Viscosity Effect on the Rate of Solution of Calcium Carbonate in Hydrochloric Acid.

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In homogeneous reactions in solution, the viscosity effect on the rate is considered to be very small. In heterogeneous reactions, there are three processes occurring: (1) the solute molecules approach and collide with the solid surface, (2) there takes place a chemical reaction; and (3) finally the products recede from the interface into the bulk of the solution. The diffusion velocities of the reactants or reaction products depend on the viscosity of the solution and, therefore, if these velocities are not very much greater than that of the chemical reaction, the observed rate will be affected by the viscosity. When metals are attacked by aqueous acids or cadmium by aqueuos iodine, the chemical change is rapid, and then the observed velocity is simply the velocity of diffusion. Thus the viscosity effect on the rate of dissolution of zinc in hydrochloric acid was already observed.(1)

On the other hand, according to Spring,(2) when marble dissolves in hydrochloric acid diffusion is rapid and the chemical change determines the observed rate. Spring's conclusion was drawn from the consideration of the apparent heat of activation. Brunner's experiments(3), however, indicated the diffusion concerned. In order to examine these observations by measuring the viscosity effect, the following experiments have been done.

Experimental. The rate of reaction is obtained by measuring the volume of carbon dioxide evolved. A well polished disk of marble of 3 cm. diameter, which is attached to a glass shaft and covered with wax or enamel all the surfaces except one face of bottom side, is rotated 485 ∼ 488 times per minute in hydrochloric acid. In order to keep the rotational velocity of the disk constant, a synchronous motor is used. Fifty cubic centimeters of the acid are contained in a bottle of capacity 250 c.c. This reaction bottle (Fig. 1) and a gas burette of carbon dioxide are placed in a thermostat of 25°C. Then the volume of carbon dioxide evolved is read at intervals of one minute after inserting the rotating disk into the acid solution. The initial concentration of hydrochloric acid varies between 0.1747 and 0.5317 N.

The relation between the velocity, that is, the volume of carbon dioxide evolved per minute, and the total volume is shown in Fig. 2. Fig. 3 and Table 1 show the effect of changing the viscosity of the acid

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(1) C. V. King and M. M. Braverman, *J. Am. Chem. Soc.*, **54** (1932), 1744.

(2) W. Spring, *Z. physik. Chem.*, **1** (1887), 209; and also Moelwyn-Huges, 'The Kinetics of Reactions in Solution', p.284 (1933).

(3) E. Brunner, *Z. physik. Chem.*, **47** (1904), 56.

solution by adding glycerine on the rate. The range of viscosities is 0.00909 (without glycerine) ~ 0.01751.

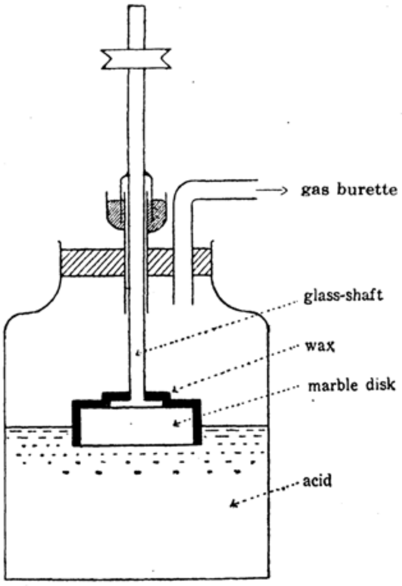

Fig. 1. Schematic View of the Reaction Bottle.

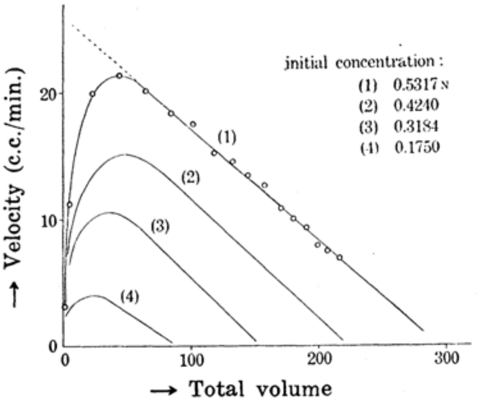

Fig. 2. Velocity Curves at Different Initial Concentrations.

