A THEORY OF THE RATE OF SOLUTION OF GAS INTO LIQUID.
II. THE RATE OF SOLUTION OF GAS INTO LIQUID CONTAINING A REACTING SUBSTANCE, AND A KINETIC DERIVATION OF THE DISTRIBUTION LAW.

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Introduction.

For the rate of solution of gas into liquid the following expression was proposed by the present writer.(1)

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(1) S. Miyamoto, this Bulletin, **7** (1932), 8; *Journal of Science of the Hiroshima University, A*, **2** (1932), 73; *Chem. News*, **144** (1932), 273.

$$\frac{dn}{dt}=\frac{p}{\sqrt{2\pi MRT}}S\,e^{-\frac{Mu_0^2}{2RT}}-\frac{c_l}{1000}S\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0'^2}{2RT}} \quad \ldots.\ (1)$$

where p is the partial pressure of the gas, M the molecular weight of the gas, R the gas constant, T absolute temperature, S the area of the boundary surface, c_l the concentration of the gas in the liquid phase expressed by moles/liter, n the number of moles of the gas in the liquid phase, and t the time.

The derivation of the above equation is based upon two assumptions, (a) that among the molecules of gas which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_o, can enter into the liquid phase, and (b) that among the molecules of gas in the liquid phase, only those, which collide with the boundary surface with velocities, whose components at right angles to the boundary surface are greater than a threshold value u_o', can escape from the liquid phase.

When the liquid is saturated with the gas,

$$\frac{dn}{dt}=0\,.$$

Then in the state of saturation,

$$\frac{p}{\sqrt{2\pi MRT}}S\,e^{-\frac{Mu_0^2}{2RT}}=\frac{c_\infty}{1000}S\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0'^2}{2RT}}, \quad \ldots\ldots.\ (2)$$

where c_∞ is the concentration of the saturated solution.

From equations (2) and (1) we have,

$$\frac{dn}{dt}=\frac{c_\infty}{1000}S\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0'^2}{2RT}}-\frac{c_l}{1000}S\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0'^2}{2RT}}, \quad \ldots..\ (3)$$

or

$$\frac{dn}{dt}=KS(c_\infty-c_l)\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

where

$$K=\frac{1}{1000}\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0'^2}{2RT}}, \quad \ldots\ldots\ldots\ldots\ldots..\ (5)$$

Equation (4) is the well known equation, experimentally obtained and theoretically interpreted by the diffusion layer theory. When equation (4) is derived by the diffusion layer theory, the constant K is naturally conditioned by different factors from the constant involved in equation (5); the former is a function of the diffusion coefficient and the thickness of the supposed diffusion layer.

According to Brunner,(1) Davis and Crandall,(2) the diffusion theory implies the existence of a stationary liquid film of a thickness of about 2×10^{-3}–2×10^{-2} cm., the exact value naturally depending upon the rate of revolution of the stirrer in the main body of the liquid. When the liquid phase is well stirred, the question is whether a stationary liquid film of this thickness really exists at the interface. A direct confirmation is necessary.

It was proved by the present writer(3) that the velocity of oxidation of sodium sulphite solution by oxygen in the presence of the molecular film of stearic acid or that of palmitic acid is almost identical with that in the absence of the molecules of these fatty acids. Now we must take into consideration from this experimental fact that when the main body of the liquid phase is well stirred, the thickness of the supposed stationary liquid film is smaller than the length of a molecule of the fatty acid(4) employed (the length of the stearic acid molecule $=26.2\times10^{-8}$ cm., and that of the palmitic acid molecule $=23.7\times10^{-8}$ cm.). When the thickness of the stationary liquid film is as small as this, the mechanism of solution of gas can not be interpreted as a diffusion process.

The second assumption made in the diffusion layer theory is that the upper layer of the stationary liquid film is saturated instantaneously with the gas. If this assumption is correct, the rate of solution of gas should be considerable when the liquid phase is stirred so violently that new surfaces are constantly formed, but it has not yet been proved experimentally.

