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

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Introduction.

The rate of solution of solid into liquid(1) is expressed generally by

$$\frac{dc}{dt} = KS(c_\infty - c) \quad \dots\dots\dots\dots\dots\dots \quad (1),$$

where c is the concentration of the dissolved substance in the liquid phase, c_∞ the saturation concentration, S the area of the boundary surface, K a constant, and t the time.

Noyes,(2) Whitney(2) and Nernst,(3) in advancing equation (1) as representing the rate of diffusion, made the assumption that a film of saturated solution is continuously present on the surface of solid phase, and that a stationary diffusion layer of adequte thickness is present at the interface. According to this theory the thickness of the diffusion

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(1) Noyes and Whitney, *Z. physik. Chem.*, **23** (1897), 689; Nernst, *Z. physik. Chem.*, **47** (1904), 52; Brunner, *Z. physik. Chem.*, **47** (1904), 56.

(2) Ibid.

(3) Ibid.

layer⁽⁴⁾ is about $2\times10^{-3}\sim5\times10^{-3}$ cm., the exact value naturally depending upon the rate of revolution of the stirrer in the main body of the liquid phase.

The rate of solution of metals or metallic oxides into acidic solution is expressed in the majority of cases by

$$\frac{dc}{dt}=-KSc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)'.$$

where c is the concentration of the acid. This equation is similarly derived by assuming that the rate of solution is the rate of diffusion of the reacting substance through an assumed diffusion layer.

There are many experimentally obtained facts which it would be difficult to interpret by the diffusion layer theory. For example,

(a) The rate of solution of metals into acidic solution is independent of the rate of stirring when the velocity of stirring is sufficiently high(5).

(b) The rate of solution differs according to the faces of the crystal concerned(6).

(c) The rate of solution is dependent on the curvature of the solid surface(7).

(d) Roller studied the relation between the rates of solution and the size of the solid particles, and concluded that no diffusion layer exists at the boundary surface(8).

Theories of the rate of solution of solid into liquid, which do not assume the existence of a diffusion layer, have been proposed by several writers(9).

The following is a new theory of the rate of solution of solid into liquid, similar to that of the rate of solution of gas into liquid proposed by the present writer,(10) and based upon the kinetic theory of gas.

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

The process of solution of solid into liquid can be divided into two processes, namely the escape of the solid molecules into the liquid phase

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(4) Brunner, *Z. physik. Chem.*, **47** (1904), 56; Wagner, *Z. physik. Chem.*, **71** (1910), 401.

(5) Centnerszwer and Zablocki, *Z. physik. Chem.*, **122** (1926), 455; Centnerszwer and Straumanis, ibid., **128** (1927), 369; Centnerszwer, ibid., **137** (1928), 352; **141**A (1929), 297.

(6) Tammann and Sartorius, *Z. anorg. Chem.*, **175** (1929), 197; Glauner, *Z. physik. Chem.*, **142** (1929), 67.

(7) Luce, *Ann. Phys.*, **11** (1929), 167; Podszus, *Z. physik. Chem.*, **92** (1917), 227.

(8) Roller, *J. Phys. Chem.*, **35** (1931), 1133; **36** (1932), 1202.

(9) Ericson-Auren, *Z. anorg. Chem.*, **18** (1898), 83; **27** (1901), 209; Palmaer, *Z. physik. Chem.*, **56** (1906), 689; Wildermann, *Z. physik. Chem.*, **66** (1909), 445.

(10) Miyamoto, *Chem. News*, **144** (1932), 273; this Bulletin, **7** (1932) 8, 388.

and the condensation of the dissolved molecules on the solid surface. Then the rate of solution of solid into liquid is generally given by

$$\frac{N}{S}\left(\frac{dn}{dt}\right)=N_1-N_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2),$$

where N is Avogadro's constant, S the area of the boundary surface, N_1 the number of molecules of the solid which enter into the liquid phase per unit area of the interface per unit time, N_2 the number of molecules which condense per unit area of the interface per unit time, n the number of moles of the dissolved substance in the liquid phase.