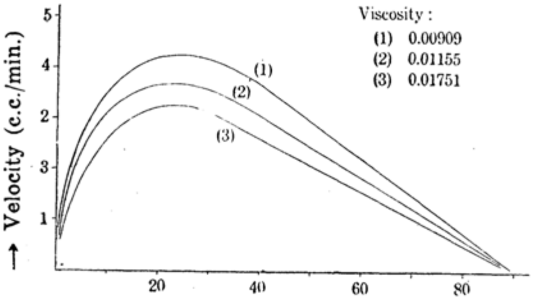

Fig. 3. Velocity Curves at Different Viscosities.

Table 1. The Effect of Viscosity on the Velocity Constant.

Glycerine %	η	k
—	0.00909	0.0495
3.78	0.00991	0.0475
5.37	0.01031	0.0433
9.77	0.01155	0.0411
14.51	0.01316	0.0377
19.16	0.01510	0.0369
23.85	0.01751	0.0344

Initial concentration of the acid: 0.1750 N.
Rotational velocity of the disk: 485 times per minute.

Discussion. As seen from Fig. 2, after about 30 c.c. of carbon dioxide has been evolved, the velocity changes linearly, which means the first order reaction occurs. The fore part of the reaction is an entirely different type. As seen from the figure, the maximum points of the velocity curves scarcely alter on using acids of different initial concentrations. The reaction before the maximum point is not simple, and there may be probably occurring following processes in this region. When the marble disk is inserted in the acid, carbon dioxide produced at the early stage will dissolve into the acid and when the neighbourhood of the disk is saturated, then for the first time bubbles of carbon dioxide are able to evolve. Further, there is time before the disk comes in perfect contact with the acid.

The reaction mechanism of the region before the maximum point seems to be very much complicated, and, therefore, only the region of the first order reaction is considered in this paper.

If the apparent reaction velocity of the linear part is denoted by v, it is proportional to the concentration of the acid, c, that is,

$$v = k c \,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where k is the velocity constant. As stated above, this heterogeneous reaction velocity consists of true chemical reaction velocity on the solid surface and the diffusion velocities of the hydroxonium ion in solution to the surface and of the reaction products to the bulk of the solution. True chemical change is considered to proceed in the two following stages:

$$CO_3^{--} + H_3O^+ \longrightarrow HCO_3^- + H_2O$$
$$HCO_3^- + H_3O^+ \longrightarrow CO_2 + H_2O$$

The second reaction of the decomposition of bicarbonate may be assumed rapid, and, therefore, one molecule of carbon dioxide is produced for one hydrogen ion; namely, the true chemical reaction velocity v_1 is proportional to c,

$$v_1 = k_1 c \,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

As to the diffusion velocities of the individual components we may assume that Nernst's theory holds. Then

$$\text{diffusion velocity} = \frac{D \cdot A}{B \cdot \delta} c \,,$$

where D is the diffusion coefficient, A the area of the solid surface, B the volume of the solution, and δ the thickness of the diffusion layer. In this reaction, notwithstanding the respective diffusion coefficients of H_3O^+, CO_2, and $CaCl_2$ may be concerned, all the constants are inversely proportional to the viscosity coefficient of the solution. Hence, the diffusion velocity v_2, in the lump, is expressed as follows:

$$v_2 = k_2 \frac{1}{\eta} c \,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where η is the viscosity coefficient.

On the marble surface, the chemical reaction takes place first, then diffusion follows. Hence, the apparent velocity v can be expressed as the sum of v_1 and v_3 added in series,

$$\frac{1}{v} = \frac{1}{v_1} + \frac{1}{v_2} \,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

From formulas (1)～(4),

$$\frac{1}{k} = \frac{1}{k_1} + \frac{\eta}{k_2} \,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

As seen from formula (5), $1/k$ is in general in the linear relation to the viscosity. If the chemical reaction is very rapid, the first term of formula (5) can be neglected and the line will cross the origin. On the contrary, if the diffusion is very rapid, the second term can be neglected and the line becomes parallel to the axis of viscosity. The actual results for this reaction are shown in Fig. 4.

