more valuable in clearing up uncertain points than did the original thesis. For this reason the author hopes that others may criticise his paper more vigorously than Mr. Sauveur has done. He is highly gratified that his comparatively unimportant and wholly tentative observations in "A Study of the Micro-Structure of Bronzes" should have drawn forth, from the distinguished engineer in charge of the Micro-Metallurgical Bureau of the famous Charlottenburg testing laboratories, one of the most valuable contributions to the science of microscopic-metallography that has appeared in any American publication.

CHEMICAL SECTION.

Stated Meeting, held December 6, 1898.

REACTION VELOCITY.

BY DR. ROBT. HART BRADBURY,
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The speed of a body moving uniformly is the distance passed over divided by the time taken to pass over it—

$$v = \frac{s}{t}$$

If the motion of the mass be not uniform, the division of the whole distance by the whole time will give simply the average speed and the velocity will be different at different points of the course. If we divide a small portion of the course, *e. g.*, 1 centimeter, by the time taken to traverse it, the result will be the average velocity over that centimeter and the variation in speed will be small; the approximation to the real velocity in that portion of the course will be close. Finally, if we consider an infinitely small portion of the path, *ds*, it is clear that the increment of velocity in passing over it will be an infinitely small quantity of the second order, or, in other words, the quotient

of an element of a path by the infinitely small time taken to traverse it,

$$\frac{ds}{dt},$$

is the rigorous mathematical expression for the speed.

Now, the law of mass action, which is the foundation of our knowledge of chemical equilibrium and of the velocity of chemical changes, asserts that the speed of a chemical process is proportional to the product of the concentrations of the reacting substances, each concentration being affected by an exponent which is equal to the number of molecules of that constituent which takes part in the change.

$$v = kC_1^{n_1}C_2^{n_2} \dots C_r^{n_r}.$$

This gives the speed of transformation from left to right in the chemical equation for the change.

For instance, if we consider the change of alcohol and acetic acid into acetic ester and water, the speed in the sense of the equation,

is expressed by

$$v = kC_1C_2,$$

since we have but two concentrations to consider, and since both substances enter the change with one molecule. By the concentration we understand the quantity in unit volume, expressed in gram-molecules.

Many chemical changes are reversible, *i. e.*, they proceed from right to left, as well as from left to right; the reaction products interact and reform the original substances. Thus, if we mix equivalent quantities of water and acetic ester, chemical transposition occurs and some acetic acid and alcohol are produced.

In reversible changes the direct reaction, *e. g.*, the production of ester and water from the alcohol and acid, and the reverse reaction, *e. g.*, the production of alcohol and acid from the ester and water, must be considered to occur together in the liquid. The observed velocity at any time

is the difference of the two. Writing v' for the speed of the reverse change there,

$$v' = k'C_1'C_2'.$$

Where C_1' and C_2' are the concentrations of the ester and the water, and if V is the observed speed, then

$$V = v - v' = kC_1C_2 - k'C_1'C_2'.$$

Introducing the possibility that each of the substances may enter the change with more than 1 molecule and making the number of substances unlimited, we have for the most general expression for the observed speed of change

$$V = v - v' = kC_1^{n_1}C_2^{n_2}C_3^{n_3} \dots - k'C_1'^{n_1'}C_2'^{n_2'}C_3'^{n_3'}.$$

In practice matters are greatly simplified by the facts that the exponents n_1, n_2 , etc., are always small numbers—no case is known where $n > 3$; that the number of substances which can simultaneously take part in a change is small, three being at present the limit in this case also; and that in many reactions the speed of the reverse reaction from right to left is so small, that it can be left out of account without introducing any serious error.

We have now to examine more narrowly the meaning of the term velocity, as applied to chemical changes. Instead of distance passed over, we have here to introduce the idea of quantity transformed and our unit, instead of centimeters, becomes gram molecules. If x is the quantity transformed in unit volume at any time, and t the time, then the average velocity for the time elapsed is

$$\frac{x}{t}$$

But the speed of a chemical change is a variable magnitude: theoretically it begins with its maximum value and sinks gradually to zero; hence the mathematical expression for velocity is the relation of an infinitely small quantity transformed to the infinitely small time taken to transform it, the differential coefficient of quantity by time.

$$\frac{dx}{dt}.$$

In the following formulation we shall make the assumption that the reaction proceeds in but one direction, or that the speed of the reverse change may be neglected.