For the derivation of equation (4) from the theory of the present writer, neither the assumption of the existence of a stationary liquid film, nor that of the instantaneous saturation of the upper layer of the film with gas is necessary.

The Initial Rate of Solution of Gas into Liquid. The initial rate of solution of gas into liquid, or the rate of solution of gas when the liquid

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(1) *Z. physik. Chem.*, **47** (1904), 99.
(2) *J. Am. Chem. Soc.*, **52** (1930), 3760.
(3) S. Miyamoto, T. Kaya and Nakata, this Bulletin **6** (1931), 133; *Journal of Science of the Hiroshima University, A*, **1** (1931), 203.
(4) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848; Adam, *Proc. Roy. Soc. London, A*, **99** (1921), 336; **101** (1922), 425, 516; **103** (1923), 676, 687.

is perfectly free from the gas, is expressed by the following equation, which is obtained by putting $c_l = 0$ in equation (4).

$$\left(\frac{dn}{dt}\right)_{\text{Initial}} = K S c_\infty \quad \text{(6)}$$

According to the diffusion layer theory, equation (6) gives the rate of diffusion of the gas molecules between the layer of concentration of saturation and that of zero.

According to the theory of the present writer the initial rate of solution of gas has a totally different character. From equations (6), (5) and (2) we have

$$\left(\frac{dn}{dt}\right)_{\text{Initial}} = \frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} . \quad \text{(7)}$$

This equation is directly obtained by putting $c_l = 0$ in equation (1). Equation (7) expresses the number of moles of gas which enter into the liquid phase per unit of time, when the liquid is perfectly free from gas molecules, the area of the boundary surface being S cm^2.

An important difference between the diffusion layer theory and the theory of the present writer is that the former assumes the instantaneous saturation of the upper layer of the liquid surface with gas, while the latter does not. According to the theory of the present writer the initial rate of solution of gas is expressed by equation (7), and a measurable time is necessary for the saturation of the upper layer of the liquid surface.

The Rate of Solution of Gas into Liquid Containing a Reacting Substance.

When the liquid contains a substance which reacts with the gas, the phenomenon is more complex. In the present paper only the initial rate of solution of gas, when the velocity of reaction between gas and reacting substance is considerable compared with the rate of solution, is discussed. Davis and Crandall(1) applied the diffusion layer theory in the following manner to the interpretation of the rate of solution of gas into liquid containing a reacting substance.

They assumed that the upper layer of the stationary liquid film is instantaneously saturated with the gas and that the gas molecules diffuse

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(1) *J. Am. Chem. Soc.*, **52** (1930), 3769.

from this layer to the reaction zone, in which the concentrations of both gas and reacting substance remain at zero, and that the molecules of the reacting substance diffuse from the layer of concentration c_m to the reaction zone, c_m being the initial concentration of the reacting substance in the main body of the liquid phase.

They assumed that the initial rate of solution, experimentally observed, is no other than the rate of diffusion in this state, and derived the following equation for the initial rate of solution.

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{\text{Initial}} = k\,(c_\infty + c_m)\,. \quad \dots\dots\dots\dots\dots\dots \quad (8)$$

Equation (8) is inadequate for the complete interpretation of the experimental facts, as will be shown in what follows. It follows from equation (8) that the initial rate of solution increases consistently with the increase of concentration of the reacting substance c_m. At the same time the decrease of the initial rate of solution caused by the decrease of solubility of gas c_∞ should be taken into account, as the solubility of gas c_∞ decreases with the increase of the concentration of the reacting substance c_m. But c_∞ generally has a small value. Therefore it is clear that when the value c_m is relatively great, the decrease of the value c_∞ is negligible, and the initial rate of solution expressed by equation (8) should increase consistently as the value c_m is increased.

Contrary to what we should expect from equation (8), the initial rate of solution actually seems to decrease with the increase of concentration c_m when the value c_m is great. For example, the initial rate of solution of carbon dioxide into sodium hydroxide solution, observed by Ledig and Weaver,(1) increases with the increase of the value c_m when the value c_m is less than about 2.5 normal, and decreases when the value c_m is further increased.

