text{Velocity} = \sqrt{\frac{\rho_1(p_1 - p_0)}{\rho_0(\rho_1 - \rho_0)}}, \quad . \quad . \quad . \quad (10)$$

where p_0 and ρ_0 respectively denote the pressure and density of the gas through which the wave is passing; p_1 denotes the maximum pressure, and ρ_1 the density at any point in the wave. Schuster[2] has suggested that Riemann's expression might be applied to the explosion wave.

Now, the total work done during an explosion of gases is evidently the sum of three factors:—

(i.) The work done by the wave.

(ii.) The work of combination, *i.e.* the heat of the reaction.

(iii.) The work of expansion as the mixed gases change from an initial volume v_0 to a final volume v_1 in the act of combination.

By equating these different terms together, and introducing the condition which must be satisfied in order that the wave may have a maximum velocity, V, consistent with Riemann's formula, (10), Chapman[3] finds that—

$$V = \sqrt{\frac{2R}{MC^2}[\{(v_0 - v_1)C_p + v_0C_v\}C_pT_0 + (C_v + C_p)Q]}, \quad (11)$$

where R is the gas constant, T_0 is the initial temperature of the gas. This relation would, no doubt, enable the rates of explosion to be calculated if the mean specific heats of the gases were known, and the other assumptions were true. Unfortunately, this information is not at hand. The equation has therefore been applied to the calculation of the mean

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[1] E. Jouguet, *Compt. Rend.*, **138**. 1685, 1904; **139**. 121, 1904.

[2] A. Schuster, *Phil. Trans.*, **184**. 152, 1893.

[3] D. L. Chapman, *Phil. Mag.* [5], **47**. 90, 1899.

specific heats of the reacting gases from the rates of explosion, and from the data so obtained Chapman has calculated back again the velocity of explosion of different mixtures, and obtained consistent results.

According to the gas laws, the elasticity of a gas is a function of the temperature T and the volume v—

$$\text{Elasticity} = f(T, v), \quad . \quad . \quad . \quad . \quad . \quad (12)$$

readily calculated from the relation—

$$pv = RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where R is a constant. When any two of these three variables —p, v, T—are known, the third may be calculated. The expression is called the *characteristic equation*, or the *equation of condition* of the gas. In dealing with a mixture of gases capable of entering into chemical union, Duhem[1] introduces a new factor, α, into equation (12)—

$$\text{Elasticity} = f(T, v, \alpha), \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where α depends upon the chemical nature of the system. The form of the function $f(T, v, \alpha)$ is not even approximately known. The elasticity of such a medium is therefore quite different from that of a mixture of chemically indifferent gases. The elasticity will be greater than an inert medium, if the reaction is exothermal without change of volume; and less, if the reaction is endothermal.

The tacit assumption is here made that a very small variation of the physical variables—v and T—will involve a variation in the chemical composition of the medium. This is not in agreement with observations made with ordinary detonating gases. The temperature and pressure of many explosive gases can be considerably modified without any perceptible sign of chemical change. It is therefore necessary to assume that, when the temperature and pressure of a gas

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[1] P. Duhem's *Traité Élémentaire Mécanique Chimique fondée sur la Thermodynamique*, Paris, 1. 255, 1897; *Théorie Thermodynamique de la Viscosité, du Frottement et des Faux Équilibres Chimiques*, Paris, 139, 1896; *Thermodynamique et Chimie*, Paris, 454, 1902; G. K. Burgess' trans., 412, 1904.

are altered, the medium will remain chemically indifferent (or continuous) until it has undergone a "preparatory" modification whereby these variables attain a certain value—the limit of false equilibrium. While the medium is in the "inert" condition, chemical action cannot take place faster than the "preparatory" step; and as long as the inert condition obtains, the velocity of propagation of chemical change will not be greater than the velocity of sound.

The experiments of Petavel[1] on the rate of increase of pressure in the explosion of gases in cylinders are here of interest. With the more explosive mixtures it was found that 0·05 second after firing the rate of rise of pressure suddenly increases, and becomes over nine times as fast as before. This change occurs when the gas is very near its "temperature of explosion." A similar result would therefore be obtained if we heated the gases, by the combustion of a certain portion of them, until the entire bulk was at the "flash point;" the gases, having then passed through the "preparatory stage," enter at once into combination throughout the whole mass, and the result is an almost instantaneous rise of pressure to the maximum effect.

In brief, Duhem employs a complex function of temperature, volume, and chemical composition of the medium, in place of Hugoniot's "adiabatic elasticity," to enable him to augment the elasticity of a gas above that employed in calculating the velocity of a sound wave.

Unfortunately, all the formulæ hitherto proposed for the rate of an explosion wave assume the existence of conditions of which we have no direct experimental evidence. But, inasmuch as the hypothetical foundations lead to conclusions in harmony with the observed results, these assumptions have been employed as working hypotheses to direct the course of further investigation—hypotheses which are only to be regarded as the "crutches of science, to be thrown away at the proper time" (Dumas); the sole justification of the various

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[1] J. E. Petavel, *Manchester Memoirs*, 46. No. 5, 1901–2; *B. A. Reports*, 655, 1900; 768, 1901.

formulæ lies in the fact that they abbreviate in one single expression a number of diverse measurements.

§ 131. Empirical Observations.

A certain number of empirical relations have been observed. The more important are given in what follows.

I. Temperature.—A rise of temperature decreases the rate of propagation of the explosion wave. For example, with a mixture of two volumes of hydrogen and one volume of oxygen, under 500 mm. pressure, the rate at 10° = 2775, and at 100° = 2738 metres per second.

II. Pressure.—A rise of pressure increases the rate of propagation. Thus, with the above mixture at 10°, when—

$p =$ 20, 30, 50, 110, 150 cm.;
$V =$ 2627, 2705, 2775, 2856, 2872 metres per sec.

Above a certain "critical pressure" an increase of pressure appears to have no effect. The critical pressure is the pressure beyond which any further increase of pressure has no effect on the velocity. Hemptinne[1] has measured the "limiting pressure" below which explosion by sparking or incandescence will not occur. Thus—

Detonating mixture of oxygen with	Limiting pressure in mm.	
	By sparking.	By incandescence.
Hydrogen	35	192
Carbon monoxide . .	58	145
Acetylene	15	45
Carbon disulphide . .	12	14

It was also observed that hydrogen and nitrogen do not combine with sparks under a pressure of 80 atm., nor does acetylene and nitrogen under a pressure of 5 to 10 atm.; the acetylene simply decomposes into carbon and hydrogen.

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[1] A. von Hemptinne, *Bull. Acad. Roy. Belg.*, **11.** 761, 1902.

III. Material of the tube.—The velocity is independent of the material of the tube. The explosion travels at the same rate in a tube of lead as in a tube of caoutchouc.

It might be pointed out that the "flame" of an explosion in a glass vessel shows the bright spectrum lines of sodium and calcium,[1] and in an iron vessel those of iron. Dixon has shown that the light produced in the explosion of electrolytic gas is mainly due to material particles knocked off the glass and volatilized by the ignited gases.

IV. Diameter of the tube.—The velocity of the explosion wave is independent of the diameter of the tube above a certain limit. For example, with the above mixture, when the diameters of the tubes were 6·5, 9, and 13 mm., the velocities were 2799, 2821, and 2819 metres per second respectively. But H. Davy's well-known experiments (*l.c.*) show that the explosion wave is damped down and even extinguished in capillary tubes.

V. Time of explosion.—The rapidity of the increase of pressure is a measure of the "explosiveness" of a substance, and the time occupied from the commencement to the moment of maximum pressure is called the **time of explosion.**

For mixtures of two volumes of hydrogen with 12, 8, 5 vols. of air, the times of explosion were 0·150, 0·026, 0·010 second respectively; and when one volume of coal gas is mixed with—

vols. of air = 13, 11, 9, 7, 5;
time of explosion = 0·28, 0·18, 0·13, 0·07, 0·05 second.[2]

When the maximum pressure is attained the explosion is complete, although it does not follow that the combustion is complete.

The "time of explosion," however, depends upon the kind of spark used for igniting the gas. The subject is of great interest, and any generalizations which might be drawn from a complete investigation of this subject must serve as a guide to

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[1] G. D. Liveing and J. Dewar, *Proc. Roy. Soc.*, **36**. 471, 1884; H. B. Dixon, *Phil. Trans.*, **200**. 315, 1903.

[2] D. Clerk's *The Gas and Oil Engine*, London, 99, 1896.

the engineer in the designing of "ignition devices" for motor cars and gas engines.

VI. The presence of inert gases.—The presence of an inert gas retards the explosion wave at a rate proportional to the volume and density of the foreign gas. For example, with mixtures of three volumes of electrolytic gas with various amounts of nitrogen, the following results were obtained :—

Nitrogen	= 0,	1,	3,	5 vols.;
V (observed)	= 2821,	2426,	2055,	1815 metres per sec.
V (calc. Berthelot)	= 2900,	2321,	1814,	1558 " "
V (calc. Dixon)	= 3416,	2731,	2122,	1813 " "
V (calc. Chapman)	= —	2412,	2035,	1811 " "

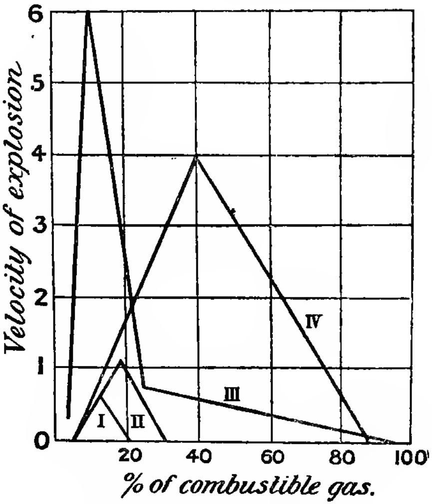

FIG. 42.—Rapidity of explosion.