Restricting the discussion to unit of volume, it is clear that if the concentrations of the several molecular species at the beginning are A, B, C, etc., that their concentrations after a time, t , during which a quantity, x , in gram molecules has been transformed, will be $(A - x)$, $(B - x)$, etc., and the velocity of the change at the time will be

$$\frac{d x}{d t} = k (A - x) (B - x) (C - x), \text{ etc.}$$

This expression becomes much simpler in the case where the concentrations of all the species, taken as always in gram molecules, are the same at the beginning—and where each enters the reaction with a single molecule. In this case the concentration of each species will remain the same through the process. That is $(B - x)$, $(C - x)$, etc., will equal $(A - x)$, and the velocity is

$$\frac{d x}{d t} = k (A - x)^n$$

where n is the number of substances which enter into the reaction. Or, in words: the velocity is proportional to the product of the concentrations of the reacting substances. In the case above, where the concentration of each of the substances is $(A - x)$, we may call this the system-concentration, and the velocity is then proportional to the system concentration affected by an exponent which is equal to the number of reacting substances. Using this simplification, we have for the reaction in which the concentration of but one substance is made to vary the reaction of the first order, as Ostwald calls it, or the monomolecular reaction according to Van't Hoff

$$\frac{d x}{d t} = k (A - x).$$

For a reaction in which two substances enter in molecular proportions, reaction of the second order of Ostwald, bimolecular reaction of Van't Hoff,

$$\frac{d x}{d t} = k (A - x)^2.$$

Finally, for a reaction in which the concentration of three substances is affected, reaction of the third order of Ostwald or trimolecular reaction of Van't Hoff,

$$\frac{d x}{d t} = k (A - x)^3.$$

Reactions in which four or more molecules are concerned are unknown.* One obtains an excellent idea of the progress of a chemical change by integrating these equations, and then making the "graph" of the resulting functions, laying off x on the axis of ordinates and t on the axis of abscissas.†

The course of the reaction is represented by a curve which rises from the time axis at first abruptly, then bends over to the right and ends by approaching asymptotically a line parallel to the time axis. The curve for the monomolecular reaction lies above that for the bimolecular, and this in turn above the curve for the trimolecular. These curves have no maxima and minima and no points of inflection, but this, of course, is evident from the differential equations, without recourse to the "graph."

The final state of things is $x = A$, that is, all the substance has been transformed. This state must evidently be reached with a velocity of zero, and cannot be passed. There is thus no inertia in a chemical change, no oscillation about the position of equilibrium, analogous to the vibration of a distorted solid.

Historically the first chemical change which was subjected to quantitative treatment was the inversion of sugar. The date of Wilhelmy's work on this subject, 1850, is an important one to chemical science, for until that time our science had contented itself almost entirely with acquiring

* Very recently a tetramolecular reaction has appeared. Compare Judson and Walker, *Journ. Chem. Soc.*, 73,410 (1898). A brief account of their work is given in a supplementary page.

† Ostwald, *Lehrbuch*, Vol. II, Part II, p. 228.

information about the final products of chemical changes, and the problem of studying the change itself had not been successfully attacked.

To devise the first successful mathematical description of a chemical change was undoubtedly a great achievement, and the very important work in reaction velocity which has been done within the last twenty-five years by Van't Hoff, Ostwald, Noyes and their students, is an outgrowth entirely of the seed which Wilhelmy planted.*

The inversion of sugar takes place under the influence of hydrogen ions and with absorption of a molecule of water. The concentration of the hydrogen ions is not altered, their action being catalytic, and the water is present in such large quantity relatively to the sugar that its concentration may be considered constant. The influence of these substances is the same throughout the change, and is incorporated in the constant k .

The change is therefore monomolecular, and is described by the equation

$$\frac{d x}{d t} = k (A - x)$$

In order to test the equation, to prove that it does as a matter of fact, describe the progress of the reaction in time, it is necessary to integrate it, to solve for k , and to ascertain whether k is in fact constant through the whole of the change.

