Kinetics of Nucleation in Supercooled Solutions.

By R. P. Rastogi.

[Reprint Order No. 5809.]

The Volmer–Frenkel theory of nucleation has been extended to supersaturated solutions of solids in liquids. It has been shown that the surface free energy can be computed from the observed maximum rate of nucleation.

THE theory of nucleation in supercooled melts has been developed by Volmer (" Kinetik der Phasenbildung," T. Steinkopff, Dresden, 1939), Frenkel (" Kinetic Theory of Liquids," Oxford Univ. Press, 1946), and Dunning (" Crystal Growth," *Discuss. Faraday Soc.*, 1949, **5**, 83). The particular case of liquid solutions seems not to have received due attention although attempts have been made to consider two-dimensional crystallization in supercooled solutions (Rastogi and Chatterji, *J. Phys. Chem.*, 1955, **59**, 1). The object of the present paper is to develop a corresponding theory of nucleation for supercooled solutions, following Frenkel, to suggest a method for computing the interfacial tension at the crystal solution interface, a knowledge of which is essential for the understanding of any mechanism of nucleation.

Maximum Rate of Nucleation.—We shall assume that in a two-component system the solution contains crystal nuclei consisting only of the solute. The nuclei will be assumed to be spherical, corresponding to the smallest possible surface energy : though not strictly true for crystals, this assumption is reasonable for calculation of the surface area, for, as Pound and LaMer pointed out (*J. Amer. Chem. Soc.*, 1952, **74**, 2323), " the difference in area between the surface of the sphere and the more probable many-sided polyhedron is small."

Let μ_A and μ_B be the chemical potential of the solute in the liquid and the solid phase respectively. At the saturation point of the solution, the chemical potential of the solute in both the phases is the same. Let us suppose that at any temperature T ($T < T_s$), g molecules agglomerate to form a nucleus ; the change in the Gibbs free energy can be expressed with reasonable accuracy as :

$$\Delta G = (\mu_B - \mu_A)g + \alpha g^{2/3} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where α is linear in surface tension. Then the probability of nucleus formation will be given by :

$$W = C \exp \{(-1/kT)[g(\mu_B - \mu_A) + \alpha g^{2/3}]\} \quad . \; . \; . \; . \; . \quad (2)$$

It can be shown that

$$\mu_B - \mu_A \approx -(L_s/T_s)(T_s - T) + (\Delta\mu)_{T,P}$$

where L_s is the heat of solution and $(\Delta\mu)_{T,P}$ is the change in chemical potential with change in concentration. If the change in concentration during the process of nucleation is assumed to be small, then

$$\mu_B - \mu_A \approx -(L_s/T_s)(T_s - T)$$

and W is given by

$$W = C \exp \{(-1/kT)[-g(T_s - T)(L_s/T_s) + \alpha g^{2/3}]\} \quad . \quad . \quad . \quad . \quad (4)$$

It is evident from equation (1) that ΔG increases as g increases, but later attains a maximum value and then decreases. The value of g for which ΔG is a maximum is given by

$$g_{\text{max.}} = \left[\frac{2}{3} \cdot \frac{\alpha T_s}{L_s(T_s - T)}\right]^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

hence the rate of nucleus formation J is given by

$$J = C \exp \left\{-\frac{\alpha}{3kT}\left[\frac{\alpha}{3} \cdot \frac{\alpha T_s}{L_s(T_s - T)}\right]^2\right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In formation of three-dimensional nuclei from vapour, diffusion plays an insignificant rôle and is practically the same throughout the volume, but in supersaturated solutions the effect of diffusion becomes pronounced. For such cases, equation (6) has to be modified as follows :

$$J = C \exp \left\{-\frac{\alpha}{3kT}\left[\frac{2}{3} \cdot \frac{\alpha T_s}{L_s(T_s - T)}\right]^2 - \frac{\Delta u}{kT}\right\} \quad . \quad . \quad . \quad . \quad (7)$$