H. Bunte[1] has investigated the velocity of propagation of explosion in mixtures of air with methane, coal gas, acetylene, and hydrogen. His results are shown graphically in Fig. 42. The diagram shows that the effects differ widely with different

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[1] H. Bunte, *Ber.*, **31**. 19, 1898.

gases. While coal gas and air can only be exploded with mixtures containing between 7 per cent. and 30 per cent. of air; acetylene and air can be exploded with all mixtures containing more than 5 per cent., and less than 81 per cent. of acetylene. This agrees with Clowes' results given on p. 449. The great rise of the acetylene curve also brings out very clearly the greater violence of explosions with acetylene than with coal gas. In the diagram, Curve I. is for methane; Curve II. for coal gas; Curve III., acetylene; and Curve IV., hydrogen.

VII. The presence of an excess of one of the reacting gases.—An excess of one of the combustible gases has the same retarding effect as an excess of a foreign gas of the same volume and density, which can take no part in the reaction. For instance, the effect of adding nitrogen (density 15) and oxygen (density 16) to three volumes of electrolytic gas is as follows:—

Velocity for pure electrolytic gas = 2821.

Nitrogen.		Oxygen.	
Volumes.	Velocity.	Volumes.	Velocity.
1	2426	1	2328
2	2055	3	1927
5	1822	5	1707

From this and similar results with other explosive mixtures, Dixon[1] argues that *when the addition of a gas retards the explosion by an amount which depends upon its volume and density, the added gas is inert so far as the propagation of the wave is concerned; and any change which the added gas might undergo is a secondary process which takes place* AFTER *the front of the explosion wave has passed by.*

This generalization has been applied to determine whether, in the combustion of gaseous carbon compounds—hydro-

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[1] H. B. Dixon, *Phil. Trans.*, **184**. 97, 1893.

carbons, or cyanogen—the carbon is first oxidized to carbon monoxide, or to carbon dioxide.

If 100 represents the rate of combustion of such a gas mixed with sufficient oxygen for burning the carbon to carbon monoxide, then, if sufficient oxygen be added for burning the carbon to carbon dioxide, the rate of explosion should be *increased* if the gases burn directly to carbon dioxide; whereas, if the gases always burn first to carbon monoxide, and the extra oxygen takes no part in the propagation of the explosion wave, the addition of an inert gas should *diminish* the rate of explosion.

Experiments were made with mixtures of methane, ethylene, and cyanogen with oxygen. The results are tabulated below. The rate of explosion, when sufficient oxygen is added for burning the carbon to carbon monoxide, is represented by 100 in each case.

Gas mixed with sufficient oxygen for burning to CO_2.	Calculated rate if the gas burns directly to—		Observed rate.
	CO_2	CO	
Methane . . .	104	92	94
Ethylene . . .	103	88	92
Cyanogen . . .	107	87	84

"These facts," says Dixon, "seem only consistent with the view that the carbon burns directly to carbon monoxide, and the formation of carbon dioxide is an after-occurrence."

In further support of this hypothesis, it was found that when sufficient oxygen was mixed with the gas to burn the carbon to carbon dioxide in one series of experiments; and nitrogen substituted for the oxygen in excess of that required for burning the carbon to carbon monoxide, in another series of experiments, the oxygen in excess of that required for burning the carbon to carbon monoxide actually retards the explosion wave more than the nitrogen. For example, with the following mixtures:—

$C_2N_2 + O_2$, $V = 2728$;
$C_2N_2 + O_2 + O_2$, $V = 2321$;
$C_2N_2 + O_2 + N_2$, $V = 2398$.

Hence it is inferred that the oxygen added to the mixture $C_2N_2 + O_2$ is as inert (so far as the propagation of the wave is concerned) as oxygen added to the mixture $2H_2 + O_2$ (Table, p. 459). Similar results were obtained with methane, ethylene, and acetylene.[1]

Horstmann, Harker, and others[2] have shown that "the law of mass action which holds good for very slow chemical reactions holds equally well for the rapid chemical combinations occurring at high temperatures, producing explosions. In rich mixtures where the active gases are but little diluted by a neutral gas the combustion is at first exceedingly rapid, but becomes slower as it proceeds, because of the diluting effects of the products. In a poor mixture, where the molecules of the reacting gases are widely separated by dilution, combustion is slow from the first." In other words, the velocity of a reaction diminishes as the mass of the products of the reaction increase. This is shown from the shapes of the curves depicted in Fig. 43, where the ordinates record the

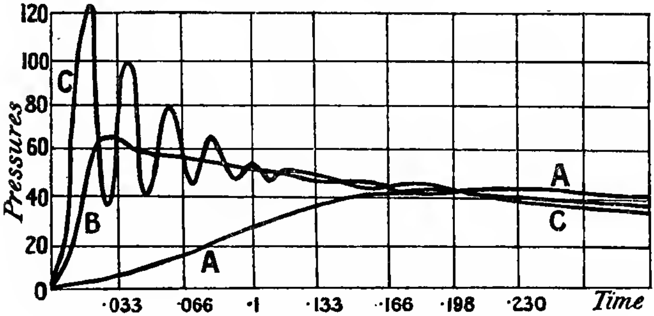

FIG. 43.—Velocity curves.

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[1] See also H. B. Dixon, "On the Burning of Carbon Compounds," *Journ. Chem. Soc.*, **69**. 774, 1896; **75**. 631, 1899.

[2] A. Horstmann, *Liebig's Ann.*, **190**. 228, 1878; *Ber.*, **10**. 1626, 1877;

amounts of gas consumed at the intervals of time represented by the abscissæ. The "amount of chemical action" is expressed in terms of the pressure per square inch above normal atmospheric pressure, viz. 14·7 lbs. per square inch. The results are tabulated below:—

Experiment.	Mixture.		Time of explosion (seconds).	Maximum pressure.
	Hydrogen.	Air.		
A	1	6	0·150	41
B	1	4	0·026	68
C	2	5	0·010	80

In Exp. *A* the pressure remained constant for some time after the maximum pressure has been attained. This appears to be due to chemical action among the gases unconsumed after the maximum pressure has been attained. In Exp. *B* the pressure falls rapidly soon after the maximum is attained; in Exp. *C* the maximum pressure is attained too rapidly for registration on the instrument used, on account of the oscillation of the piston in its spring.

Nernst[1] has raised the objection to the application of the law of mass action to such experiments as these because, "we do not know whether equilibrium is really established at the moment of ignition." The answer is that the measurements do not refer to the equilibrium at the temperature of the explosion, but to the equilibrium attained as the gases cool down behind the explosion wave.

VIII. The presence of water vapour.—Water vapour appears in many cases to act like an inert gas. Thus with an electrolytic mixture of hydrogen and chlorine the velocity of the explosion wave is 1745 metres per second in the dry gas, and 1720 in

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12. 1006, 1879; H. B. Dixon, *Phil. Trans.*, **175.** 617, 1884; D. Clerk, *Proc. Inst. Civil Engineers*, **69.** iii., 1, 1881–2; **85.** iii., 1, 1885–6; J. A. Harker, *Zeit. phys. Chem.*, **9.** 673, 1893.

[1] W. Nernst's *Theoretische Chemie*, Stuttgart, 1900; C. S. Palmer's trans. of the 1893 edit., 575, 1895.

the moist gas. The same thing may be said of dry and moist mixtures of oxygen with hydrogen, ethylene, or with cyanogen. On the other hand, water vapour undoubtedly plays an important part in some chemical reactions which take place in the explosion wave. Thus, no explosion occurs with a dry mixture of two volumes of carbon monoxide and one volume of oxygen. If, however, the following amounts of water vapour be present—

Water vapour = 1·2, 2·3, 3·7, 5·6, 9·5, 15·6, 38·4%;
V = 1676, 1737, 1713, 1782, 1742, 1666, 1266.

The presence of water vapour is necessary for this reaction; the speed of the explosion wave increases as the amount of water vapour increases; a maximum velocity is attained when between 5 and 6 per cent. of water vapour is present;[1] more water vapour retards the progress of the explosion wave like an inert gas. According to Dixon's interpretation, these phenomena may be due to the fact that the carbon monoxide "is oxidized by steam and not directly by the oxygen." See "Catalysis."

IX. Incompleteness of the combustion in the explosion wave.—D. Clerk[2] thinks that in an explosion of gas, the combustion is not completed instantly, but that the unburnt particles are still combining while the products of combustion are cooling. The evidence has already been quoted in reference to curve *A*, Fig. 43, p. 469. R. Bunsen[3] seems to have been under the impression that when the mixture $2H_2 + O_2$ is exploded, only one-third of the gaseous mixture is burnt, and "no further combination takes place until the gas has cooled down to a temperature at which explosion can begin again when another one-third is burnt." A. von Oettingen and A. von Gernet[4]

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[1] The numbers given in the table correspond with the vapour pressures of water at the respective temperatures of 10°, 20°, 28°, 35°, 45°, 55°, and 75°. The change in the velocity due to rise of temperature does not affect the point the numbers are intended to illustrate.