Integrating we get

$$-\log. (A - x) = k t + C.$$

C , the constant of integration, is easily eliminated by recalling the fact that x , the change in concentration of the sugar and t , the time, are both zero at the beginning.

Introducing this condition we have

$$-\log. A = C, \text{ and}$$

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

* Wilhelmy's original paper has been reprinted with notes by Ostwald, *Klassiker d. Exakten Wissenschaften*, No. 29.

All the quantities in this expression for k are known or may be determined; t is simply the elapsed time.

A is the original concentration of the sugar, and x is easily ascertained at any moment by the polariscope. The results showed that the value of k is in fact constant, and that the differential equation must be regarded as a valid description of the change.

The differences in the value of k (from '001321 to '001499) are due to variations in temperature of the solution.

Temperature has a great influence on reaction velocity, and at present in all work of this kind the temperature of the solution is carefully maintained constant.

Another classical case of the monomolecular reaction is the decomposition of arsine. From the chemical equation

we might predict that the reaction would require the simultaneous meeting of four molecules, and would be tetramolecular.

Such a change would be described by the equation

$$\frac{dx}{dt} = k(A - x)^4$$

It has already been remarked that no tetramolecular reaction is known. In fact, trimolecular reactions are extremely rare. The reaction in question is eminently monomolecular, and the same logarithmic formula employed for the sugar inversion, gives values for k which are remarkably constant.

So far, the kinetic theory of the molecule has not been of much value in dealing with chemical phenomena. Nevertheless, a recent remark of Van't Hoff is of interest in this connection. The slow progress of a monomolecular reaction of this kind shows that not all the molecules are in the same condition. If they were, either none would decompose or they would all decompose at once. This reminds us of Maxwell's conception that the molecules of a gas possess all possible temperatures distributed about the mean value.*

* *Vorlesungen über Theoret. Chem.*, Vol. I, p. 187.

Another distinctly monomolecular reaction is the splitting up of di-brom-succinic acid into mono-brom-maleic acid and hydrobromic acid.

*

The bimolecular reaction.

In this case the concentration of two substances is changed as a result of the reaction, hence the equation is

$$\frac{dx}{dt} = k(A - x)^2$$

Integrating we obtain at once

$$\frac{1}{A - x} = kt + C$$

and remembering that x and t are simultaneously zero,

$$\frac{1}{A} = C$$

$$k = \frac{x}{At(A - x)}$$

The reactions whose progress is described by this formula are numerous. Among the most important are the saponifications of the esters; for instance, the action of sodium hydroxide on acetic ester, which, in the usual notation, is:

or in terms of the theory of electrolytic dissociation,

Reactions of this type have been investigated with special thoroughness by Warder, Reicher, Ostwald and Arrhenius, and it has been shown that, in general, the reac-

* *Van't Hoff-Cohen*. "*Studien zur Chemischen Dynamik*," p. 117; where there is an interesting instance of the possibility of detecting the presence of a mixture of isomers by investigation of the reaction velocity.

tion is bimolecular. Among other bimolecular reactions is the hydrolysis of acetamide by acids *e. g.* *

This is apparently trimolecular, but the water is present in such large quantity that its concentration may be considered constant. Further, the reaction between sodium hydroxide and sodium mono-chlor-acetate,

investigated by Schwab, under Van't Hoff's direction.†

Some of the most interesting of the recent work in this field is the investigation of the action of bases upon γ and δ lactones, carried out in Ostwald's laboratory, by Paul Henry.‡

From the older standpoint the reaction is, for butyro-lactone

or, more accurately,

In either case the reaction is accomplished by the meeting of two molecules, both of which are reduced in concentration as a result, and is therefore bimolecular. Henry placed 190 cubic centimeters of a solution of the base to be investigated, NaOH, KOH, Ba(OH)₂ etc., in a thermostat, and added 10 cubic centimeters of a $\frac{1}{10}$ normal solution of the lactone. The concentration of the base was so chosen that it became $\frac{1}{200}$ normal by the additional dilution to 200 cubic centimeters, the lactone, of course, be-

* Ostwald, *Lehrbuch d. All. Chemie*, Vol. II, Part II, p. 215.

† *Studien zur Chemischen Dynamik*, p. 14.

