A THEORY OF THE RATE OF SOLUTION OF GAS INTO LIQUID.

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A theory of the rate of solution of gas into liquid, which may be much probable not only for the interpretation of the phenomena already studied by many writers, but also for the interpretation of the rate of oxidation of sodium sulphite solution, was described in the previous papers.(1) The present paper is intended to discuss the new theory in comparison with other theories.

Noyes and Whitney(2) interpreted the rate of reaction at solid-liquid interfaces by the theory based upon the assumptions that the process is composed of two stages, namely extremely rapid reaction in the interfacial layer and slow diffusion of the reactants and resultants from the layer. Nernst(3) extended this diffusion theory and proposed that the reaction velocity in heterogeneous systems is generally composed of two stages above described.

Adeney and Becker(4) had studied the rate of solution of air, oxygen and nitrogen from the surface of bubbles of known magnitude into water, and proposed the following equation to interpret the experimental results,

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(1) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 13[illegible]; S. Miyamoto and A. Nakata, ibid., **6** (1931), 18; S. Miyamoto, T. Kaya and A. Nakata, ibid., **6** (1931), 140.

(2) *Z. physik. Chem.*, **23** (1897), 689.

(3) Ibid., **47** (1904), 52.

(4) *Phil. Mag.*, **38** (1919), 317; **39** (1920), 385; **42** (1921), 87.

$$\frac{dw}{dt} = SAp - f\frac{S}{v}w\,, \qquad (1)$$

where A is the initial rate of solution per unit area, f the coefficient of escape from the liquid per unit area and volume, S the area of the boundary surface, v the liquid volume, p the gas pressure and w the weight of gas dissolved.

Donnan and Masson⁽¹⁾ modified the equation of Adeney and Becker, and proposed the following equations.

$$\frac{dw}{dt} = k_2(kc_g - c_l)\,, \qquad (2)$$

when the system obeys Henry's law, and

$$\frac{dw}{dt} = k_2[f(c_g) - c_l]\,, \qquad (2')$$

when Henry's law does not hold.

In these equations, c_g is the concentration of absorbable gas in the gas phase, c_l the corresponding concentration in the liquid phase, k the Henry's law coefficient, and k_2 a constant. The above mentioned equations may be expressed by a slight rearrangement in the form,

$$\frac{dw}{dt} = k[c_\infty - c_l] \qquad (3)$$

where c_∞ is the concentration of saturated solution, and k a constant.

For the rate of solution of gas into liquid, the following expression was proposed by Lewis, Whitman and Keats,⁽²⁾

$$\frac{dw}{dt} = k_p[p_g - p_l] \qquad (4)$$

where p_g and p_l are the partial pressure of the absorbable component in the gas phase and in the liquid phase respectively.

Whitman and Keats⁽³⁾ assumed the existence of a stationary gas film and a stationary liquid film at the boundary surface and proposed the following equation for the rate of absorption.

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(1) *J. Soc. Chem. Ind.*, **39** (1920), 236.

(2) Lewis, *J. Ind. Eng. Chem.*, **8** (1916), 825; Whitman and Keats, ibid., **14** (1922), 185.

(3) Ibid.

$$\frac{dw}{dt} = k_p(p_1 - p_2) = k_c(c_2 - c_3) \ldots\ldots\ldots\ldots \quad (5)$$

where $p_1 - p_2$ is a partial pressure gradient of the solute in the gas film, and $c_2 - c_3$ is a concentration gradient in the liquid film, k_p and k_c being constants.

Davis and Crandall⁽¹⁾ assumed that the upper surface of the liquid film is almost instantaneously saturated with the gas and interpreted the results of their research on the rate of solution of oxygen into water by the equation,

$$\frac{1}{S}\left(\frac{dn}{dt}\right) = k_l(c_\infty - c_l)\ , \ \ldots\ldots\ldots\ldots \quad (6)$$

where c_∞ is the saturation concentration of the dissolved gas, c_l the concentration of the gas in the liquid phase, k_l a constant, n the number of moles of the gas in the liquid phase, and S the area of the boundary surface.