[2] D. Clerk, *l.c.*; A. Witz, *Ann. phys. chim.* [5], **30.** 289, 1883; *Compt. Rend.*, **99.** 187, 1884; **100.** 1131, 1885.

[3] R. Bunsen, *Pogg. Ann.*, **131.** 161, 1867.

[4] A. von Oettingen and A. von Gernet, *Wied. Ann.*, **33.** 586, 1888.

tried to prove Bunsen's principle of successive partial explosions by photographing the explosion flame as it travels through a tube containing the gaseous mixture. The explosion wave is indeed often followed by secondary waves running parallel with the first. Oettingen and Gernet state that this phenomenon is due to the fact that successive explosions are initiated at the electrodes, as Bunsen has described. H. B. Dixon[1] has however shown that the secondary waves of Oettingen and Gernet are not really waves of combustion, but are waves of compression, which travel to and fro among the products of combustion. Bunsen's conclusion is based upon a wrong interpretation of the experimental work, p. 184.

H. B. Dixon and W. H. Smith[2] have shown that *incompleteness of combustion is characteristic of the explosion wave*, and is not observed in ordinary eudiometric combustions. With a detonating mixture of carbon monoxide and oxygen, about 1 per cent. of the original detonating gas remained unburnt after the passage of the explosion wave.

§ 132. The Maximum Temperature attained in an Explosion.

The specific heat of a substance is the amount of heat required to raise the temperature of one gram of the substance 1°. Assuming that the specific heat of the substance remains constant, the number of units of heat, Q (calories), required to raise the temperature of m grams of the substance $\theta°$ C. is—

$$Q = mC\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C denotes the specific heat of the given substance.

Now let Q denote the amount of heat developed during any chemical reaction, say the formation of carbon dioxide from a mixture of equal volumes of carbon monoxide and oxygen, and further assume that the gases enter into chemical union at the moment of explosion, so that no carbon dioxide

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[1] H. B. Dixon, *Phil. Trans.*, **200**. 315, 1903.

[2] H. B. Dixon and W. H. Smith, *Manchester Memoirs* [4], **2**. 2, 1889.

is formed after the explosion. Then, θ will denote the temperature of the explosion, m the amount of gas (products of combustion) in grams heated up to the maximum temperature during the explosion. We know that 28 grams of carbon monoxide develop 67,700 units of heat when burnt to 44 grams of carbon dioxide. Let 0·15 be the specific heat of carbon dioxide when the volume of the heated gas is kept constant. From (1), therefore—

$$\text{Temp. of explosion} = \frac{67{,}700}{44 \times 0{\cdot}15} = 10{,}200^\circ \text{ C. (nearly)}. \quad (2)$$

Mallard and Le Chatelier have found the temperature of the carbon monoxide flame, burning in oxygen, is 3200° C. The calculated result, (2), is much too large. Some of the suppositions upon which the calculation is based are therefore erroneous. What are these assumptions? The more prominent are (i.) that no heat is conducted or radiated away from the burning gas; (ii.) that combustion is complete; (iii.) that the products of combustion do not dissociate at the high temperature attained by the burning gas; (iv.) that the specific heat of the carbon dioxide remains constant throughout a long range of temperature.

Let us examine the last assumption first. The experimental evidence inclines in favour of the view that the specific heat of a gas does increase with rise of temperature.[1] The actual relation between the temperature and specific heat is not known. For convenience it is customary to assume that this relation may be expressed by the series—

$$C = a + b\theta + c\theta^2 + \ . \ . \ . \ ,$$

where a, b, c, . . . are constants whose numerical values *should* be determined from the experimental data. For very

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[1] The evidence is not convincing, but see V. H. Regnault, *Relation des experiences*, **2.** 1, 1841; E. Wiedemann, *Wied. Ann.*, **2.** 195, 1877; H. B. Dixon and F. W. Rixon, *B. A. Reports*, 697, 1900; E. H. Stevens, *Phys. Gesell. Verh.*, Berlin, 54, 1901; *Drude's Ann.*, **7.** 285, 1902; H. Petrini, *Zeit. phys. Chem.*, **16.** 97, 1895; A. Kalähne, *Drude's Ann.*, **11.** 225, 1903; J. H. van't Hoff, *Boltzmann's Festschrift*, 233, 1904.

small changes of temperature, $d\theta$, the corresponding quantity of heat will be dQ—

$$\therefore\ dQ = mC.d\theta;$$

or—

$$dQ = m(a + b\theta + c\theta^2 + \ . \ . \ .)d\theta.$$

By integration between the limits of temperature θ_0 and θ_1, we get—

$$Q = m\{a(\theta_1 - \theta_0) + \tfrac{1}{2}b(\theta_1 - \theta_0)^2 + \tfrac{1}{3}c(\theta_1 - \theta_0)^3 + \ . \ . \ .\}. \quad (3)$$

The combustion of carbon monoxide in pure oxygen gas may be taken to illustrate the application of formula (3). It is known that 28 grams of carbon monoxide unite with 16 grams of oxygen to form 44 grams of carbon dioxide, and that in the union 67,700 units of heat are evolved. The specific heats of carbon dioxide at constant volume C_v and at constant pressure C_p, referred to the molecular weight in grams, taken between 0° and 1000° C., are respectively—

$$C_v = 6{\cdot}3 + 0{\cdot}005640\theta - 0{\cdot}00000108\theta^2;$$
$$C_p = 8{\cdot}3 + 0{\cdot}005640\theta + 0{\cdot}00000108\theta^2,$$

according to Mallard and Le Chatelier.[1]

Substitute these values, $a = 8{\cdot}3$, $b = 0{\cdot}00564$, $c = -0{\cdot}00000108$, and $m = 1$, in (3). The quantity of heat required to raise the temperature of a gram-molecule of carbon dioxide from 0° to 2000° will then be—

$$Q = 8{\cdot}3(2000) + 0{\cdot}0028(2000)^2 - 0{\cdot}00000036(2000)^3 = 26{,}360 \text{ cal.}$$

But the heat of combination of carbon monoxide with pure oxygen is 67,700 calories taken at constant pressure; 26,360 of these are employed in heating the carbon dioxide to 2000°, hence the remaining 41,340 calories are available for heating the gas above 2000° C. If we now employ Berthelot and Vieille's[2] expression for the specific heat of carbon dioxide between 2000° and 4000°—

$$C_v = 16{\cdot}1 + 0{\cdot}0015, \text{ and } C_p = 18{\cdot}1 + 0{\cdot}0015,$$

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[1] E. Mallard and H. le Chatelier, *Compt. Rend.*, **91.** 825, 1880; **93.** 1014, 1881.

[2] M. Berthelot and P. Vieille, *Compt. Rend.*, **95.** 1280, 1882; **96.** 116, 1218, 1358, 1882; *Ann. Chim. Phys.* [6], **4.** 17, 1885.

we can compute the temperature to which the carbon dioxide will be heated in virtue of the 41,340 calories. From (1)—

$$Q = 18{\cdot}1(\theta - 2000) + 0{\cdot}00075(\theta - 2000)^2.$$

But $Q = 41,340$, hence—

$$0{\cdot}000{\cdot}75\theta^2 + 15{\cdot}1\theta = 74,740\;;$$

consequently—

$$\theta = 4000^\circ \text{ (nearly).}$$

Mallard and Le Chatelier, as we have just seen, found the maximum temperature of the flame to be 3200°, by means of the Le Chatelier pyrometer.

In a similar manner, using the values—

$$C_v = 5 + 0{\cdot}00062\theta\;; \text{ and } C_p = 7 + 0{\cdot}0062\theta,$$

for the specific heat of nitrogen at temperatures up to 2000°, and—

$$C_v = 3{\cdot}5 + 0{\cdot}0016\theta, \text{ and } C_p = 5{\cdot}5 + 0{\cdot}0016\theta,$$

for the specific heat of the same gas between 2000° and 4000°, we may compute the maximum temperature developed by the combustion of carbon monoxide in air. In the preceding manner—

$$2CO + O_2 + 4N_2 = 2CO_2 + 4N_2.$$

We find that the calculated value of $\theta = 2322°$; Mallard and Le Chatelier find by measurement, $\theta = 2050°$. For mixtures of coal gas and air, D. Clerk (*l.c.*) gives the following numbers :—

Volumes of air mixed with one volume of coal gas.	Temperature ° C.	
	Observed.[1]	Calculated.
14	806	1786
13	1033	1912
12	1202	2058
11	1220	2228
9	1557	2670
7	1733	3334
6	1792	3808

---

[1] That is, calculated from the *observed* pressure.

The differences between the theoretical and the observed values are due to the uncertainty of the values of the specific heats at high temperatures; to the loss of heat by radiation and conduction; to the dissociation of the products of combustion at the temperature of observation, etc., which will be considered in the next section.

The maximum temperature developed in the explosion wave by the combustion of a mixture of carbon monoxide and oxygen may be readily calculated by using C_v in place of the C_p employed above. The value $\theta = 4300^c$ is thus obtained. The comparison of the calculated with the observed values is quite another matter.[1]

§ 133. Pressure.

A study of the pressure developed during the explosion of a mixture of gases is of great technical importance. The motive power of a gas-engine or of a motor-car, for example, is derived from the pressure produced by the explosion of certain hydrocarbons and air, much in the same way that the pressure of steam in a steam-engine is used to propel the piston of the engine.