The rate of solution of oxygen into sodium sulphite solution decreases with the increase of the concentration of sodium sulphite when the concentration is greater than about 1 normal.(2) It is to be expected that the initial rate of solution of oxygen into concentrated sodium sulphite solution is less than that into dilute solution.

Equation (8) can not interpret these experimental facts.

This disaccord between equation (8), theoretically derived from the diffusion theory, and the experimentally observed facts would appear to

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(1) *J. Am. Chem. Soc.*, **46** (1924), 650.

(2) S. Miyamoto and T. Kaya, this Bulletin, **6** (1931), 264; *Journal of Science of the Hiroshima University, A*, **2** (1932), 59.

be due to the assumption, employed for the derivation of equation (8), viz. that the upper layer of the liquid surface is instantaneously saturated with the gas.

The present writer is of the opinion that the initial rate of solution of gas in the presence of the reacting substance is expressed by equation (7) exactly as in the case of pure liquid. This does not mean that the presence of the reacting substance in the liquid phase has no effect upon the initial rate of solution of gas. As the value u_o, in equation (7), is a constant depending upon the nature of the liquid phase, it varies with the change of concentration of the reacting substance in the liquid phase, and the initial rate of solution increases or decreases as the value u_o decreases or increases.

Equation (7) does not contain a term c_∞. This means that the initial rate of solution does not depend upon the solubility of gas. According to the theory of the present writer the solubility of gas is expressed as a function of $u_o^2 - u_o'^2$ as will be seen in equation (9), while the initial rate of solution as a function of u_o only.

The initial rate of solution of carbon dioxide into sodium hydroxide solution, observed by Ledig and Weaver,(1) is interpreted according to the new theory in the following way. At low concentrations the initial rate of solution increases with the increase of concentration of sodium hydroxide as the value u_o decreases, and at high concentrations the initial rate of solution decreases with the increase of concentration of sodium hydroxide as the value u_o increases.

In the case of the rate of solution of oxygen into sodium sulphite solution the value u_o does not appear to be much effected by the increase of concentration of sodium sulphite at low concentrations, as the rate of solution of oxygen is independent of the concentration of sodium sulphite.(2) The direct observation of the initial rate of solution of oxygen into sodium sulphite solution will be carried out on a later occasion.

A collaborator of the present writer is now studying the rate of solution of oxygen into alcoholic solution of anhydrous stannous chloride, and it has proved that the initial rate of solution is not much effected by the increase of concentration of stannous chloride at low concentrations, while the initial rate of solution decreases as the concentration of stannous chloride increases at high concentrations.(3) This phenomenon is to be interpreted exactly as in the case of sodium sulphite solution.

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(1) Loc. cit.

(2) Loc. cit.

(3) The result of this experiment will be published shortly.

The Solubility of Gas. From equation (2) we have,

$$c_\infty = \frac{1000}{RT} p\, e^{-\frac{M}{2RT}(u_0^2 - u_0'^2)} \qquad \dots\dots\dots\dots\dots\dots \quad (9)$$

The solubility of gas c_∞ moles / liter is given by equation (9) according to the present theory. The solubility is not a function of u_o only, but that of $u_o^2 - u_o'^2$.

The Calculation of u_0 and u_0'. From equation (7) we can calculate the value u_o, if the initial rate of solution of gas be determined, and when the value of u_o and the solubility c_∞ are known, the value of u_o' is calculated from equation (9). In the case of oxygen and water the value of u_o is⁽¹⁾

$$u_o = 1.65 \times 10^5 \text{ cm./sec. at } 15°\text{C.},$$

and the solubility of oxygen at 15°C. is

$$c_\infty = 1.50 \times 10^{-3} \text{ moles/liter.}$$

The calculated value of u_o' from equation (9), using these values, is

$$u_o' = 1.49 \times 10^5 \text{ cm./sec.}$$

This means that among the molecules of oxygen in water, only those which collide with the interface with velocities whose components at right angles to the boundary surface are greater than a threshold value 1.49×10^5 cm./sec., are able to escape from the liquid phase.