According to Maxwell's distribution law, the number of molecules, whose components of energies of vibration at right angles to a fixed plane lie between ε and $\varepsilon+d\varepsilon$, among N' molecules is given by

$$dN=\frac{N'}{kT}e^{-\frac{\varepsilon}{kT}}d\varepsilon \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3),$$

where k is Boltzmann's constant.

Then the number of molecules, per unit area of the solid surface, whose energies of vibration at right angles to the interface are greater than a threshold value ε_0, is given by

$$N_x=\frac{N_0}{kT}\int_{\varepsilon_0}^{\infty}e^{-\frac{\varepsilon}{kT}}d\varepsilon=N_0e^{-\frac{\varepsilon_0}{kT}}=N_0e^{-\frac{N\varepsilon_0}{RT}},$$

where N_0 is the number of molecules which make up unit area of the solid surface.

Now an assumption is proposed. Among the molecules of which the surface of the solid consists, only those, whose components of energies of vibration at right angles to the interface are greater than a threshold value ε_0, are able to enter into the liquid phase. Then it is clear that the value N_1 is proportional to N_x and is given by

$$N_1=\beta N_x=\beta N_0e^{-\frac{N\varepsilon_0}{RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4),$$

where β is a constant.

On the above mentioned assumption it easily follows that the value ε_0 depends upon the characteristic qualities of solid and liquid, and also upon pressure and temperature. The packing of the molecules in the solid surface will have a great influence on the value of ε_0. When the solid surface is convex, the value ε_0 is of course smaller and consequently the value N_1 is greater than when the solid surface is plane.

The rate of condensation or the value N_2 is obtained in the following way. By Maxwell's distribution law of velocities the number of molecules whose components of velocities at right angles to a fixed plane lie between u and $u+du$ among N'' molecules in the liquid phase is given by

$$dN = \frac{N''}{\sqrt{\frac{2\pi RT}{M}}} e^{-\frac{Mu^2}{2RT}} du \quad \dots\dots\dots\dots\dots\dots \quad (5),$$

where M is the molecular weight of the dissolved substance, R the gas constant, and T the absolute temperature.

Now the following assumption is proposed. Among the molecules, which collide with the solid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0, can condense on the solid surface.

This assumption has great probability in view of the fact that in the majority of cases the collisions between gas molecules and surface are perfectly inelastic, that is, every gas molecule which collides with the solid surface condenses(11). The greater the component of velocity at right angles to the interface, the more inelastic will be the collision. According to this assumption the value N_2 is given by

$$N_2 = \int_{u_0}^{\infty} \frac{cN}{\sqrt{\frac{2\pi RT}{M}}} u e^{-\frac{Mu^2}{2RT}} du = cN\sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \quad \dots\dots \quad (6),$$

where c is the concentration of the dissolved substance expressed as the number of moles per c.c.

The value u_0 depends upon the natures of solid and liquid, temperature and pressure, and the value N_2 increases or decreases as the value u_0 decreases or increases. From equations (2), (4) and (6) we have

$$\frac{dn}{dt} = S\left(\frac{\beta N_0}{N} e^{-\frac{N\varepsilon_0}{RT}} - c\sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}}\right) \quad \dots\dots\dots\dots \quad (7).$$

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(11) Langmuir, *J. Am. Chem. Soc.*, **38** (1916), 2257; **54** (1932), 2801; Egerton, *Phil. Mag.*, **33** (1917), 33.

In the state of saturation,

$$\frac{dn}{dt} = 0 \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (8).$$

From equations (7) and (8) we have

$$\frac{\beta N_0}{N} e^{-\frac{N\varepsilon_0}{RT}} = c_\infty \sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_0^2}{2RT}} \quad \dots\dots\dots\dots \quad (9),$$

where c_∞ is the concentration of the saturated solution. From equations (7) and (9) we have

$$\frac{dn}{dt} = S\sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_0^2}{2RT}} (c_\infty - c) \quad \dots\dots\dots\dots \quad (10).$$

Now

$$c = \frac{n}{v} \quad \dots\dots\dots\dots\dots\dots \quad (11),$$

where v is the volume of the liquid phase.