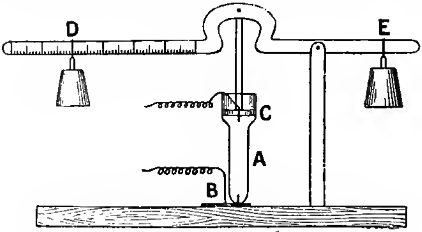

FIG. 44.—Bunsen's app. (diagrammatic).

The pressure developed during an explosion was first measured by Hirn.[2] Bunsen[3] then took up the subject,

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[1] See W. Macnab and E. Ristori, *Proc. Roy. Soc.*, 66. 221, 1900.

[2] G. A. Hirn, *Polytechnisches Centralblatt*, Leipzig, 1861.

[3] R. Bunsen, *Gasometrische Methoden*, Braunschweig, 319, 1877; *Phil. Mag.* [4], 34. 489, 1867.

working with an apparatus shown diagrammatically in Fig. 44. *A* is a piece of strong glass tubing resting on a sheet of tinfoil, *B*, which is in contact with a piece of platinum wire sealed through the lower end of *A*. The tube *A* is filled with gas and closed by a steel plate, *C*, connected with a lever, *DE*. The pressure on the plate *C* can be regulated and measured by adjusting the weights *D* and *E* along the arms of the lever. A wire is connected with *C* so that a spark can be passed through the gas. When the gas is exploded the outward pressure of the exploding gas on *C* is balanced by moving the weight *E* along the arm *D* until the plate *C* is just kept in position.

Bunsen found that for a mixture of carbon monoxide and oxygen the plate *C* remained at rest under a pressure of 10·2 atm., and that it was lifted up when the pressure was 10·04 atm. Similarly, for an electrolytic mixture of hydrogen and oxygen gases, Bunsen obtained a pressure of 9·5 atm.

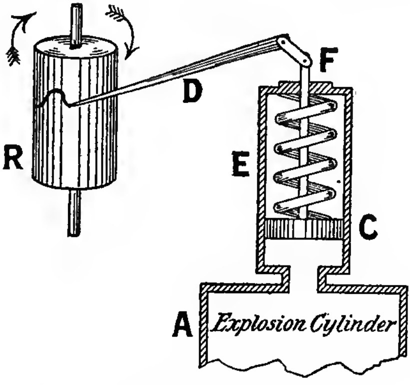

FIG. 45.—Clerk's app. (diagrammatic).

Berthelot and Vieille, Mallard and Le Chatelier, and Clerk, replaced Bunsen's lid with a light piston, *C* (Fig. 45), moving against a spring, *E*. Clerk's arrangement is shown diagrammatically in Fig. 45.[1]

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[1] D. Clerk, *Proc. Inst. Civil Engineers*, **85**. iii., 1, 1885-6; *The Gas*

The piston rod *F* works against a movable arm, *D*, which presses a pencil-point against a revolving cylinder, *R*, rotated by clock-work. The gases are exploded in the steel cylinder *A*; the pressure developed causes the piston *C* to rise. This alters the vertical position of the pencil-point connected with *D*, a record of the height of the piston rod is thus obtained on the paper attached to the revolving cylinder.

Petavel[1] has replaced the spiral spring by a metal tube, the longitudinal compression of which gives the indication. The compression of the tube is small, and within the elastic limits of the material. This small movement is magnified by the method of the "reflecting mirror and beam of light."

The results obtained by the investigators mentioned above confirm, in the main, the results of Hirn and of Bunsen. The observed pressures were always less than those calculated from the estimated maximum temperature of the gas during explosion.

For a mixture of carbon monoxide and oxygen, this temperature has been estimated (p. 478) at 10,200° C. During the combustion, however, there is a decrease in the volume of the gases, such that the final volume is but $\frac{2}{3}$ of the original. From the gas law—

$$p = \frac{v_1}{v_0} p_0 (1 + \tfrac{1}{273}\theta), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where v_0 and v_1 are the volumes of the gases at 0° and normal pressure p_0 before and after combustion. Hence—

$$p = \tfrac{2}{3} p_0 (1 + \tfrac{10200}{273}) = 25 \text{ atm. (nearly)},$$

when the normal pressure p_0 is one atmosphere. Bunsen observed 10·12 atm. The following table shows the observed and calculated pressures obtained by Clerk (*l.c.*) for various mixtures of air and coal gas :—

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and Oil Engine, London, 96, 1896; G. C. Douglas, *Engineer*, **63**. 308, 1887; **94**. 442, 1902.

[1] J. E. Petavel, *Manchester Memoirs*, **46**. No. 5, 1901-2; *B. A. Reports*, 655, 1900; 768, 1901

Volumes of air mixed with one volume of coal gas.	Maximum pressures.	
	Observed.	Calculated.
14	55	105
13	67	111
12	75	118
11	76	127
9	93	149
7	102	183
6	105	127

The numbers prove that if the theoretical pressures are calculated from right premises (theories or hypotheses), *only about* 50 *per cent. of the available energy is utilized in the explosions of the gas engine.* It is therefore of vital importance to find how the energy has been lost.

As a matter of fact, Grover[1] obtained "maximum pressures" even less than those of Clerk, but Wimperis[2] has shown that the discrepancy was due "to the presence of a film of water of varying extent" in the explosion cylinders employed by Grover.

It is easy enough to express the relation between the volume of air v (say, in cubic feet) and the maximum pressure p (say, in lbs. per square inch) in the form of a mathematical expression without theoretical basis. Thus, Perry[3] writes—

$$p = 136 - 6{\cdot}57v.$$

But this does not help us to answer the question—

§ 134. Where has the Lost Energy gone?

While all observers agree as to the deficit, there is some disagreement as to the mode of explaining it. Four guesses have been made.

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[1] F. Grover's *A Practical Treatise on Oil and Gas Engines*, Manchester, 1897.

[2] H. E. Wimperis, *Engineer*, **96**. 511, 1903.

[3] J. Perry's *The Steam Engine and Oil and Gas Engines*, London, 440, 1904.

I. Hirn's theory of cooling.—When explosion occurs a point is reached at which the cooling effect of the enclosing walls is so great that heat is conducted away more rapidly than it is evolved by the explosion. The maximum pressure thus falls short of what it would be if no heat were conducted away during the progress of the explosion. "The maximum explosion pressure," says Witz,[1] "depends on the ratio of the cooling surface of the cylinder to the volume of the gas." But Clerk (*l.c.*) has shown that this theory is quite inadequate to explain the greater part of the loss. The maximum pressure is practically independent of the nature and capacity of the explosion vessel. Bunsen (*l.c.*) and Berthelot (*l.c.*) also obtained almost the same results with mixtures of hydrogen and oxygen, and yet the former used a small vessel a few cubic centimetres, capacity, while the latter used a vessel of 4000 cc. capacity.

II. Bunsen's theory of dissociation.—Here it is supposed that the products of combustion dissociate at the high temperature attained during the explosion. Perry (*l.c.*) accepts this explanation. The heat absorbed during the dissociation lowers the temperature of the burning gases and reduces the pressure in a corresponding way. "If dissociation were the sole cause," says Clerk (*l.c.*), "then, as water must dissociate more at a high temperature than at a lower, the apparent evolution of heat should be less at 1700° than at 900° . . . but this is not the case—

Max. temp. of explosion, 900° ; apparent evolution of heat, 55 % ;
Max. temp. of explosion, 1700° ; apparent evolution of heat, 54 %.

Some other cause than dissociation must therefore be acting to check the increase of temperature so powerfully at 900°."

This argument is ingenious. We must remember that the dissociation of carbon dioxide is only just perceptible at 1700°.[2] It is indeed doubtful if the dissociation, at 1700°,

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[1] A. Witz' *Traité Théorique et Pratique des Moteurs à Gaz*, Paris, 1892–99.

[2] C. Langer and V. Meyer's *Pyrochemische Untersuchungen*, Braunschweig, 64, 1885.

could be detected by the experiment of Clerk. Moreover, at the high pressure under which the explosion takes place, it is very doubtful whether there is any dissociation at all (see p. 173). Indeed, Clerk himself obtained practically the same result with mixtures compressed before ignition, again proving that dissociation cannot be detected under the conditions of the experiment.

III. Mallard and Le Chatelier's theory of variable specific heats.—Mallard and Le Chatelier assume that the specific heat of a gas rises with the temperature. I have already shown, on p. 473, that *if* we accept certain values for the specific heats of different gases at the high temperature of the explosion, we get results in close agreement with theory. For example, we have seen that the temperature of burning carbon monoxide is 4300° C. Hence, from (1)—

$$p = \tfrac{2}{3}p_0(1 + \tfrac{4300}{273}) = 11{\cdot}17 \text{ atm.},$$

which agrees fairly well with the number 10·12 found by Bunsen.

With the aid of Mallard and Le Chatelier's values for the specific heats of gases at high temperatures, supplemented by another hypothesis as to "the rate of cooling during explosion," Wimperis[1] has *made* his "calculated" pressures agree with those observed by Clerk.

The theory of variable specific heats seems to be the favourite mode of accounting for the lost energy, but Clerk (*l.c.*) raises the objection that "if it were entirely true that specific heat increases with increasing temperature, a great proportion of heat would apparently be evolved at the lower temperature, which is not always the case."

