

Chapter 5

REACTION-DIFFUSION KINETICS IN SOLID-LIQUID AND SOLID-GAS SYSTEMS

The melting points of the components of a reaction couple are most frequently different. Therefore, there is a certain range of temperature in which one of the components is in the solid state, while the other is in the liquid state. If soluble, the solid substance will dissolve in the liquid phase. The dissolution process should clearly affect the growth kinetics of a chemical compound layer at the solid-liquid interface.

If a solid interacts with a gas, the reaction product may happen to be appreciably volatile at a given temperature. Then, the rate of its evaporation must also be taken into account in kinetic equations.

The effect of dissolution in the solid-liquid system and of evaporation in the solid-gas system on the growth rate of a chemical compound layer will now be established. Substance *A* will be assumed to have a higher melting point than substance *B*. As before, substance *B* is considered to be insoluble in phase *A*.

5.1. Main relationships governing dissolution of solids in liquids

Let us briefly analyse the process of dissolution of a solid substance in a liquid. Assume that the interaction of substances *A* and *B* takes place at temperature T_2 (see Fig.1.1). The solubility of component *A* in liquid *B* at this temperature is c_s , kg m^{-3} or mol m^{-3} . If the instantaneous concentration, c , of *A* in *B* is below this value, then solid *A* will dissolve in liquid *B*.

Consider first the case where the chemical compound A_pB_q is not formed between initial substances *A* and *B* during dissolution. The rate of dissolution of any solid in the liquid phase is known to be described by the equation

$$\frac{dc}{dt} = k \frac{S}{v} (c_s - c) \quad (5.1)$$

where c is the concentration of the dissolved substance in the bulk of the liquid phase at time t , c_s is the saturation concentration (solubility of A in B) at a given temperature, k is the dissolution-rate constant, S is the surface area of the solid in contact with the liquid, and v is the volume of the liquid.

An equation of this type was first proposed by A. Shchukarev in 1896.²⁹⁴ A year later, A.A. Noyes and W.R. Whitney derived a similar equation.²⁹⁵ Its validity was then verified experimentally by L. Bruner and St. Tolloczko²⁹⁶ and E. Brunner.²⁹⁷

According to W. Nernst,²⁹⁸ the dissolution-rate constant can be expressed as follows

$$k = \frac{D_A}{\delta} \quad (5.2)$$

where D_A is the coefficient of diffusion of the atoms of the dissolving substance A across the diffusion boundary layer adjacent to the surface of the solid into the liquid phase, and δ is the thickness of the diffusion boundary layer.

Note that equation (5.1) follows immediately from Fick's laws on the assumption of a quasi-stationary distribution of the concentration of components within the diffusion boundary layer. Indeed, if in this layer $\partial c_A / \partial t \approx 0$, then the second Fick law yields $\partial c_A / \partial x \approx \text{const}$. It means that the distribution of the concentration of component A within this layer is close to linear (Fig.5.1). Anywhere outside of this layer, the concentration of A is assumed to be the same and equal to an instantaneous value, c . This implies sufficiently intensive agitation of the liquid. In such a case, the flow of A atoms across the diffusion boundary layer under the condition of constancy of the surface area of the dissolving solid is

$$j_A = -D_A \left(\frac{\partial c_A}{\partial x} \right)_s = -D_A \frac{c_s - c}{\delta}. \quad (5.3)$$

In terms of the concentration of substance A in the bulk of liquid B the flow, j_A , can be written as follows

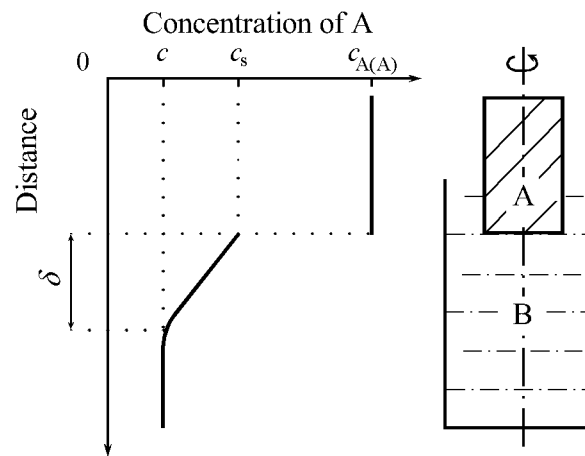


Fig.5.1. Schematic diagram to illustrate the process of dissolution of a solid *A* in a liquid *B* in the case where no chemical compound layer is formed at their interface.

Not on scale; in fact, the thickness, δ , of the diffusion boundary layer is very small in comparison with the height of the column of the liquid phase .

$$j_A = \frac{v}{S} \frac{dc}{dt}. \quad (5.4)$$

Equation (5.1) is then obtained by combining equations (5.2)-(5.4).