The idea of Davis and Crandall is similar to that of Nernst, Noyes and Whitney, and the equation (6) is quite the same as the equation (3). When the gas reacts with a component in the liquid phase, the rate of absorption of the gas would depend upon the concentration of the solute. Davis and Crandall⁽²⁾ proposed the following equation for the rate of solution when the reaction velocity is very great,

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{\text{initial}} = k_l(c_\infty + c_m)\ , \ \ldots\ldots\ldots\ldots \quad (6')$$

where c_m is the concentration of the reacting solute in the main body.

A New Theory of the Rate of Solution of Gas into Liquid.

The above mentioned theories are based upon two assumptions; the existence of a stationary film of liquid or stationary films of liquid and gas, and the instantaneous saturation of the upper layer of the stationary film with the gas. These assumptions will not be satisfied in some cases, as will be discussed in the later. The existence of stationary film of such thickness as the diffusion theory requires will be questionable, when the bulk of the liquid is well agitated with a proper stirrer, and the assumption of instantaneous saturation of the upper layer of the liquid with gas can not be adopted to interpret the rate of oxidation of sodium sulphite solution.

The theory of the present writer⁽³⁾ is based upon quite different assumptions, as will be described in the following.

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(1) *J. Am. Chem. Soc.*, **52** (1930), 3757.
(2) Ibid., **52** (1930), 3769,
(3) The theory, described in the previous papers, loc. cit., was slightly revised.

The process of solution of gas into liquid can be separated in two processes, namely the penetration of gas molecules into the liquid phase, and the escape of the gas molecules from the liquid phase. Then the rate of solution of gas into liquid can generally be expressed by

$$\frac{N}{S}\frac{dn}{dt} = N'' - N''' , \quad \ldots\ldots\ldots\ldots \quad (7)$$

where n is the number of moles of the absorbable gas, N Avogadro's constant, N'' the number of molecules of gas which enters into the liquid phase per unit area of the interface per unit of time, N''' the number of molecules of the gas which escapes the liquid phase per unit area per unit of time, and S the area of the boundary surface.

According to the kinetic theory of gases, the value N'' should be a fraction of the number of molecules which collide with the unit area of the interface per unit of time, N', then,

$$N'' = \beta N' , \quad \ldots\ldots\ldots\ldots \quad (8)$$

where β represents the ratio of the number of molecules which penetrate into the liquid phase and the number of molecules which collide with the liquid phase, N' being the number of molecules which collide with the unit area of the boundary surface per unit of time.

By Maxwell's distribution law of velocities,

$$dN = \frac{N}{\sqrt{\pi}\alpha} e^{-\frac{u^2}{\alpha^2}} du , \quad \ldots\ldots\ldots\ldots \quad (9)$$

where dN means the number of molecules whose components of velocities at right angles to one definite plane lies between u and $u+du$ among N molecules, and

$$\alpha^2 = \frac{2RT}{M} , \quad \ldots\ldots\ldots\ldots \quad (10)$$

where R the gas constant T the absolute temperature, and M the molar weight of the gas. It is then easily be seen that the value N' can be expressed by

$$N' = \int_0^\infty \frac{N}{V\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{Np}{\sqrt{2\pi MRT}} , \quad \ldots\ldots\ldots\ldots \quad (11)$$

Where V is the molar volume of the gas, N Avogadro's constant, P the partial pressure of the gas, N/V being the number of molecules per unit volume of gas.