IV. Clerk's theory of incomplete combustion ("after burning").[2]—In Fig. 46 is shown a curve recorded on the revolving cylinder of Clerk's apparatus, Fig. 45, when a mixture of one volume of hydrogen and six volumes of air was fired in the explosion cylinder. The curve brings out

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[1] H. E. Wimperis, *Engineer*, **94**. 354, 1902; **96**. 511, 1903; A. Slaby, *Calorimetrische Untersuchungen*, Berlin, 1893.

[2] See p. 471 for "incomplete combustion in the explosion wave."

very clearly the fact that the explosion is followed by a very slow fall of pressure. In another experiment the maximum pressure was attained 0·026 second after ignition, and it required 1·5 second, *i.e.* sixty times as long, to regain atmospheric pressure. Consequently, although the explosion may be finished, complete combustion must be going on at a rate sufficiently fast to compensate for the loss of heat by the cooling action of the walls.

Clerk (*l.c.*) believes that this phenomenon is an adequate explanation of the discord between the theoretical and the observed results, and that there is no need to assume any considerable dissociation or variation of specific heat of the products of combustion. This conclusion is fully in accord with the law of mass action, as pointed out on p. 472.[1]

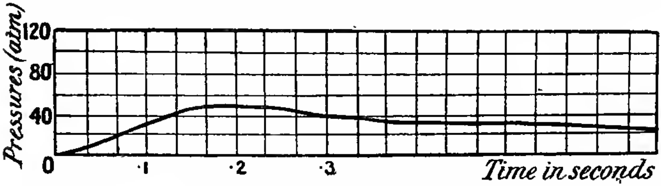

FIG. 46.—Velocity curve.

Incidentally it may be noted that the rate of cooling must be rather slow, because, at the end of 0·66 second, the mixture was still 20 lbs. per square inch in excess of the normal atmospheric pressure.

§ 135. Fugitive or Transitory Pressures.

The observed maximum pressure, 10·12 atm., is not sufficient to raise the temperature of the gas in the explosion wave to the ignition point[2] of the mixture of gases, for we

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[1] Grover (*l.c.*) has made the interesting observation that if an explosive mixture of coal gas and air be diluted with the products of a previous explosion, the maximum pressure is increased.

[2] E. Mallard and H. le Chatelier, *Recherches*, 89, 1883.

have already found that a pressure of 19 atm. is required for this purpose. If, then, the explosion occurs in the layer of compressed gas (p. 454), the upper limit of the pressure in the explosion wave itself will be—

$$p = \frac{2 \times 19}{3}\left(1 + \frac{4900}{273}\right) = 240 \text{ atm. (nearly).}$$

Notice should here be taken of the greater explosive power of a compressed gas. This fact is utilized in gas engines, say, of the "Otto" type.

We must remember that the pressures measured by Bunsen, and by Berthelot and Vieille, are really mean or "effective" pressures produced by the whole mass of gas. Mallard and Le Chatelier, working with the extremely sensitive manometer of M. Despretz,[1] found that in mixtures which burnt very rapidly local variations of pressure were produced in the vicinity of the explosion wave far greater than those measured by Bunsen. These **fugitive or transitory pressures**, as Mallard and Le Chatelier call them, are produced either in the compression wave which travels in front of the explosion wave, or else in the explosion wave itself.

H. B. Dixon[2] sought an approximate idea of the magnitude of the transitory or fugitive pressures by exploding the gases in tubes known to be capable of withstanding a certain pressure.[3] For instance, "four green glass tubes were tested by compressed air at fifty atmospheres. All these tubes withstood the explosion of carbon monoxide and oxygen, and of hydrogen and oxygen. Two of these tubes were blown to pieces by the explosion of equal volumes of cyanogen and oxygen, and a third was fractured by compressed air at 78 atmospheres."

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[1] Described in O. Guttmann's *The Manufacture of Explosives*, London, **2**. 352, 1895.

[2] H. B. Dixon and J. C. Cain, *Manchester Memoirs* [4], **8**. 174, 1894; H. B. Dixon, R. H. Jones, and J. Bower, *Phil. Trans.*, **200**. 333, 1903.

[3] See W. P. Bradley and A. W. Browne, *Journ. Phys. Chem.*, **8**. 37, 1904.

According to Chapman (*l.c.*) the maximum pressure developed during an explosion is given by the expression—

$$p = \frac{MV^2}{v_0} \cdot \frac{C_v}{C_p + C_v} + p_0,$$

where, it will be remembered, M, V, v_0, and p_0 respectively denote the sum of the molecular weights of the components of the mixture, the velocity of the explosion wave, the original volume of the mixture, and the initial pressure. "The pressure for an explosion of equal volumes of cyanogen and oxygen," says Chapman, "calculated from this formula, is 57 atmospheres. Dixon, Jones, and Bower (*l.c.*), by breaking glass tubes, obtain the value 58 atmospheres." Unfortunately we are here again confronted with the unknown specific heats; the argument consequently appears to run in a circle, in spite of the fact that the selected values for the specific heats give satisfactory results when employed in two ways.

§ 136. Origin of the Explosion Wave.

The more powerful the igniting spark the less the distance traversed by the wave of compression before the explosion wave is established. The explosion wave is set up instantly when a suitable detonator of mercury fulminate is used to ignite the gas. If, however, the charge of fulminate be too strong, a wave of compressed gas is set up, which travels more rapidly than the explosion wave. The latter is then extinguished, in consequence of the agitation of the gas caused by the compression wave. Le Chatelier,[1] for example, found that the explosion wave was set up in a mixture of carbon monoxide and oxygen by means of a charge of 0·05 grm. of fulminate and extinguished by a charge of 0·75 grm.

Under ordinary circumstances, when the gas is fired by an electric spark, the explosion wave is set up when the combustion has travelled a few feet along the tube containing the

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[1] H. le Chatelier, *Compt. Rend.*, **130**. 1755, 1900.

gas. This preliminary wave of burning gas is called a **wave of progressive combustion.**

Professor Dixon has a lecture experiment to illustrate the "striking contrast" of the quiet burning of a mixture of carbon monoxide and oxygen in a short tube where no wave is generated with the violence of the explosion when a wave is set up in the gas. "A test tube full of the mixture may be ignited by a taper, when the quiet passage of the blue flame down the tube can be followed by the eye; the tube is then refilled and screwed on to the end of a few feet of leaden pipe filled with the mixture; the test tube is surrounded by metal gauze and a thick glass cylinder. On applying a flame to the open end of the pipe, or by passing a spark near the extremity, a loud report is heard, and the test tube is reduced to powder."

Mallard and Le Chatelier[1] have paid special attention to the phenomena which precede the development of the explosion wave. They have photographed the wave of progressive combustion on a revolving cylinder covered with a film of sensitive paper, and observed—

(1) That when a mixture, such as nitric oxide and carbon disulphide, is ignited at the open end of the tube, the flame travels a certain distance at a uniform velocity.

(2) At a certain point in the tube vibrations are set up which alter the character of the flame, and these vibrations become more and more intense, the flame swinging backwards and forwards with oscillations of increasing amplitude.

(3) That the flame either goes out altogether, particularly in narrow tubes, or the rest of the gas denotes with extreme velocity.

These phenomena are illustrated by the two photographs, Figs. 47 and 48.

Fig. 47 shows a photograph of the flame travelling through a mixture of carbon disulphide with six times its volume of nitric oxide. The flame advances with a uniform velocity up to a certain point; vibrations are then set up

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[1] E. Mallard and H. le Chatelier, *Recherches*, Paris, 1883.

which die down, recommence, and the flame dies out altogether a moment after.

Fig. 48 shows a photograph of a mixture of cyanogen and oxygen gases. The gas was ignited by an electric spark at the point *a* near the end of the tube (*O*, Fig. 49). The wave of combustion passed along the tube with a gradually increasing velocity, until at the point *b* (*Q*, Fig. 49) an explosion wave is set up. This photograph was taken under the following conditions: The wave of combustion travelled along the tube from left to right; the wheel upon which the sensitive film was placed rotated vertically downwards on the side nearest the explosion tube. The effect of the two motions on the film is much the

Fig. 47.—(After Le Chatelier.)

Fig. 48.—(After Dixon.)

same as if one were to draw a piece of chalk horizontally along a blackboard while the board was moving downwards. Fig. 49 will perhaps help one to form a mental picture of the process. *OQ* is the wave of progressive combustion, *QR* the explosion wave.

The distance traversed by the wave combustion at any point on the photographed wave is found by drawing the line *QM* (Fig. 49); the distance traversed by the rotating wheel may be represented by the line *OM*. The rate of propagation of the wave at the point *Q* will obviously be represented by the slope of the tangent to the curve *OQ* at the point *Q*. The

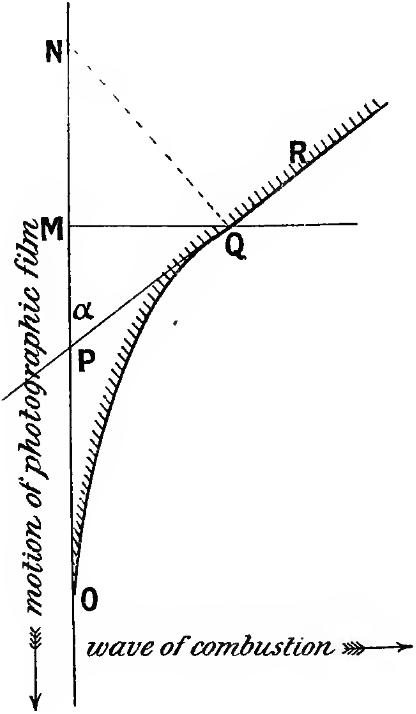

FIG. 49.

greater the slope of the curve the greater the velocity of the wave. The gradually increasing slope of the curve shows that the velocity of the wave is gradually increasing. A straight line, *QN*, means that a wave is travelling with a uniform velocity. If the left-to-right slope of the curve *OQ* means that the wave is travelling from left to right, then the right-to-left slope of the curve *QN* means that a wave also travels from right to left.[1]

We have seen that when a mixture of, say, acetylene and oxygen is ignited by an electric spark, a flame is propagated along the tube with a gradually increasing velocity. This wave of progressive combustion gradually merges into a true explosion wave. The straightness of the curve *bc* (Fig. 48, or *QR*, Fig. 49) shows that the wave of combustion now travels with a uniform velocity. In opposition to the views of Le Chatelier,[2] Dixon and Bradshaw have shown that in no case is there any discontinuity between the "period of acceleration" and the explosion wave proper. Dixon, Dawson, and Bradshaw[3] state that the apparent discontinuity between the period of acceleration and the explosion wave proper, observed by Le Chatelier, is simply a photographic effect technically known as "halation."

