ART. XXVIII.—*On the Velocity of Chemical Reactions*; by
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IN investigating the laws of physical chemistry it is expedient for the physicist to devise and develop the methods of measurement, and for the chemist to apply them. In the following pages are described two methods of measuring the velocity of chemical reactions. The velocity of a chemical reaction is the rate at which a chemical compound appears or disappears during that reaction. The changes in the quantity of this compound present during successive intervals of time are measured by the changes in some property of the chemical system during the intervals. This property is usually either a chemical or a physical one.

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In the first of the following methods the basis of the measurement is the change in the index of refraction of the system, and in the second the change in its volume.

The first method is applicable to those chemical systems only that are transparent. It is substantially the following. Rays of light from an illuminated slit *S* (Fig. 1) passing through a long focus lens *L* and the tube *a b c d* form a distant image *S*₁ of *S*. The slit *S* is perpendicular to the plane of the diagram which represents a horizontal section of the apparatus. The tube *a b c d* has plane glass ends *a b* and *c d*; and a plane glass plate *a c* divides it into two wedge-shaped compartments. The ends *a b* and *c d* are not quite parallel to each other, so that if the two compartments are filled with liquids having the same index of refraction there will be a slight resultant refraction of the light rays that pass through the tube. The rays of light that pass outside of the tube therefore will form an image *S*₂ a little to one side of *S*₁. It is evident that if the liquid in one compartment (the wedge *a c d* for instance) is undergoing a chemical change its index of refraction in general will vary and the image *S*₁ will move sideways. The distance that *S*₁ has moved will be a measure of the change that has taken place in the index of refraction and, therefore, of the amount of substance in *a c d*, that has reacted. The displacements of *S*₁ can be determined by comparing its distances from *S*₂ which remains stationary.

In order to obtain a complete record of the position of S_1 a photographic plate S_1S_2 is placed in a vertical position at the images S_1 and S_2 and just in front of it a screen. A narrow horizontal slit cut in the screen allows a small part of the light only to pass through. At any instant of time, therefore, there will be two small spots of light on the plate at the intersections of the two images S_1 and S_2 with the projection of the slit on the plate. A system of cog-wheels allows the photographic plate to fall slowly during the reaction so that two lines are drawn on it, one of them straight due to the fixed image S_2 and the other curved due to the moving image S_1 . The curved line represents the reaction in that the abscissas are proportional to the intervals of time and the ordinates represent (but are not proportional to) the quantities of the substance that have reacted. After the reaction is completed the plate is drawn up and lowered again and the image S_1 traces a third line that is practically straight. This line may be taken as the zero line and the distances between it and the curved one are (at least in some cases) proportional to the amounts of the original compounds left in the solution.

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Fig. 2 is a reduced copy of a photograph representing the inversion of a 25 per cent solution of cane sugar, the inversion being accelerated by the addition of hydrochloric acid. The middle horizontal line represents the position of the image S_1 twenty-four hours after the reaction had started. The vertical lines were drawn with a dividing engine after the plate had been developed. The distance between two successive lines repre-

sents fifteen minutes. This distance was determined on a separate plate by lighting a magnesium burner for an instant every hour at some distance in front of the horizontal slit, and by measuring on the dividing engine the distance between the lines thus formed. A heavy vertical line to the extreme right of the plate (not seen in the copy) is a magnesium flash-light line and represents the instant at which the hydrochloric acid and sugar solution were mixed.

The photographic plate was fastened in a frame hung on a fine iron wire that was wrapped around a cylinder on the axle of one of the wheels in the works of a clock. The escapement of the clock was operated by an electro-magnet the circuit of which was made and broken by the swing of the pendulum of a standard clock. On account of the escapement the downward motion of the plate was by jerks, but as each jerk carried the plate only about $\frac{1}{20}$ th of a mm. this is not apparent from the photograph.

It is evident from the way in which the fifteen-minute lines are drawn that no correction need be made for the shrinkage of the gelatine films, for practically the same shrinkage takes place on one plate as on another. The shrinkage too reduces all the ordinates of the curve in the same proportion, and if the relative positions of the images are always determined by measurements on a photographic plate no correction need be applied to the ordinates.

The object of having two wedge-shaped compartments is to reduce the dispersion of the light passing through them as much as possible, indeed white light from an incandescent lamp can be used. The solution in the wedge $ab d$ is the same as that in $ac d$ except that in it the reaction has already taken place. Under these circumstances the indices of refraction in the two wedges are very nearly equal and a slow change of a few degrees in temperature does not displace the image S_1 since such a change affects the index of refraction in both solutions practically to the same extent.

In the above described experiment the dimensions of the apparatus were as follows: SL (Fig. 1) = 150^{cm} ; $LS_2 = 250^{\text{cm}}$; $ab = 1^{\text{cm}}$; $ad = 5.3^{\text{cm}}$; $Lb = 15^{\text{cm}}$, approximately. The breadth of the slit in front of the figure was $.2^{\text{mm}}$, and its distance from the figure about $.3^{\text{cm}}$.