Now an assumption is proposed. Among the molecules, which collide with the liquid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0, are able to enter into the liquid phase. Then value N'' will be expressed by

$$N'' = \int_{u_0}^{\infty} \frac{N}{V\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \;\ldots\ldots\; (12)$$

From (8), (11) and (12) it is seen that

$$\beta = e^{-\frac{Mu_0^2}{2RT}} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; (13)$$

From the similar assumption, that among the molecules of gas in the liquid phase, only those, which collide with the interface with the velocities whose components at right angles to the boundary surface are greater than a threshold value u'_0, are able to escape the liquid phase, we can obtain the value N''' from the Maxwell's distribution law,

$$N''' = \int_{u'_0}^{\infty} \frac{c_l N}{1000} \frac{1}{\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{c_l N}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \;\ldots\ldots\; (14)$$

where c_l is the concentration of the gas in the liquid phase, N Avogadro's constant, $c_l N/1000$ being the number of molecules of the gas per unit volume of the liquid. The concentration of the gas in the liquid phase will depend upon the depth of the liquid, and strictly speaking, the mean value of the concentrations of the effective region should be employed for the value c_l, but when the bulk of the liquid is stirred, its concentration may be employed as a first approximation.

From the equations (7), (12) and (14) we have

$$\frac{N}{S}\frac{dn}{dt} = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} - \frac{c_l N}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}},$$

or

$$\frac{dn}{dt} = \frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} - \frac{c_l}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \;\ldots\ldots\; (15)$$

This is the general equation for the rate of solution of gas into liquid, obtained from the new theory. The values of u_0 and u'_0 depend upon the nature of gas and liquid.

The initial rate of solution, or the rate of solution of gas when the liquid is perfectly free from the gas, can be obtained from the above equation by putting $c_l = 0$,

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = \frac{p}{\sqrt{2\pi MRT}} S \cdot e^{-\frac{Mu_0^2}{2RT}}, \quad \ldots\ldots\ldots\ldots\ldots \quad (16)$$

When the liquid is saturated with the gas, $dn/dt = 0$. Then at the state of saturation,

$$\frac{p}{\sqrt{2\pi MRT}} Se^{-\frac{Mu_0^2}{2RT}} = \frac{c_\infty}{1000} S \sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_0'^2}{2RT}}, \quad \ldots\ldots\ldots\ldots \quad (17)$$

where c_∞ is the concentration of the saturated solution.

Then the equation (15) can be expressed in the form

$$\frac{dn}{dt} = KS(C_\infty - C_l), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

where

$$K = \frac{1}{1000}\sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_0'^2}{2RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

The equation (18) is quite the same as the equation (3). Thus the equation (3), experimentally obtained and theoretically explained by old theories, was also derived from the new theory.

The equations (15), (16) and (18) were derived without the assumption of the existence of stationary boundary films, and these equations will also be satisfied, when the bulk of the liquid phase is quiescent and the existence of a stationary liquid film should be taken into considerations. In this case,

$$n = n_1 + n_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

where n is the total number of moles of the absorbed gas in the liquid phase, and n_1 and n_2 the number of moles of the gas in the stationary liquid film and in the bulk of liquid respectively.

$$\frac{dn}{dt} = \frac{dn_1}{dt} + \frac{dn_2}{dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (21)$$

Now,

$$\frac{N}{S}\frac{dn_1}{dt} = xN'' - yN''' - K(c_s - c_l) \quad \ldots\ldots\ldots\ldots\ldots \quad (22)$$

where xN'' is a portion of gas molecules which enter into liquid phase per unit of area per unit of time, yN''' a portion of gas molecules which escape the liquid phase per unit of area per unit of time, $K(c_s - c_l)$ the number of molecules of gas which enter into the bulk of liquid from the stationary film by diffusion, c_s the concentration of gas at the upper surface of the film, c_l the concentration in the bulk of liquid, N Avogadro's constant, S the area of the boundary surface, and x and y the constants less than 1.

$$\frac{N}{S}\frac{dn_2}{dt} = (1-x)N'' - (1-y)N''' + KS(c_s - c_l). \quad \dots\dots\dots\dots \quad (23)$$

From the equations (21), (22) and (23),

$$\frac{N}{S}\frac{dn}{dt} = N'' - N''' \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (24)$$

From the equations (12), (14) and (24) we have

$$\frac{dn}{dt} = \frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} - \frac{cS}{1000}\sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}},$$

which is the equation (15), and by a slight rearrangement,

$$\frac{dn}{dt} = KS(c_\infty - c),$$

which is the equations (18). In this case the mean value of concentrations of the effective region should be employed for the value c.