The wave of progressive combustion, that is the flame of increasing velocity which is anterior, in point of time, to the true explosion wave, is preceded by a wave of compressed gas, which travels on in front of the wave of combustion like "the undulations of the sea which precede the prow of a steamer;" or the mass of compressed air which Mach and Boys have shown to precede a projectile moving with a great velocity. This may be proved by the following experiment:[4] A mixture

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[1] Since $PM \tan \alpha = QM$, if *PM*, the rate of rotation of the wheel, and the magnitude of the angle α are known, it is easy to calculate the velocity of the wave at any point on the curve *OQ*.

[2] H. le Chatelier, *Compt. Rend.*, **130**. 1755, 1900.

[3] H. B. Dixon, B. Dawson, and L. Bradshaw, *Phil. Trans.*, **200**. 346, 1903.

[4] Unpublished experiment by Dixon and Bradshaw. If *E* is closed by an indiarubber stopper, the gas will not be ignited by the wave of compression.

of two volumes of hydrogen and one volume of oxygen is placed in a tube drawn out at one end in such a way that the funnel-shaped end *D* (Fig. 50) is followed by a piece of capillary tubing, *E*. The other end of the tube is sealed off. The detonating gas is then ignited by an electric spark at *A*. As the wave of combustion, *B*, travels along the tube from left to right, it is preceded by the wave of compression, *C*. When the wave of compression reaches *E*, the gas will be there ignited, owing to the heat generated during the compression of the gas, and this in spite of the fact that the actual wave of combustion has only traversed the tube as far as the point *D*.

The wave of compression does not travel so fast as the explosion wave, so that the wave of progressive combustion is always gaining on the wave of compression. Hence if the tube *AD* be long enough to allow of the development of the explosion wave, the latter will overtake the former, and the gas is not ignited at the point *E*.

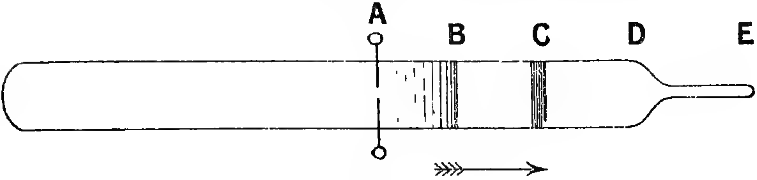

FIG. 50.

§ 137. Secondary Waves

The photographic study of explosion waves has revealed the existence of a whole series of secondary waves. For example—

(i.) Dixon has shown that at the moment the explosion wave is developed a wave of compression also travels backwards in the burned gases. Thus, on referring to the diagram (Fig. 48), the explosion wave travels from the point *b* (*Q*, Fig. 49) to the right, but another wave, *d* (*QN*, Fig. 49), starts from the same point and travels to the left. Dixon calls this a **retonation wave**;[1] Le Chatelier, *l'onde rétrograde.*

The retonation wave may, under certain conditions, travel backwards through the apparently "burnt" gases as rapidly as the explosion wave itself. The energy necessary for this must be due to chemical action. (See p. 22.) Combustion has therefore not been completed when the retonation wave returns.

The period of acceleration is distinguished not only by a slower propagation of the flame, *i.e.* of ignition, but also by a slower process of combustion. In the initial period, the molecules of the gas may meet many times before chemical reaction occurs; while in the explosion wave, the molecules may be so intensely agitated that most of the collisions between the reacting molecules are chemically fruitful. At the point of origin of the explosion wave, the rise of pressure must be exceedingly rapid, owing to the increase of chemical action, and this pressure appears to produce not only the forward explosion wave, but also the sudden backward "retonation" wave of compressed gas which passes through the gases still slowly burning behind the explosion wave. This compression wave must raise the temperature of the ignited gases, and so quicken the residual burning; its propagation is therefore analogous to that of the explosion wave itself, but modified by the extent to which the slow combustion has proceeded.[2]

(ii.) When the explosion wave is completely or partially arrested against the closed extremity or in a contracted portion of the tube, another wave of compression is also sent backward through the burnt gas. Dixon calls this a **reflexion wave**; Le Chatelier, *l'onde réfléchie.*

(iii.) When two explosion waves, generated simultaneously at different parts of the gaseous mixture, meet together, their

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[1] H. B. Dixon now calls the "explosion wave" a "detonation wave." At the place where the wave of progressive combustion ends the "detonation wave" goes forwards, while the "retonation wave" goes backwards.

[2] H. B. Dixon, *Phil. Trans.*, **200.** 339, 1903.

simultaneous extinction gives rise to two waves of compression, which proceed in the same direction as the explosion waves which they have succeeded. These waves are called **collision waves** by Dixon; *l'onde prolongée* by Le Chatelier.

The velocity of each of these waves varies with the density of the gaseous mixture through which they travel. Le Chatelier has obtained the measurements recorded in the following table by the method described in the footnote, p. 488.

Kind of wave.	Velocity in metres per second.		
	$C_2H_2+O_2$	$2CO+O_2$	C_2H_2+2NO
Explosion wave . .	2990	1900	2850
Retonation wave . .	2300	—	1140
Reflexion wave. . .	2250	1000	1350
Collision wave . . .	2050	—	—

These secondary waves, in turn, are reflected from the extremities of the tubes. In short tubes, a whole series of reflected waves cross and recross one another until they gradually die out altogether. Le Chatelier found that a retonation wave travelled backwards from an explosion wave in a mixture of acetylene and oxygen at the rate of 2300 metres per second; after reflection from the end of the tube it travelled at the rate of 1350 metres per second; then 1080 metres, and then 980 metres. Sound and undulatory movements of the gas still further complicate the movements of the flame rushing through the detonating mixture.

§ 138. Explosion of Solid and Liquid Substances.

So far we have dealt principally with the explosion of gaseous mixtures, but a great deal of empirical work has been done on the explosion of solid and liquid substances. It is possible that liquid and solid explosives like gases have a characteristic constant—the explosion wave. The velocity of explosion of dynamite and nitroglycerine in open air and in leaden tubes[1] is as follows :—

	Abel.	Berthelot.
Nitroglycerine .	1620	1300
Dynamite . . .	6090	2500

Berthelot could not prepare tubes strong enough to measure accurately the rate of propagation of the explosion in liquid methyl nitrate.

The practical application of liquid and solid explosives to military and mining operations has attracted a good deal of attention to this subject. The commercial value of an explosive depends largely on the amount of work that it can be made to perform. The intensity of the action depends on the volume of gases developed during the explosion, on the heat produced during the reaction, and on the velocity of explosion of the substance.

Measurements of the volume of the gases and of the thermal change which accompany an explosion have been made for the more important explosives. But the gases collected are not necessarily those existing at the high temperature of the explosion, but of the products after they have cooled down to atmospheric temperatures. For technical purposes, therefore, the intensity of action, that is of the pressure developed by the explosion, is determined practically by suitable instruments. A description of these instruments, etc., must be sought in text-books devoted to this subject. For example—

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[1] F. A. Abel, *Phil. Trans.*, **156**. 269, 1866 ; **157**. 181, 1867 ; **159**. 489, 1869 ; **164**. 337, 1874 ; *Compt. Rend.*, **69**. 105, 1869 ; **78**. 1227, 1301, 1362, 1874 ; **79**. 204, 294, 1874 ; **83**. 1011, 1876 ; *Proc. Roy. Soc.*, **13**. 204, 1864 ; **15**. 417, 1867 ; **17**. 395, 1869 ; **22**. 408, 1874 ; *Journ. Chem. Soc.*, **20**. 505, 1867 ; **23**. 41, 1870 ; *Phil. Mag.* [4], **32**. 145, 1866 ; **33**. 545, 1867. M. Berthelot, *Compt. Rend.*, **112**. 16, 1891 ; *Ann. Chim. Phys.* [6], **23**. 485, 1891.

M. Eissler's *Modern High Explosives*, London, 1893; and *A Handbook of Modern Explosives*, London, 1897.

O. Guttmann's, *The Manufacture of Explosives*, London, 1895.

M. Berthelot's *Sur la force des matières explosive sur la thermodynamique*, Paris, 1883; C. N. Hake and W. Macnab's trans., *Explosives and their Powers*, London, 1892.

D. Clerk's and W. H. Deering's articles in T. E. Thorpe's *Dictionary of Applied Chemistry*, London, **2**. 47, 64, 1891.