That the distance of the image S_1 at any time from its final position after the reaction has been completed is very approximately proportional to the amount of cane sugar left in the solution at that time, may be seen from the following reasoning. The proof is based upon the assumptions that the density d and the specific index of refraction $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ of the solution

(where n is the ordinary index of refraction) are additive functions of the constituents (see Nernst, *Theoretische Chemie*). Granting these, it follows that the difference between the value of $\frac{n^2-1}{n^2+2}$ at any time and its final value must be proportional to the amount z of cane sugar remaining at that time. Denoting this difference by Δ we have

$$\Delta \frac{n^2-1}{n^2+2} = k z$$

Approximately for small changes

$$\Delta \frac{n^2-1}{n^2+2} = \frac{d}{dn} \left(\frac{n^2-1}{n^2+2} \right) \Delta n = \frac{6n}{(n^2+2)^2} \Delta n$$

Hence

$$\Delta n = \frac{(n^2+2)^2}{6n} k z$$

If n (Fig. 3) is the index of refraction of the already reacted solution

$$\begin{aligned} \frac{n_1}{n} &= \frac{\sin \beta}{\sin \alpha} = \frac{\sin (\alpha + \Delta \alpha)}{\sin \alpha} \\ &= 1 - \cot \alpha \sin \Delta \alpha \end{aligned}$$

approximately, and therefore,

$$\cot \alpha \sin \Delta \alpha = 1 - \frac{n_1}{n} = \frac{\Delta n}{n}$$

or

$$\sin \Delta \alpha = \frac{\Delta n}{n \cot \alpha}$$

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If D is the distance from the solution to the screen

$$\frac{y}{D} = \frac{\sin \Delta \alpha}{\cos \Delta \alpha}$$

$$\therefore y = D \sin \Delta \alpha \text{ approximately}$$

Hence

$$y = \frac{D(n^2+2)^2}{n^2 \cot \alpha} k z$$

n does not vary more than .1 per cent, and if n lies between 1.3 and 1.4, which it usually does, the expression $\frac{(n^2+2)^2}{n^2}$ is practically constant.

Hence y is proportional to z , or the displacement of the image from its final position is proportional to the quantity of cane sugar in the solution.

Whether or not y is proportional to z in any particular case should and can be tested experimentally as follows. Take equal quantities by weight of a solution that has already reacted and of one that is just beginning to react. Mix them together and obtain a curve as above. This mixture is equivalent to a solution that has reacted half way, and the total change in the position of S_1 as indicated by the curve should be $\frac{1}{2}$ that in the case of the original solution. Such a curve photographed for the inversion of sugar proved the proportionality to within about $\frac{1}{2}$ of a per cent. If y is found not to be proportional to z a number of mixtures must be made with varying quantities of new and old solutions, and the relation between y and z determined.

The distances between the lines on the photographic plate corresponding to the different instants of time can be measured by means of a micrometer microscope of low power. I have found it more satisfactory, however, to place a glass scale over the plate and take the readings with a small lens, illuminating both scale and plate by means of a mirror below them.

The following table contains the results of such measurements on the plate representing the inversion of sugar. The first column contains the time t expressed in minutes; the second, the distances y in centimeters between the curve and the line drawn 24 hours later (the value of y for $t = 0$ being extrapolated), and the third, the percentage of cane sugar left in the solution.

t	y	% sugar	k
0	25.5	25.	2.3026
15	21.2	20.78	.00535
30	17.9	17.54	.00490
45	15.4	15.09	.00463
60	13.25	12.99	.00454
75	11.3	11.07	.00455
70	9.75	9.56	.00449
105	8.5	8.33	.00441
120	7.4	7.25	.00435
135	6.4	6.27	.00433
150	5.55	5.44	.00431
165	4.85	4.75	.00427
180	4.3	4.22	.00419
195	3.95	3.87	.00405
210	3.6	3.53	.00395
225	3.3	3.23	.00385

According to Gouldberg and Waage's law the rate at which the cane sugar disappears should be proportional to the amount left in the solution. Hence $\frac{dz}{dt} = -kz$

Or integrating between t_1 and t

$$k(t-t_1) = \log_e \frac{z_1}{z} = 2.3026 \log_{10} \frac{z_1}{z}$$

or
$$k = \frac{2.3026}{t-t_1} \log_{10} \frac{z_1}{z}$$

The third column in the table contains the values of $\frac{k}{2.3026}$ calculated by this formula, using the value $t_1 = 15$ minutes so as to avoid extrapolation. It appears that k as calculated above

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is not a constant. The decrease in its value indicates that the velocity of the reaction is greater at the beginning or less at the end than would be expected from Gouldberg and Waage's law. During the reaction, of course, the amount of water present changes perceptibly, but not enough to account for the large variation of k . The total change during the entire reaction is less than 2 per cent. The deviation from Gouldberg and Waage's law may be due to the relatively large quantity of hydrochloric acid in the solution. To decide whether it is or not will be the object of further investigation.