Then, neglecting the change of volume of the liquid phase due to the dissolution of the solid substance; we have,

$$\frac{dc}{dt} = \frac{1}{v}\frac{dn}{dt} = \frac{S}{v}\sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_0^2}{2RT}} (c_\infty - c) \quad \dots\dots\dots \quad (12),$$

or

$$\frac{dc}{dt} = KS(c_\infty - c) \quad \dots\dots\dots\dots\dots\dots \quad (13),$$

where

$$K = \frac{1}{v}\sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_0^2}{2RT}} \quad \dots\dots\dots\dots\dots\dots \quad (14).$$

Thus equation (1) has been derived from the new theory without the assumption of a diffusion layer.

Equation (1)′ is similarly derived as follows:—It is assumed that, among the molecules which collide with the solid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0, can react with the solid.

Then from equation (6) the rate of solution is expressed by

$$-\frac{N}{S}\frac{dn}{dt} = cN\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0^2}{2RT}} \qquad \ldots\ldots\ldots\ldots\ (15),$$

where n is the number of moles of the reacting substance and c its concentration. Now

$$c = \frac{n}{v} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (16),$$

where v is the volume of the liquid phase. From equations (15) and (16) we have

$$\frac{dc}{dt} = -\frac{c}{v}S\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0^2}{2RT}} \qquad \ldots\ldots\ldots\ldots\ (17),$$

or

$$\frac{dc}{dt} = -KSc \qquad \ldots\ldots\ldots\ldots\ldots\ (18),$$

where

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

Thus equation (1)′ has been obtained.

The Initial Rate of Solution. The initial rate of solution, or the rate of solution when the liquid is perfectly free from solid substance, is obtained from equation (7) by putting $c = 0$.

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = \frac{\beta S N_0}{N}\,e^{-\frac{N\varepsilon_0}{RT}} ,$$

or

$$\left(\frac{dc}{dt}\right)_{\text{initial}} = \frac{\beta S N_0}{Nv}\,e^{-\frac{N\varepsilon_0}{RT}} \qquad \ldots\ldots\ldots\ldots\ (20).$$

The initial rate of solution is a function of ε_0 only.

From equations (9) and (20) we may also express the initial rate of solution by the following equation.

$$\left(\frac{dc}{dt}\right)_{\text{initial}} = \frac{Sc_\infty}{v}\sqrt{\frac{RT}{2\pi M}}\,e^{-\frac{Mu_0^2}{2RT}} \qquad \ldots\ldots\ldots\ldots\ (20)'.$$

The Solubility of Solid.

From equation (9) the solubility of a solid, c_∞ moles per c.c., is given by

$$c_\infty = \frac{\beta N_0}{N}\sqrt{\frac{2\pi M}{RT}}\,e^{-\frac{1}{RT}\left(N\varepsilon_0 - \frac{Mu_0^2}{2}\right)} \quad \dots\dots\dots\dots (21).$$

The solubility of a solid is quite independent of the initial rate of solution. The solubility is expressed as a function of ε_0 and μ_0, but the initial rate of solution as a function of ε_0 only. Now the value N_0, the number of molecules which compose unit area of the solid surface, is generally given by

$$N_0 = \gamma\left(\frac{N}{v_m}\right)^{\frac{2}{3}} = \gamma\left(\frac{\rho N}{M}\right)^{\frac{2}{3}} \quad \dots\dots\dots\dots (22),$$

where N is Avogadro's constant, v_m the molar volume, ρ the density of the solid, M the molecular weight, γ a constant, the value of which depends upon the arrangement of the molecules of the solid. From equations (21) and (22) we have

$$c_\infty = \beta\gamma N^{-\frac{1}{3}}\left(\frac{2\pi}{R}\right)^{\frac{1}{2}} M^{-\frac{1}{6}} \rho^{\frac{2}{3}} T^{-\frac{1}{2}} e^{-\frac{1}{RT}\left(N\varepsilon_0 - \frac{Mu_0^2}{2}\right)} \quad \dots (23).$$