Discussion.

The rate of oxidation of sodium sulphite solution and the effect of many substances on the velocity were investigated by many writers.(1) The present writer has also studied the rate of oxidation of the same substance under special conditions, and from the following reason an assumption, that the rate of oxidation obtained by the present writer is equivalent to the rate of solution of oxygen into water, free from oxygen, was proposed.

(1) The rate of oxidation of sodium sulphite solution, obtained, is the maximum value, which does not increase further with the increase of concentration of sodium sulphite. It was also found that this maximum value is not a specific value of sodium sulphite solution. The maximum velocities

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(1) Bigelow, *Z. physik. Chem.*, **26** (1898), 493; Titoff, *Z. physik. Chem.*, **45** (1903), 641; Bäckstrom, *J. Am. Chem. Soc.*, **49** (1927), 1465; Alyea and Bäckstrom, *J. Am. Chem. Soc.*, **51** (1929), 90.

of oxidation of sodium sulphite, stannous hydroxide and ferrous hydroxide are identical under the same conditions.⁽¹⁾

(2) The rate of oxidation of sodium sulphite solution does not increase above this maximum value with the further increase of concentration of sodium sulphite, on the contrary it decreases when the concentration is very great.⁽²⁾ The total quantity of these substances oxidized during a definite time interval in a same vessel is not greater than that when they are oxidized alone. The rate of absorption of oxygen by the solution does not increase by mixing them.⁽³⁾

(3) The maximum rate of oxidation of sodium sulphite solution is proportional to the area of the interface of the solution.⁽⁴⁾ It was also confirmed that this maximum value is proportional to the partial pressure of oxygen.⁽⁵⁾

(4) As was described in the previous paper,⁽⁶⁾ the rate of solution of oxygen, calculated from the maximum rate of oxidation of sodium sulphite solution, has nearly the same value as the initial rate of solution of oxygen into water, observed directly by several writers.

From these reasons, the maximum rate of oxidation of sodium sulphite solution is equivalent to the rate of solution of oxygen into water, free from oxygen, which is expressed by the equation (16), according to the theory of the present writer. From the equation (16), the value u_0 was calculated,⁽⁷⁾ using the maximum rate of oxidation of sodium sulphite solution, observed, and was found that the value u_0 is 1.65×10^5 cm./sec., approximately 3.4 times the root-mean-square velocity of oxygen gas and is independent of temperature in the range 15°—35°C.

The diffusion theory assumes the existence of a stationary film at the interface. According to the new theory the equation (3) was obtained when the stationary film is not exist, as when the stationary film exists. When the liquid phase is quiescent, the existence of a stationary liquid film will be very probable, but when the liquid phase is well stirred, the assumption that a stationary liquid film of such thickness as that, calculated by Brunner⁽⁸⁾ and Crandall⁽⁹⁾ from the diffusion theory (2×10^{-2}—2×10^{-3} cm.), exists at the interface, can not be accepted without direct confirmations.

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(1) Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **3** (1928), 98; **3** (1928), 137.
(2) Miyamoto and Kaya, ibid., **6** (1931).
(3) Miyamoto, this Bulletin, **2** (1927), 192; **4** (1959), 132. .
(4) Miyamoto and Nakata, ibid., **6** (1931), 9.
(5) Miyamoto, Kaya and Nakata, ibid., **5** (1930), 229.
(6) Miyamoto and Nakata, ibid., **6** (1931), 22.
(7) Ibid.
(8) *Z. physik. Chem.*, **47** (1904), 99.
(9) *J. Am. Chem. Soc.*, **52** (1930), 3760.