Clearly, this derivation of equation (5.1) is valid only in the case of the diffusional regime of dissolution of substance *A* in liquid *B* when the overall rate of the process is limited by the rate of transition of the *A* atoms across the diffusion boundary layer. However, the equation itself is also applicable for another, decomposition controlled regime of dissolution when the rate-determining step is the separation of the *A* atoms from the solid surface due to their interaction with the *B* atoms at the solid-liquid interface.

Indeed, it seems obvious that a variation of the concentration of any dissolving solid substance in a liquid is directly proportional to both the area of its surface contacting with the liquid and the difference between the saturation concentration (solubility) at a given temperature and the instantaneous concentration of *A* in *B*, and is inversely proportional to the volume of the liquid phase. Therefore, the general form of equation (5.1) remains unchanged for either dissolution regime of any solid in any liquid. The difference lies in the character of the dependence of the dissolution-rate constant, *k*, upon the thickness, δ , of the diffusion boundary layer.²⁹⁹⁻³⁰³

It is clear that under conditions of decomposition control the rate of dissolution of a solid in a liquid is independent of the thickness of the diffusion boundary layer and hence of the intensity of agitation of the liquid. By contrast, in the case of diffusion control the intensity of agitation of a liquid has a strong effect on the thickness of the diffusion boundary layer, thus influencing the value of the dissolution-rate constant, *k*.

Most frequently, the process of dissolution of solid substances in liquids is investigated using the rotating disc technique.²⁹⁹⁻³⁰⁹ The main advantage of this method is an equal accessibility of the surface of the rotating disc, *i.e.* the dissolution of its surface (or the deposition of the reaction product on it) should proceed uniformly.²⁹⁹

According to V.G. Levich²⁹⁹ (see also Refs.300,302,304), the thickness of the diffusion boundary layer at the rotating disc surface is determined by the equation

$$\delta = 1.61D^{1/3} \nu^{1/6} \omega^{-1/2} \quad (5.5)$$

where ν is the kinematic viscosity of the liquid phase, $\text{m}^2 \text{s}^{-1}$, ω is the angular speed of

the disc rotation, rad s^{-1} . For simplicity, the subscript A at D_A was omitted.

From equations (5.2) and (5.5), it follows

$$k = 0.62D^{2/3}\nu^{-1/6}\omega^{1/2}. \quad (5.6)$$

This equation allows the determination of the diffusion coefficient, D , of the atoms of the dissolving substance across the diffusion boundary layer, knowing the value of the dissolution-rate constant, k , and *vice versa*. It is essential to remember, however, that equation (5.6) holds for Schmidt's numbers, Sc , exceeding 1000.

The Schmidt number is a dimensionless parameter equal to the quotient of dividing the kinematic viscosity by the diffusion coefficient: $Sc = \nu/D$ (for more detail, see Refs.299,300,302). Usually, for liquids $Sc < 1000$. In such a case, more precise calculations can be carried out using the equation

$$k = 0.554I^{-1}D^{2/3}\nu^{-1/6}\omega^{1/2} \quad (5.7)$$

in which the factor I is a (slight) function of the Schmidt number: $I = f(Sc)$. The dependence of I on Sc is presented in Table 5.1.^{300,306}

Equation (5.7) was proposed by T.F. Kassner.³⁰⁶ It is valid for $Sc > 4$. In the range $10 < Sc < 10^3$ typical of liquid metals the difference in the results of calculations with the use of equations (5.6) and (5.7) varies from about 17 % to 3 %.³⁰⁰

In many cases, the solid disc indeed dissolves in a liquid uniformly over the entire surface, as in Fig.5.2a.³⁰⁹ Sometimes, however, spiral etch patterns reproducing the lines of laminar flow of the liquid^{299,300,304} are seen on the surface of the disc after its dissolution in the liquid phase. An example is shown in Fig.5.2b.³⁰⁹ This takes place when the velocity of movement of the solid-liquid interface relative to its initial position exceeds a certain limiting value.

It is clear that the occurrence of visible etch patterns provides evidence for the violation of the condition of an equal accessibility of the rotating disc surface. Therefore, when investigating the dissolution process, the diameter of a disc is to be chosen in such a way as to ensure that, for the pre-determined volume of a liquid, the depth of dissolution of the disc should not exceed a critical value for that particular system.