A Kinetic Derivation of the Distribution Law.

In equation (9) c_∞ is expressed by the number of moles per liter. If c_∞ be expressed by the number of moles per c.c., equation (9) becomes

$$c_\infty = \frac{p}{RT} e^{-\frac{M}{2RT}(u_0^2 - u_0'^2)} \qquad \dots\dots\dots\dots\dots\dots \quad (10)$$

Equation (10) expresses the relation between the solubility and the partial pressure of gas. At constant temperature, the value $u_o^2 - u_o'^2$ can be considered to be constant, and then we have from equation (10)

$$c_\infty = k\, p\,, \qquad \dots\dots\dots\dots\dots\dots \quad (11)$$

where

$$k = \frac{1}{RT} e^{-\frac{M}{2RT}(u_0^2 - u_0'^2)} \qquad \dots\dots\dots\dots\dots\dots \quad (12)$$

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(1) S. Miyamoto and A. Nakata, this Bulletin, **6** (1931), 21; *Jonrnal of Science of the Hiroshima University, A*, **1** (1931), 143.

Equation (11) is Henry's law, and the constant k, according to the present theory, has the value given by equation (12). Now,

$$\frac{p}{RT}=\frac{1}{v}=c_g\,, \qquad \text{(13)}$$

where c_g is the concentration of gas in the gas phase. From equations (10) and (13) we have

$$\frac{c_\infty}{c_g}=e^{-\frac{M}{2RT}(u_0^2-u_0'^2)}\,, \qquad \text{(14)}$$

or

$$\ln\frac{c_\infty}{c_g}=\frac{\frac{Mu_0'^2}{2}-\frac{Mu_0^2}{2}}{RT}\,. \qquad \text{(14')}$$

If the values of E_{xo} and E_{xo}' are given by

$$\frac{Mu_0^2}{2}=E_{x.0}\,, \qquad \frac{Mu_0'^2}{2}=E'_{x.0}\,, \qquad \text{(15)}$$

we obtain by substituting these values in equation (14),

$$\ln\frac{c_\infty}{c_g}=\frac{E'_{x.0}-E_{x.0}}{RT}\,. \qquad \text{(16)}$$

Equations (14) and (16) also give Henry's law.

The distribution of a substance between two liquid phases can be treated in exactly the same way. Consider a case in which a substance is distributed between two liquid phases A and B in one and the same molecular state. Then the rate of increase of the substance in phase B is expressed by

$$\frac{N}{S}\,\frac{dn}{dt}=N_1-N_2 \qquad \text{(17)}$$

where N is Avogadro's number, N_1 the number of molecules which transfer through unit area of the boundary surface from phase A to phase B per second, N_2 the number of molecules which transfer through unit area of the interface from phase B to phase A per second, S the area of the boundary surface, n the number of moles of the substance in phase B, and t the time.

Now the following assumptions are proposed.

(a) Among the molecules of the distributed substance in phase A, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_1, are able to enter into phase B, and

(b) Among the molecules of the substance in phase B, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_2, are able to enter into phase A.

By Maxwell's distribution law, among N molecules, the number of molecules, whose components of velocities at right angles to a fixed plane lie between u and $u+du$, is expressed by

$$dN = \frac{N}{\sqrt{\frac{2\pi RT}{M}}} e^{-\frac{Mu^2}{2RT}} du \, .$$

Then it is clear that N_1 is expressed by the following equation.