§ 139. Sensitiveness to Explosion.

In order that an explosion initiated at one point may be propagated throughout the whole mass, it is necessary that the temperature and pressure may have certain critical values which are determined by the nature of the substance. This "critical value" determines the sensitiveness of the substance to explosion.

One substance may be sensitive to a slight change of temperature, another to changes of pressure, another to shocks, and another to friction. For example, silver oxalate detonates at 130°, mercury fulminate at about 190°, and nitrogen sulphide at 207°, yet the fulminate is the most sensitive to shock or friction.

Sensitiveness to explosion also depends on the state of aggregation of the explosive.

As a general rule, sensitiveness increases with temperature, that is to say, a substance becomes more liable to explosion the nearer it is to the temperature at which decomposition sets in. In the neighbourhood of this temperature a substance appears to be in a state of "chemical tension," as Berthelot calls it. Thus celluloid does not detonate under the hammer at ordinary temperatures, but it will do so when heated to 160–180°—a temperature near which celluloid begins to decompose.

§ 140. Influence of Pressure on Explosives.

It is generally agreed that the explosion of gunpowder does not differ from ordinary combustion except that it is more rapid. The close relation between the pressure and the rate of combustion was recognized in some measure as early as the seventeenth century, when Robert Boyle[1] found that grains of gunpowder might be fused without explosion, when dropped on to a red-hot plate in a vacuous vessel. The observation was confirmed by C. Huyghens, Bianchi, and F. Hawksbee.[2] According to the latter, the sulphur might be sublimes from gunpowder in vacuo by the application of heat. Nitroglycerine, too, burns quietly in vacuo. Although mercury fulminate detonates in vacuo, yet the explosion is not communicated to particles in the immediate vicinity, not contiguous, as would be the case in air.

Mitchell[3] observed that "time fuses" burnt slower on high mountains, and St. Robert has expressed the relation between the pressure (p) and the velocity (v) of the combustion of gunpowder by means of the formula—

$$v = Ap^{\frac{2}{3}},$$

where A is a constant, and p varies between 722 and 405 mm. of mercury.

The retardation under diminished pressure is supposed to be due to the escape of the heated gases before they have time to heat the contiguous particles of gunpowder. In other words, the lower the pressure the more easily the hot products of combustion escape and carry with them the heat necessary for the ignition of the adjacent particles. On the other hand, by increasing the pressure the rate of combustion increases very rapidly. For example, Castan has estimated the velocity of combustion of gunpowder in the interior of a large bore cannon to be 0·32 metre per second, whereas it only attains one-third of this value when burnt in the open air.

Liquid acetylene is an explosive compound resembling

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[1] R. Boyle's *New experiments on the relation betwixt flame and air, and about explosions*, London, 1672; *Collected Works*, London, 3, 248, 1743.

[2] Bianchi, *Compt. Rend.*, **55**. 97, 1862; M. Berthelot, *l.c.*

[3] J. Mitchell, *Proc. Roy. Soc.*, **7**. 316, 1855; E. Frankland, *Journ. Roy. United Service Inst.*, 5, 1861; *Phil. Trans.*, **151**. 629, 1861; *Experimental Researches in Pure, Applied, and Physical Chemistry*, London, 844, 1877.

gun-cotton; acetylene gas at atmospheric pressures will not detonate by red-hot platinum wire, electric spark, or a mercury fulminate cartridge, but under two atmospheres pressure acetylene can be exploded by any one of these agents;[1] and compressed ozone may decompose with explosion.[2]

The resistance of air to the escape of the gaseous products of the decomposition of gunpowder obviously depends on the rate at which these products are liberated. The quicker the evolution of gas the greater the resistance of the air. Hence the "shock" given to the particles of air in the neighbourhood of the explosion depends on the velocity of decomposition of the explosive.

§ 141. Susceptibility of Explosives to Shocks.

As a general rule, the addition of energy is necessary to decompose a compound which has been formed with the evolution of heat. In order to decompose a gram of water at the ordinary temperature, an amount of energy must be added equivalent to that which would be liberated if 1630 kilograms were to fall a height of one metre. On the other hand, the decomposition of a compound which has been formed with the absorption of heat is relatively easily effected. A few strokes of a heavy hammer upon a small crystal of potassium chlorate, wrapped up in a piece of platinum foil and placed on an anvil, will be sufficient to produce a perceptible decomposition.

In order that a "shock" may effect the decomposition of a substance, it is necessary that energy should be communicated to the neighbouring particles so as to determine "step by step" the decomposition of the whole mass. The fall of a hammer is just able to produce a perceptible decomposition of potassium chlorate, but the same blow would bring about the explosion of a large mass of nitroglycerine. On the other hand, if the nitroglycerine be mixed with a siliceous earth, the

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[1] M. Berthelot and P. Vieille, *Ann. Chim. Phys.* [7], **11.** 5, 1897.

[2] P. Hautefeuille and J. Chappius, *Compt. Rend.*, **91.** 522, 1880.

dynamite, as the mixture is called, is but very slightly susceptible to shock. The porous structure of the silicate militates against the communication of energy from one particle to the next. An explosion of gunpowder in contact with nitroglycerine will cause the explosion of the latter, but not dynamite. Both these substances, however, explode under the influence of the violent shock imparted by the explosion of mercury fulminate. Hydrogen arsenide decomposes slowly at ordinary temperatures and pressures. It cannot be made to decompose "explosively" by an electric spark, but it will detonate when fired by a mercury fulminate cartridge.[1] Acetylene requires 137 cm. of mercury pressure before it can be exploded by an incandescent platinum wire, while a pressure of 100 cm. suffices if a mercury fulminate cartridge is used.[2]

§ 142. Explosion by Influence.

Abel has compared the effect of firing mercury fulminate and nitroglycerine in contact with gun-cotton. He found that ten times as much nitroglycerine as mercury fulminate was required to explode similar specimens of gun-cotton. An explosion was also induced in a charge of silver fulminate placed at the end of a tube by the explosion of a similar charge at the other end. This effect was not interfered with by placing diaphragms across the tube. Abel bases his explanation of these facts on the assumption that there is a synchronism between the vibrations induced in air or in ether, by mercury fulminate, and the natural period of vibration of the molecules. The superior detonating power of mercury fulminate is thus attributed to the fact that it can produce vibrations in gun-cotton which are not produced by nitroglycerine.

Champion and Pellet's experiments[3] are sometimes quoted

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[1] M. Berthelot's *Sur la Force des matières explosifs*, Paris, **1.** 114, 1888.

[2] M. Berthelot and P. Vieille, *Ann. Phys. Chim.* [7], **13.** 1, 1898; *Compt. Rend.*, **123.** 523, 1896; **124.** 988, 996, 1000, 1897.

[3] P. Champion and H. Pellet, *Compt. Rend.*, **75.** 210, 712, 1872.

in support of Abel's theory of "synchronous vibration." Small portions of nitrogen iodide were placed on a vibrating fiddle-string, and it was found that the detonation was only produced when the string vibrated with a frequency exceeding 60 vibrations per second. M. Berthelot[1] tried the effect of mechanical vibrations on chemical change by swinging vessels containing ozone, hydrogen arsenide, hydrogen peroxide, sulphuric acids and ethylene, and persulphuric acid on the prongs of a tuning-fork (100 vibrations per second), and also by exposing these substances to longitudinal vibrations (7200 per second) by pressing the vessels against the revolving disc of Koenig's wave syren. No effect could be detected. Nor should we expect any, for any vibrations capable of producing chemical change must be comparable as to period with that of the molecular vibrations.

Although the explosion of a charge at one end of a tube, in Abel's experiment, was not stopped by a diaphragm, yet Abel found that smoothness or roughness of the walls of the tube exercised a very considerable influence. We are therefore not justified in assuming that the vibrations causing explosion were transmitted through the material of the tube itself. But the result is just what we should expect if a wave of compressed air sent down the tube caused the explosion. When the wave impinges against the diaphragm in the tube the elasticity of the diaphragm causes another wave to be sent off on the other side.

The success of a detonator depends on the time of explosion, and on its density. If the time of explosion be too long, that is to say, if the detonator does not liberate the products of decomposition quickly enough to raise the temperature of a small portion of the explosive to the "critical" temperature, there will be no explosion, even though the explosive be shattered to fragments by the detonator. Vieille has proved that the instantaneous rise of pressure of nitroglycerine is not

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[1] M. Berthelot, *Ann. Chim. Phys.* [5], **20.** 265, 1880; *Sur la force des matières explosives*, Paris, **1.** 125, 1883; R. Threlfall, *Phil. Mag.* [5], **21.** 165, 1886.

so great as that of mercury fulminate. The fact that very large charges of nitroglycerine are able to bring about the explosion of gun-cotton shows that the "shock" imparted by small charges of nitroglycerine is very nearly great enough to raise the substance to its temperature of explosion. Some detonators which just fail to explode nitroglycerine at ordinary temperatures do so when the temperature of the nitroglycerine is raised.

In Abel's experiment the violence of the impact of the wave of compressed air set up at one end of the tube against the fulminate at the other end of the tube was, no doubt, sufficient to raise the substance to its temperature of explosion; so might Champion and Pellet's result be explained by the "suddenness" of the impact of the nitrogen iodide against the air, without the assumption of synchronic vibrations. But see p. 358.