Diameter values between 1 and 2 cm are practicable. With smaller discs, edge

Table 5.1. Dependence of the correction factor, I , of the Kassner equation upon the Schmidt number, $Sc^{299,300}$

Sc^{-1}	I	Sc^{-1}	I	Sc^{-1}	I
0.001	0.9209	0.010	0.9564	0.100	1.0368
0.002	0.9286	0.020	0.9747	0.110	1.0412
0.003	0.9341	0.030	0.9877	0.120	1.0451
0.004	0.9385	0.040	0.9981	0.130	1.0488
0.005	0.9424	0.050	1.0068	0.140	1.0521
0.006	0.9457	0.060	1.0143	0.150	1.0552
0.007	0.9487	0.070	1.0209	0.160	1.0580
0.008	0.9515	0.080	1.0268	0.180	1.0631
0.009	0.9541	0.090	1.0321	0.200	1.0675

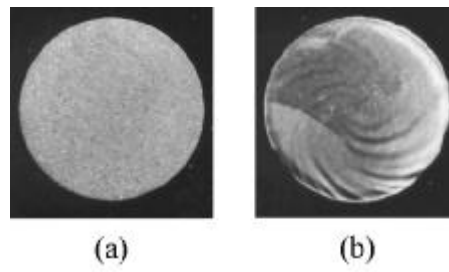


Fig.5.2. Niobium (a) and molybdenum (b) discs (12 mm diameter) after their dissolution in liquid aluminium at 700°C and an angular speed of the disc rotation of 25.0 rad s^{-1} . Dissolution time is 7200 s ($St/v = 19440 \text{ s m}^{-1}$).³⁰⁹

effects become significant.^{299,300} Greater discs are not very convenient from the point of view of experimental set-up.

The volume of the liquid phase usually varies between 10 and 50 cm³. The diameter of the column of the liquid phase is 2 to 3 times greater than that of the disc. The distance between the disc surface and the bottom of the liquid-phase column is of the order of the disc diameter or a little greater. The depth of immersion of the disc into the liquid is around half the disc diameter. Typical rotational speeds, ω , lie in the range 5-100 rad s⁻¹.

Note that both a small disc in the large volume of a liquid and a large disc in the small volume of a liquid will hardly produce reliable data on the dissolution kinetics of the solid in the liquid. In the former case, the small disc will not ensure sufficient convective agitation of the liquid phase. In the latter, the threshold of turbulence may happen to be exceeded. Turbulence is known to occur at Reynolds numbers in excess of 10⁵. The Reynolds number, $Re = \omega r^2/\nu$, r being the disc radius, is a dimensionless parameter characterising the hydrodynamic regime of flow of liquids.^{299,300} Reproducible results are readily obtained if the flow is laminar.

It should be emphasised that the simplest way of avoiding the formation of deep etch patterns, namely, by reducing the time of the solid-with-liquid interaction, does not seem to be the best one because it only masks the phenomenon, not eliminating its cause. Therefore, it appears to be much more reasonable to increase the disc diameter and to reduce the volume of the liquid phase (within acceptable limits and taking account of other restrictions^{22,299,300,305}), so that during dissolution of a solid from zero up to saturation concentration of A in B no etch patterns will occur onto the disc surface.

Integration of equation (5.1) with the initial condition $c = 0$ at $t = 0$ yields

$$c = c_s \left[1 - \exp\left(-\frac{kSt}{\nu}\right) \right] \quad (5.8)$$

or in another form

$$\ln \frac{c_s}{c_s - c} = k \frac{St}{\nu}. \quad (5.9)$$

If the initial concentration of the dissolving substance in the liquid is equal to c_0 , then

$$\ln \frac{c_s - c_0}{c_s - c} = k \frac{St}{v}. \quad (5.10)$$

Equations (5.1), (5.8)-(5.10) indicate that the process of dissolution of a solid in a liquid is characterised by the two quantities: the saturation concentration or solubility, c_s , and the dissolution-rate constant, k . At constant pressure, the former only depends upon temperature. The second is in addition dependent upon the hydrodynamic conditions of flow of the liquid. Experimental determination of these quantities will be considered in detail in the next sections.

5.2. Experimental investigation of the dissolution process of a solid in a liquid

The process of dissolution of a solid in a liquid can readily be investigated using a rapid-quenching device like that shown schematically in Fig.5.3. Depending on the nature of substances to be studied, this may be carried out either in vacuum, or in a protective atmosphere (inert gases, hydrogen, nitrogen, *etc.*), or under a flux.^{197,303,309}

To heat the materials under investigation to the required temperature and to maintain it, the electric-resistance furnace 1 is employed. The specimen 2 of a solid substance is connected, by means of the protective tube 3, with the shaft 5, being rotated by the electric motor 4. The shaft is free to move in the vertical direction and can be fixed in the required position by the stopper 6. The temperature is measured with the help of the thermocouple 7. The flux 8 is used both to pre-heat the solid specimen to the experimental temperature and to protect the liquid 9 from oxidation by atmospheric air.

Consider the main features of the process of dissolution of some transition metals in liquid aluminium as an example.^{169,303,304-308} Cylindrical specimens of a transition metal, 11.28 ± 0.01 mm diameter and 5-6 mm high, were machined from 12-13 mm diameter rods produced by arc melting the metal under investigation. The disc surface was then ground flat and polished mechanically.

Immediately before the experiment, the solid specimen was rinsed with ethanol and dried. Then, it was pressed into a high-purity graphite tube, 16 mm diameter, to protect its lateral surface from the liquid-metal attack. Therefore, only the disc surface,