The osmotic pressure, p_∞, of the saturated solution is given in the ideal case by

$$p_\infty = RTc_\infty = \beta\gamma N^{-\frac{1}{3}}(2\pi R)^{\frac{1}{2}} M^{-\frac{1}{6}} \rho^{\frac{2}{3}} T^{\frac{1}{2}} e^{-\frac{1}{RT}\left(N\varepsilon_0 - \frac{Mu_0^2}{2}\right)} \quad .. (24).$$

From equation (21) we have

$$\ln c_\infty = \frac{-\left(N\varepsilon_0 - \frac{Mu_0^2}{2}\right)}{RT} - \frac{1}{2}\ln T + \ln\frac{\beta N_0}{N}\sqrt{\frac{2\pi M}{R}} \quad \dots.. (25).$$

For the temperature range within which the values ε_0, u_0, N_0 may be taken as constant, we have from equation (25)

$$\ln c_\infty = \frac{A}{RT} - \frac{1}{2}\ln T + B \quad \dots\dots\dots\dots (26),$$

where

$$\left.\begin{aligned} A &= -\left(N\varepsilon_0 - \frac{Mu_0^2}{2}\right) \\ B &= \ln\frac{\beta N_0}{N}\sqrt{\frac{2\pi M}{R}} \end{aligned}\right\} \qquad \text{................ (27).}$$

From Clapeyron-Clausius equation we have⁽¹²⁾

$$\frac{d \ln c_\infty}{dT} = \frac{-Q}{RT^2} \qquad \text{.................... (28).}$$

By putting

$$Q = Q_0 + \alpha T \qquad \text{...................... (29),}$$

in equation (28) we have

$$\frac{d \ln c_\infty}{dT} = \frac{-(Q_0+\alpha T)}{RT^2}$$

This equation represents the relation between the solubility and the temperature over the temperature range for which Q may be expressed by equation (29). By integrating this equation we have

$$\ln c_\infty = \frac{Q_0}{RT} - \frac{\alpha}{R}\ln T + \beta \qquad \text{............... (30),}$$

where β is the integration constant. Equation (26) derived kinetically has a form analogous to equation (30) derived thermodynamically.

Discussion.

As equations (1) and (1)′ have been derived according to the new theory, it is certain that this theory can be used to interpret any experimental fact that can be interpreted by the diffusion theory. It is hardly necessary to mention that the same theory can also be applied when the bulk of the liquid phase is quiescent, in which case the existence of a diffusion layer must be taken into consideration.

From equations (7) and (17) the rate of solution is dependent upon the values ε_0 and u_0. The fact, experimentally verified, that the rate of solution differs at different faces of the crystal,⁽¹³⁾ is thus explained:—

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(12) Eucken, „Lehrbuch der chemischen Physik,“ S. 345.

(13) Loc. cit.

The values ε_0 and u_0 are dependent not only on the chemical natures of the solid and the liquid but also on the packing of the molecules in the solid surface. The results of Roller's investigations(14) can be similarly interpreted by means of equation (7).

The solubility of the solid depends upon the curvature of the solid surface.

(a) Hulett(15) found that the solubility of gypsum increases when the size of the particle is less than 2×10^{-4} cm.

(b) Dundon and Mack(16) observed an increase in the solubility of gypsum between $0.2\times10^{-4}\sim0.5\times10^{-4}$ cm. in size, and Dundon(17) extended these observations to other powders.

These facts are interpreted easily from equation (21), obtained by the present theory.

Nernst(18) had proposed that a diffusion layer of adequate thickness normally exists at the interface between different phases. But there are a number of experimentally obtained facts which contradict the existence of the Nernst diffusion layer.