$$N_1 = \int_{u_1}^{\infty} \frac{c_1 N}{\sqrt{\frac{2\pi RT}{M}}} u\, e^{-\frac{Mu^2}{2RT}} du = c_1 N \sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_1^2}{2RT}}, \quad \ldots\ldots (18)$$

where c_1 is the concentration of the substance in phase A, expressed by moles per c.c. Similarly N_2 is expressed by

$$N_2 = \int_{u_2}^{\infty} \frac{c_2 N}{\sqrt{\frac{2\pi RT}{M}}} u\, e^{-\frac{Mu^2}{2RT}} du = c_2 N \sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_2^2}{2RT}}, \quad \ldots\ldots (19)$$

where c_2 is the concentration of the substance in phase B expressed by moles per c.c. From equations (17), (18) and (19) we obtain

$$\frac{dn}{dt} = c_1 S \sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_1^2}{2RT}} - c_2 S \sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_2^2}{2RT}}$$

$$= S \sqrt{\frac{RT}{2\pi M}} \left(c_1 e^{-\frac{Mu_1^2}{2RT}} - c_2 e^{-\frac{Mu_2^2}{2RT}} \right) . \quad \ldots\ldots\ldots\ldots (20)$$

In the state of equilibrium

and

$$\left.\begin{aligned} & c_1 = c_{1.\infty}\,, \qquad c_2 = c_{2.\infty}\,, \\ & \frac{dn^{\cdot}}{dt} = 0 \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (21)$$

From equations (20) and (21) we obtain

$$c_{1.\infty}\, e^{-\frac{M\,{}_1^2}{2RT}} - c_{2.\infty}\, e^{-\frac{Mu_2^2}{2RT}} = 0\,, \quad \cdots\cdots\cdots\cdots\cdots \quad (22)$$

or

$$\frac{c_{1.\infty}}{c_{2.\infty}} = e^{\frac{1}{RT}\left(\frac{Mu_1^2}{2} - \frac{Mu_2^2}{2}\right)}\,. \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (23)$$

If $E_{x.1}$ and $E_{x.2}$ are expressed by

$$E_{x.1} = \frac{Mu_1^2}{2}\,, \qquad E_{x.2} = \frac{Mu_2^2}{2}\,, \quad \cdots\cdots\cdots\cdots\cdots \quad (24)$$

we obtain by substituting these values in equation (23)

$$\frac{c_{1.\infty}}{c_{2.\infty}} = e^{\frac{1}{RT}(E_{x.1} - E_{x.2})} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (25)$$

or

$$\ln \frac{c_{1.\infty}}{c_{2.\infty}} = \frac{1}{RT}(E_{x.1} - E_{x.2})\,. \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (26)$$

When the temperature is constant, the values of u_1 and u_2 or those of $E_{x.1}$ and $E_{x.2}$ are constant and we have

$$\frac{c_{1.\infty}}{c_{2.\infty}} = \text{const.}$$

Equations (23), (25) and (26) give the distribution law derived according to the present theory.

The distribution law is usually derived thermodynamically by making the chemical potentials of the distributed substance in the two liquid phases equal in the state of equilibrium.(1) The chemical potentials μ_1 and μ_2 are expressed by

$$\left.\begin{aligned} \mu_1 &= K_1 + RT \ln x\,, \\ \mu_2 &= K_2 + RT \ln y\,, \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (27)$$

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(1) R. Lorenz, *Z. anorg. allgem. Chem.*, **178** (1929), 346.

where x and y are the mole fractions of the substance in the two phases respectively. At equilibrium

$$\mu_1 = \mu_2$$

and we have

$$\ln \frac{x}{y} = \frac{1}{RT}(K_2 - K_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

It is an interesting fact that equation (26), derived kinetically, has a form analogous with equation (28), obtained thermodynamically.

Summary.

(1) The initial rate of solution of gas into liquid was developed from a new theory of the rate of solution based upon the assumptions. (a) that among the molecules of gas, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_o, can enter into the liquid phase, and (b) that among the molecules of gas in the liquid phase, only those, which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value u_o' can escape from the liquid phase.

The equations derived from the new theory were compared with those obtained from the diffusion layer theory.

(2) The solubility of gas was expressed as a function of u_o and u_o'.

(3) The values of u_o and u_o' were calculated in the case of oxygen and water at 15°C.

(4) Henry's law was derived by means of the new theory.

(5) The distribution of a substance between two liquid phases was discussed in exactly the same manner.

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