‡ *Zeitschrift für Phys. Chemie*, 10, p. 96.

coming $\frac{1}{200}$ normal at the same time. After the lapse of a time, t , counted in minutes, the value of x was determined by titrating the remaining alkali with dilute hydrochloric acid of known strength. In the case of the strong bases, potassium, sodium and barium hydroxides, the values of k were constant within the limits of error. With the weak bases a different behavior was to be expected: thus with ammonia, it is obvious that ammonium ions must accumulate in the liquid during the process; this will force back the dissociation of the ammonium hydroxide, reduce the concentration of the hydroxyl ions and cause the value of k to diminish with increasing time. In conformity with this, it was found that with ammonium hydroxide and methylamine hydroxide the value of k decreased as the time increased. It is interesting to notice the verification of another prediction of the theory of electrolytic dissociation. Since the stronger bases are dissociated with practical completeness at moderate dilutions, it was to be expected that no increase in their efficiency in converting the lactones into salts of the γ -oxy-acids would be noticed with increasing dilutions; with ammonia or other weak bases, we should expect increasing dissociation and increasing values of k . This conclusion was strikingly verified by experiment. Finally, we must notice Henry's interesting experiments on the saponification of acetic ester by barium hydroxide. In this case the old and the new view of the state of substances in solution make opposed predictions. From the older point of view the reaction is

Here, since the ethyl acetate enters, the reaction with two molecules, and the baryta with one, the speed is given by an equation of the form

$$\frac{d x}{d t} = k (A - x)^2 (B - x) \quad (1)$$

where A is the original concentration of the ester and B that of the base.

On the other hand, according to the more recent conception, the reaction is

and requires an equation of the simple form

$$\frac{d x}{d t} = k (A - x) (B - x), \quad (2)$$

A being again the concentration of the ester and B that of the hydroxyl, which, of course, is the same as the equivalent concentration of the base. The results showed that it was possible to get constant values of k by means of a form of equation (2), indicating that the hydroxyl ions exist free in the liquid, and that it is to them that the basic properties are due. In all work of this kind it is indispensable to keep the temperature constant; otherwise constant values of k cannot be obtained. Moro* investigated the production of the alkali salts of ethyl-sulpho-thio-carbonic acid from carbon disulphide, alcohol and potassium or sodium hydroxide

The purpose of the research was to find a typical trimolecular reaction, in which the three substances were different. This was not attained, because it was found necessary to work in dilute alcoholic solution, which, of course, made the concentration of the alcohol constant. In the case of the potassium salt, satisfactory constants were not obtained, but the reaction is probably bimolecular.† Bimolecular also were the reactions in which the same xanthates were produced from carbon disulphide and potassium or sodium ethylate:

For the trimolecular reaction, making the same restrictions as before, that the speed of the reverse change may be neglected and that the equivalent concentrations of the three substances are constantly the same, we have

$$\frac{d x}{d t} = k (A - x)^3$$

* *Gazzetta Chimica Italiana*, Vol. XXVI, p. 494 (1896).

† Curiously enough, with the sodium salt the reaction is accurately bimolecular.

Integrating

$$\frac{I}{2(A-x)^2} = k t + C.$$

The value of the constant of integration is again given by the fact that x and t are simultaneously zero. This gives us

$$\frac{I}{2 A^2} = C$$

$$k = \frac{I}{2t} \left(\frac{I}{(A-x)^2} - \frac{I}{A^2} \right)$$

or

$$k = \frac{I}{t} \left(\frac{2 A x - x^2}{2 A^2 (A-x)^2} \right)$$

Trimolecular reactions are rare; nevertheless, the three possible types are all known. The case where the three molecules are the same is represented by the polymerization of cyanic acid

which has been studied by Van't Hoff. Two molecules of one substance react with one of another in the reduction of ferric chloride by stannous chloride, the basis of the well-known rapid volumetric method for iron

This reaction has been shown to be trimolecular by Noyes. Finally, all three molecules are different in the oxidation of ferrous chloride by potassium chlorate and hydrochloric acid,

According to the chemical equation, this change requires the simultaneous meeting of thirteen molecules; yet the researches of Noyes and Wason leave no doubt that it is trimolecular.

[To be concluded.]