(a) Langmuir(19) has concluded from the studies on adsorption, that only a monomolecular film exists at the interface between solid and gas, and interpreted a number of phenomena according to his theory.

(b) As mentioned above, the rate of solution of metals into acidic solutions is independent of the rate of stirring when the stirring speed is sufficiently high;(20) the rates of solution at the different faces of a crystal are different;(6) the rate of solution of solid depends upon the curvature of the solid surface(21). These facts are difficult to interpret by the diffusion layer theory.

(c) The diffusion layer theory demands the existence of a diffusion layer whose thickness is $20\times10^{-4}\sim50\times10^{-4}$cm. at the interface between solid and liquid(22). On the contrary Spangenberg(23) found optically that the thickness of the stationary layer at the interface between sodium chloride crystal and its saturated solution, if it exist, must be less than 0.4×10^{-4}cm. Bulkley(24) showed from the measurements of flow through

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(14) Loc. cit.
(15) *Z. physik. Chem.*, **37** (1901), 385; **47** (1904), 357.
(16) *J. Am. Chem. Soc.*, **45** (1923), 2479.
(17) Ibid., **45** (1923), 2658.
(18) *Z. physik. Chem.*, **47** (1904), 52.
(19) *Trans. Farad. Soc.*, **17** (1921), 621.
(20) Loc. cit.
(21) Loc. cit.
(22) Loc. cit.
(23) *Z. Krist.*, **59** (1923), 383.
(24) *Bureau Standards, J. Res.*, **6** (1931), 89.

capillary tubes that the liquid moves at least up to 0.03×10^{-4} cm. from the solid surface.

From the study of the effect of molecular films of fatty acids on the rate of oxidation of sodium sulphite solution the present writer and his collaborators(25) have concluded that no Nernst diffusion layer exists at the interface between liquid and gas, when the bulk of liquid phase is stirred at high speed.

(d) From the study of the initial rate of solution of oxygen into alcoholic solutions of anhydrous stannous chloride the present writer and his collaborator(26) have shown that the effect of the change of concentrations of stannous chloride on the initial rate of solution does not satisfy the equation derived from the diffusion layer theory.

Roller(14) concluded from the results of his study that no theoretical Nernst film exists at the interface between solid and liquid. The present writer is also of the opinion that no diffusion layer of such thickness as that demanded by the diffusion layer theory exists at the interface between different phases when the bulk of the phases is stirred at a sufficiently high speed.

Summary.

(1) A theory of the rate of solution of solid into liquid was proposed, which is based upon the assumptions that among the molecules, which compose the solid surface, only those, whose components of energies of vibration at right angles to the interface are greater than a threshold value ε_0, can enter into the liquid phase, and that among the molecules 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 condense on the solid surface.

According to this theory the rate of solution is expressed by

$$\frac{dc}{dt} = \frac{S}{v}\left(\frac{\beta N_0}{N} e^{-\frac{N\varepsilon_0}{RT}} - c\sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{Mu_0^2}{2RT}}\right),$$

which can be transformed into the following equation.

$$\frac{dc}{dt} = KS(c_\infty - c)\ .$$

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

(26) Miyamoto and Utunomiya, this Bulletin, **53** (1932), 1096; *J. Science of the Hiroshima University*, A, **3** (1933), 193.

(2) According to the present theory the solubility of solid is given by

$$c_\infty = \frac{\beta N_0}{N}\sqrt{\frac{2\pi M}{RT}}\,e^{-\frac{1}{RT}\left(N\varepsilon_0-\frac{Mu_0^2}{2}\right)}$$

or

$$c_\infty = \beta\gamma N^{-\frac{1}{3}}\left(\frac{2\pi}{R}\right)^{\frac{1}{2}} M^{-\frac{1}{3}}\rho^{\frac{2}{3}}\,T^{-\frac{1}{2}}\,e^{-\frac{1}{RT}\left(N\varepsilon_0-\frac{Mu_0^2}{2}\right)}$$

(3) The experimental facts obtained by a number of writers have been interpreted in the light of the present theory.

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