The second method is based upon the change in the volume of the chemical system during the reaction. In order to measure the change in volume the system is placed in a spiral glass tube (Fig. 4), on one end of which is sealed a capillary tube A B and on the other end a ground stopper and cup C. The reacting system may fill the entire spiral or only a part of it, the rest being filled with a liquid that does not combine with the given system. If the volume increases during the reaction, the cup A and most of the tube A B are filled with mercury. If the volume decreases, the cup and only a small part of the tube are filled. Evidently during the change of volume the mercury is drawn in or pushed out through the capillary tube and the positions of the end of the mercury column measure the amount of change.

The particular form represented (Fig. 4) was adopted, first, in order that the temperature of the system should remain that of a bath in which the spiral is immersed owing to the large surface presented to the bath; and second, in order that the tube might be filled, and the first reading of the position of the mercury column taken as soon after the reaction started as possible. The liquid is first poured in at C and allowed to fill the spiral, the tube A B and the cup A. Mercury is then poured into A and finally the stopper inserted at C. A little practice in manipulating the stopper and tilting the whole tube will enable one to set the dividing surface between the mercury and the other liquid at any desired point in the capillary tube. The tube A B is graduated or a graduated scale is fastened to it.

In most cases the change in the volume of a system is small. Hence, if the temperature of the apparatus varies during the reaction, even by a small amount, the consequent change in volume will be a large fraction perhaps of the change we wish to measure. It is, therefore, necessary to immerse the spiral tube in a delicate thermostat. In the following experiment on the inversion of a 25 per cent solution of cane sugar the electrical thermostat described by my assistant Mr. Lory and myself in this Journal for March, 1900, was used. The temperature of the bath did not vary as much as $\frac{1}{2000}$ th of a degree except once, and then the variation was only about $\frac{1}{1000}$ th of a degree.

In this experiment the spiral tube contained about 100^{cc} of the solution. The length of the capillary tube A B was 36^{cm}, and its cross section about 1^{sq mm}. The temperature was 25°·872 C.

The first two columns of the following table contain the readings of the end of the mercury column, on a metal scale attached to the capillary tube, together with the corresponding intervals of time *t* in minutes.

After allowing the apparatus to stand 24 hours and the reaction to become practically completed, the bath was heated up again to 25°·872 C., allowing all of the mercury which had been drawn into the spiral to run out. The end of the mercury column then stood at the mark ·20, which is the zero corresponding to zero quantity of cane sugar in the solution. The third column in the table contains the readings referred to this zero.

Under the assumption that the volume of the solution is an additive function of the constituents, these latter distances representing the changes in volume should be proportional to the quantities of cane sugar left in solution. The last column

contains the values of $\frac{k}{2.3026}$ calculated from the formula

$$\frac{k}{2.3026} = \frac{1}{t-t_1} \log_{10} \frac{z_1}{z}$$

<i>t</i>	cm.	cm.	$\frac{k}{2.3026}$
0			
20	34.55	34.35	
41	29.66	29.46	.00318
55	26.87	26.67	.00314
70	24.28	24.08	.00308
85	21.61	21.41	.00316
100	19.83	19.63	.00303
115	17.86	17.66	.00304
130	16.12	15.92	.00303
145	14.99	14.79	.00292
160	13.80	13.60	.00287
175	12.70	12.50	.00284
190	11.85	11.65	.00276
205	10.96	10.76	.00272
220	10.63	10.43	.00259
235	9.92	9.72	.00255
250	9.37	9.17	.00249
265	8.80	8.60	.00245

We see that *k* decreases, indicating as before that the velocity is less rapid at the end than would be expected from Gouldberg and Waage's law.

If desired, a complete record of the position of the mercury column could be obtained by any of the methods for recording the readings of a mercury thermometer.

The chief advantages of the above described methods are, first that the chemical system is not disturbed during the reaction; second, that no time is lost in titration or other chemical tests for the state of the system, thus making it possible to investigate rapid reactions; third, that it is not necessary for the experimenter to make observations during the reaction, which is a tedious piece of work if the velocity is very small; and fourth, the curves are drawn by purely mechanical processes, thus avoiding the influence of the personal equation.

A third method based upon the change in the index of refraction of the chemical system as measured by the motion of interference bands is being perfected.

In conclusion I wish to thank my assistant, Mr. F. C. Blake, for the care with which he has helped me obtain the above data. He and his brother, Mr. J. C. Blake, are at work applying the methods to hitherto uninvestigated reactions.

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