As clearly seen, the velocities of the chemical reaction and the diffusion are both measurable, and according to the estimation from the figure these two processes concern in the same order under present conditions. This conclusion will be ascertained by following another experiment.

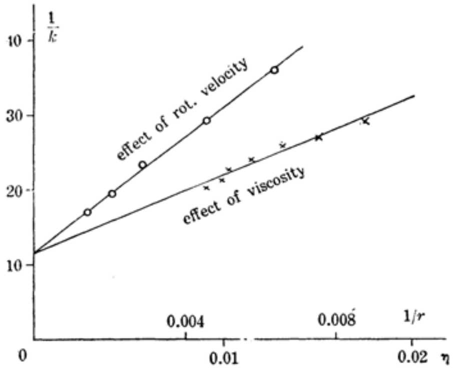

Fig. 4. Effects of Viscosity and Rot. velocity on the Velocity Constant.

The rate of the same reaction has been measured by changing the rotational velocity of the disk. The results are shown in Table 2.

Table 2. The Effect of Rotational Velocity of the Disk on the Velocity Constant.

r (Number of rotation per minute)	158	220	349	484	683
k	0.00633	0.00455	0.00287	0.00207	0.00146

Initial concentration of the acid: 0.1750 N. Viscosity: 0.00909.

The thickness of the diffusion layer δ may depend on the rotational velocity r. If δ is assumed to be inversely proportional to r, the diffusion velocity will be expressed as,

$$v_2 = k_3 r c \,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Hence,

$$\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_3 r} \,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Similary to (5), $1/k$ is in linear relation to $1/r$.

The graphical representation of the results is given in Fig. 4, and the cross point of the line with the axis, which indicates the value of $1/k_1$, coincides very well with that of the line of viscosity effect.

On the Calculation of the Energy of Activation from the Temperature Coefficient of the Rate. Moelwyn-Hughes(2) calculated the heat of activation of the reaction between marble and hydrochloric acid from the temperature coefficient of the rate which had been observed by

Spring(2), and found $E_{15^\circ-35^\circ} = 6,300$ calories. In this calculation, however, the viscosity effect of this reaction was not taken into consideration. This is not correct. As stated above, this reaction is affected by viscosity, and by increasing temperature the viscosity is decreased. Hence, in the calculation of the apparent heat of activation from the temperature coefficient of the rate, the acceleration due to viscosity decrease must be eliminated.

Spring used a 5% acid solution and the observed ratio of the velocity constant of 35°C to that of 15°C was 2.05. The viscosity coefficients of this concentration are measured by the present authors as 0.00781 at 35°C and 0.01210 at 15°C. If the same amount of the viscosity effect as observed in the present experiment holds in the reaction in the 5% solution, the velocity constant of the latter reaction will become 1.23 times as much by changing the temperature from 15° to 35° owing only to the viscosity change. Hence, the increase of the rate in the ordinary meaning on raising the temperature becomes $k_{35^\circ}/k_{15^\circ} = 1.82$. By using this, the apparent heat of activation is corrected to 5,400 instead of 6,300 calories.

Generally, if a reaction is affected by viscosity, its effect must be taken into consideration in calculating the energy of activation from the temperature coefficient of the rate.

Summary.

The viscosity effect on the rate of reaction between marble and hydrochloric acid has been measured. The mechanism of the region of the first order reaction has been considered and the results show that the true chemical reaction on the marble surface and the diffusions of the reactant and reaction products concern in the same order in this reaction. The same conclusion is obtained from the experiments of changing the rotational velocity of the marble disk. The apparent heat of activation, which was calculated by Moelwyn-Hughes from the temperature coefficient of the rate, has been corrected by considering the viscosity effect.

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