As a result of the study on the oxidation velocity of sodium sulphite solution by oxygen in the presence of molecular film of fatty acid,(1) it was ascertained that when the bulk of sodium sulphite solution is well agitated, the thickness of stationary film, if it exist, should be less than the length of a molecule of palmitic acid (23.7×10^{-8} cm.).

The result of the measurement of the oxidation velocity of sodium sulphite solution studied by the present writer, will be difficult to be interpreted by the diffusion theory, which requires the existence of a stationary film whose thickness is about 10^4 times the value confirmed experimentally(1). The fact that the rate of oxidation of sodium sulphite solution is independent of the concentration of sodium sulphite in the range of about 0.3—0.7 normal, will also be difficult to be explained by the diffusion theory, according to which the interface is instantaneously saturated with gas. The equation (6′)

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{\text{initial}} = k_l(c_\infty + c_m) ,$$

which is based upon the assumption that the upper layer of the surface film is almost instantaneously saturated with gas, does not hold in the case of the oxidation of sodium sulphite solution. The oxidation velocity is independent of the concentration in the range above described; it depends upon the concentration when the concentration is very small. According to the theory of the present writer, the rate of oxidation of sodium sulphite solution is less than the initial rate of solution of oxygen into water, when the concentration of sodium sulphite is very small, and the rate of oxidation is greater than the initial rate of solution of oxygen into water, when the concentration of sodium sulphite solution is in the range of 0.3—0.7 normal. In the former case, the rate of oxidation depends upon the concentration of sodium sulphite solution, and in the latter case, the rate of oxidation is equivalent to the initial rate of solution of oxygen into water, free from oxygen, which is expressed by the equation (16), and is independent of the concentration of sodium sulphite solution.

The rate of solution of oxygen into sodium sulphite solution decreases when the concentration of sodium sulphite solution is very great,(2) as was above described. This fact will be explained by the equation (6′), which is based upon the diffusion theory, if the decrease of solubility of gas c_∞ be taken into consideration, but the diffusion theory is not satisfied for the interpretation of the initial stage of the rate of oxidation of sodium sulphite solution, as was above described. According to the new theory it is easily

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(1) Miyamoto, Kaya and Nakata, this Bulletin, **6** (1931), 133.

(2) Miyamoto and Kaya, this Bulletin, **6** (1931).

explained by the consideration that in this stage the rate of oxidation is also equivalent to the rate of solution of oxygen into the solution, free from oxygen, which is expressed by the equation (16), but the value u_0, which depends upon the nature of the liquid phase, increases with the increase of the concentration of sodium sulphite solution.

The coincidence of the oxidation velocities(1) of sodium sulphite, stannous hydroxide and ferrous hydroxide in sodium hydroxide solution under the same conditions by air is also a favourable experimental fact to the theory of the present writer. The maximum oxidation velocity of sodium sulphite solution is proportional to the partial pressure of oxygen, as the new theory requires. The maximum oxidation velocity is equivalent to the value expressed by the equation (16).

In conclusion it can be described that the new theory interprets not only the experimental facts which are explained by the diffusion theory, but also those, which will be difficult to be explained by the old theory.

The new theory is very reasonable in the point of view that it does not assume the existence of a stationary liquid film at the interface, since the existence of a stationary liquid film of such thickness as that calculated by the diffusion theory is questionable, when the bulk of the liquid is well agitated with a stirrer.

Summary.

(1) A theory of the rate of solution of gas into liquid was proposed, which is based upon the assumptions 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_0, can enter into the liquid phase, and 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_0', can escape the liquid phase.

(2) A short discussion of the theory in comparison with the old theories was described.

(3) Rate of oxidation of sodium sulphite solution, which will be difficult to be explained by the old theory, was interpreted by the new theory.

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(1) Loc. cit.