APPENDIX

Table for calculating the Factor $\log_{10}\frac{a}{a-x}$ of Unimolecular Reactions

It is easy to see that—

$$\log\frac{a}{a-x} = \log\frac{1}{1-\frac{x}{a}} = \log\frac{1}{1-z},$$

where we have written—

$$z = \frac{x}{a}.$$

This fraction must be less than unity. The following table contains numerical values of the expression $\log_{10}\frac{1}{1-z}$ for values of z between 0·001 and 0·999. To illustrate its use, take the data for $t = 4$ on page 31; here $x = 49·3 - 13·8 = 35·5$.

$$\therefore z = \frac{x}{a} = \frac{35·5}{49·3} = 0·720.$$

From the table, when $z = 0·720$—

$$\log_{10}\frac{1}{1-z} = 0·5528;\ \therefore \frac{1}{4}\log_{10}\frac{1}{1-z} = \frac{0·5528}{4} = 0·138.$$

Tables of reciprocals and products are very handy for calculating up the results of bi- and ter- molecular reactions.

z.	·000	·001	·002	·003	·004	·005	·006	·007	·008	·009
0·00	0000	0004	0009	0013	0017	0022	0026	0031	0035	0039
0·01	0044	0048	0052	0057	0061	0066	0070	0074	0079	0083
0·02	0088	0092	0097	0101	0106	0110	0114	0119	0123	0128
0·03	0132	0137	0141	0146	0150	0155	0159	0164	0168	0173
0·04	0177	0182	0186	0191	0195	0200	0205	0209	0214	0218
0·05	0223	0227	0232	0237	0241	0246	0250	0255	0259	0264
0·06	0269	0273	0278	0283	0287	0292	0297	0301	0306	0311
0·07	0315	0320	0325	0329	0334	0339	0343	0348	0353	0357
0·08	0362	0367	0372	0376	0381	0386	0391	0395	0400	0405
0·09	0410	0414	0419	0424	0429	0434	0438	0443	0448	0453
0·10	0458	0462	0467	0472	0477	0482	0487	0491	0496	0501
0·11	0506	0511	0516	0521	0526	0531	0535	0540	0545	0550
0·12	0555	0560	0565	0570	0575	0580	0585	0590	0595	0600
0·13	0605	0610	0615	0620	0625	0630	0635	0640	0645	0650
0·14	0655	0660	0665	0670	0675	0680	0685	0691	0696	0701
0·15	0706	0711	0716	0721	0726	0731	0737	0742	0747	0752
0·16	0757	0762	0768	0773	0778	0783	0788	0794	0799	0804
0·17	0809	0814	0820	0825	0830	0835	0841	0846	0851	0857
0·18	0862	0867	0872	0878	0883	0888	0894	0899	0904	0910
0·19	0915	0921	0926	0931	0937	0942	0947	0953	0958	0964
0·20	1069	1075	1080	1085	1091	1096	1002	1007	1013	1018
0·21	1024	1029	1035	1040	1046	1051	1057	1062	1068	1073
0·22	1079	1085	1090	1096	1101	1107	1113	1118	1124	1129
0·23	1135	1141	1146	1152	1158	1163	1169	1175	1180	1186
0·24	1192	1198	1203	1209	1215	1221	1226	1232	1238	1244
0·25	1249	1255	1261	1267	1273	1278	1284	1290	1296	1302
0·26	1308	1314	1319	1325	1331	1337	1343	1349	1355	1361
0·27	1367	1373	1379	1385	1391	1397	1403	1409	1415	1421
0·28	1427	1433	1439	1445	1451	1457	1463	1469	1475	1481
0·29	1487	1494	1500	1506	1512	1518	1524	1530	1537	1543
0·30	1549	1555	1561	1568	1574	1580	1586	1593	1599	1605
0·31	1612	1618	1624	1630	1637	1643	1649	1656	1662	1669
0·32	1675	1681	1688	1694	1701	1707	1713	1720	1726	1733
0·33	1739	1746	1752	1759	1765	1772	1778	1785	1791	1798
0·34	1805	1811	1818	1824	1831	1838	1844	1851	1858	1864
0·35	1871	1878	1884	1891	1898	1904	1911	1918	1925	1931
0·36	1938	1945	1952	1959	1965	1972	1979	1986	1993	2000
0·37	2007	2013	2020	2027	2034	2041	2048	2055	2062	2069
0·38	2076	2083	2090	2097	2104	2111	2118	2125	2132	2140
0·39	2147	2154	2161	2168	2175	2182	2190	2197	2204	2211
0·40	2218	2226	2233	2240	2248	2255	2262	2269	2277	2284
0·41	2291	2299	2306	2314	2321	2328	2336	2343	2351	2358
0·42	2366	2372	2381	2388	2396	2403	2411	2418	2426	2434
0·43	2441	2449	2457	2464	2472	2480	2487	2495	2503	2510
0·44	2518	2526	2534	2541	2549	2557	2565	2573	2581	2588
0·45	2596	2604	2612	2620	2628	2636	2644	2652	2660	2668
0·46	2676	2684	2692	2700	2708	2716	2725	2733	2741	2749
0·47	2757	2765	2774	2782	2790	2798	2807	2815	2823	2832
0·48	2840	2848	2857	2865	2874	2882	2890	2899	2907	2916
0·49	2924	2933	2941	2950	2958	2967	2976	2984	2996	3002

s.	·000	·001	·002	·003	·004	·005	·006	·007	·008	·009
0·50	3010	3019	3028	3036	3045	3054	3063	3072	3080	3089
0·51	3098	3107	3116	3125	3134	3143	3152	3161	3170	3179
0·52	3188	3197	3206	3215	3224	3233	3242	3251	3261	3270
0·53	3279	3288	3298	3307	3316	3325	3335	3344	3354	3363
0·54	3372	3382	3391	3401	3410	3420	3429	3439	3449	3458
0·55	3468	3478	3487	3497	3507	3516	3526	3536	3546	3556
0·56	3565	3575	3585	3595	3605	3615	3625	3635	3645	3655
0·57	3665	3675	3686	3696	3706	3716	3726	3737	3747	3757
0·58	3768	3778	3789	3799	3810	3820	3830	3840	3851	3862
0·59	3872	3883	3893	3904	3915	3925	3936	3947	3958	3969
0·60	3979	3990	4001	4012	4023	4034	4045	4056	4067	4078
0·61	4089	4101	4112	4123	4134	4145	4157	4168	4179	4191
0·62	4202	4214	4225	4237	4248	4260	4271	4283	4295	4306
0·63	4318	4330	4342	4353	4365	4377	4389	4401	4413	4425
0·64	4437	4449	4461	4473	4486	4498	4510	4522	4535	4547
0·65	4559	4572	4584	4597	4609	4622	4634	4647	4660	4672
0·66	4685	4698	4711	4724	4737	4750	4763	4776	4789	4802
0·67	4815	4828	4841	4855	4868	4881	4895	4908	4921	4935
0·68	4949	4962	4976	4989	5003	5017	5031	5045	5058	5072
0·69	5086	5100	5114	5129	5143	5157	5171	5186	5200	5214
0·70	5229	5243	5258	5272	5287	5302	5317	5331	5346	5361
0·71	5376	5391	5406	5421	5436	5452	5467	5482	5498	5513
0·72	5528	5544	5560	5575	5591	5607	5622	5638	5654	5670
0·73	5686	5702	5719	5735	5751	5768	5784	5800	5817	5834
0·74	5850	5867	5884	5901	5918	5935	5952	5969	5986	6003
0·75	6021	6038	6055	6073	6091	6108	6126	6144	6162	6180
0·76	6198	6216	6235	6253	6271	6289	6308	6326	6345	6364
0·77	6383	6402	6421	6440	6459	6478	6498	6517	6536	6556
0·78	6576	6596	6615	6635	6655	6676	6696	6716	6737	6757
0·79	6778	6799	6819	6840	6861	6882	6904	6925	6946	6968
0·80	6990	7011	7033	7055	7077	7100	7122	7144	7167	7190
0·81	7212	7235	7258	7282	7305	7328	7352	7375	7399	7423
0·82	7447	7471	7496	7520	7545	7570	7595	7620	7645	7670
0·83	7696	7721	7747	7773	7799	7825	7852	7878	7905	7932
0·84	7959	7986	8013	8041	8069	8097	8125	8153	8182	8210
0·85	8239	8268	8297	8327	8356	8386	8416	8447	8477	8508
0·86	8539	8570	8601	8633	8665	8697	8729	8761	8794	8827
0·87	8861	8894	8928	8962	8996	9031	9066	9101	9136	9172
0·88	9208	9245	9281	9318	9355	9393	9431	9469	9508	9547
0·89	9586	9626	9666	9706	9747	9788	9830	9872	9914	9957
0·90	10000	10044	10088	10132	10177	10222	10269	10315	10362	10410
0·91	10458	10506	10555	10605	10655	10706	10757	10809	10862	10915
0·92	10969	11024	11079	11135	11192	11249	11308	11367	11427	11486
0·93	11549	11612	11675	11739	11805	11871	11938	12007	12076	12147
0·94	12218	12291	12366	12441	12518	12596	12676	12757	12840	12924
0·95	13010	13098	13188	13279	13372	13468	13565	13665	13768	13872
0·96	13979	14089	14202	14318	14437	14559	14685	14815	14949	15086
0·97	15229	15376	15528	15686	15850	15921	16198	16383	16576	16787
0·98	16990	17212	17447	17696	17959	18239	18539	18861	19208	19586
0·99	20000	20458	20969	21849	22218	23010	23979	25229	26990	30000

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