where Δu is the activation energy for diffusion, following Frenkel (*Sowjet Physik*, 1932, **1**, 498) and Becker (*Proc. Phys. Soc.*, 1940, **52**, 71). Expression (7) shows that when the degree of supersaturation is small the velocity is very small, but that it increases rapidly as T decreases until it attains a maximum value. The maximum value of J can be found as follows. Differentiating expression (7) with respect to T and putting $\mathrm{d}J/\mathrm{d}T$ equal to zero, we get

$$\frac{(T_s - T)^3}{T_s^2(3T - T_s)} = \frac{4}{27} \cdot \frac{\alpha^3}{L_s^2} \cdot \frac{1}{\Delta u} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This equation should be satisfied when $T = T_{\text{max.}}$, the temperature at which the rate is maximum. If $T_s/T_{\text{max.}} = x$, equation (8) yields :

$$\frac{(x - 1)^3}{x^2(3 - x)} = \frac{4}{27} \cdot \frac{\alpha^3}{L_s^2} \cdot \frac{1}{\Delta u} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The maximum rate is given by

$$J_{\text{max.}} = C \exp \left\{-\frac{\Delta u}{kT_{\text{max.}}}\left[1 + \frac{\alpha(x - 1)}{(3 - x)}\right]\right\} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

When x is sufficiently close to 1, equations (9) and (10) yield :

$$(x - 1)^3 = \frac{8}{27} \cdot \frac{\alpha^3}{L_s^2} \cdot \frac{1}{\Delta u}$$

and

$$J_{\text{max.}} = C \exp (-\Delta u/kT_{\text{max.}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

It is clear from equations (7) and (9) that the temperature of maximum velocity is not so sensitive to the magnitude of the activation energy of self-diffusion as is the rate.

Computation of Interfacial Tension.—Attempts were made to measure the rate of formation of nuclei in supersaturated solutions but this was not achieved satisfactorily. Even under controlled conditions, growth of the nuclei was the greatest disturbing factor. For nucleation in melts, these and other difficulties have been solved to a great extent by Vonnegut (*J. Colloid Sci.*, 1948, **3**, 563) by a procedure based on the idea that, if the bulk liquid is subdivided into a great many tiny droplets isolated from each other, the more active foreign nuclei would be crowded into a few of the droplets and their effect would thus be confined in a small part of the total mass. It is doubtful whether this technique can be applied to nucleation in solution as the phase separation involves changes in concentration. The theory cannot be checked against experiment even if the rate could be determined experimentally, since the constant and the interfacial tensions are not known. However, equation (9) can be used to compute the value of interfacial free energy at the crystal–solution interface. A method for the estimation of this important quantity has been suggested by Pound and LaMer (*loc. cit.*), but there are limitations to their procedure. However, with the knowledge of temperature of maximum velocity alone, equation (9) can more conveniently yield the value of interfacial free energy. The experimental determination of $T_{\text{max.}}$ is not difficult. In fact Tammann has described a method (*Z anorg. Chem.*, 1914, **87**, 248) in which a temperature gradient is generated in a tube filled with a supercooled melt; the point at which most crystals appear corresponds to the temperature of the maximum velocity of formation of nuclei.

Unfortunately no such data exist for solutions. Hence, it is difficult to get an accurate estimate of interfacial tensions at the crystal–solution interface. However, the lower limit of interfacial tensions can be calculated as follows. The temperature of maximum velocity can never be higher than that of spontaneous crystallization, because, however pure the solution may be, it is not possible to free it from foreign nucleation catalysts. Hence, if we use the temperature of spontaneous crystallization instead of the temperature of maximum velocity we can get the lower limit for the interfacial free energy from equation (9). We have tried to calculate " α " for several systems for which the data for temperature of spontaneous crystallization are available (Chatterji and Bose, *J. Indian Chem. Soc.*, 1949, **26**, 283; 1943, **20**, 183). The activation energy of self-diffusion was calculated from the viscosity data (*ibid.*, 1948, **25**, 39) by using the relation η = Const. exp. ($\Delta u/kT$), though this relation is strictly valid only for dilute solutions. The values of heats of solution were taken from International Critical Tables. In the absence of data, the heat of solution was taken to be equal to the heat of fusion. The calculated values of the minimum possible interfacial free energy for certain systems are given in the Table. These values seem to be somewhat high, although by using the Ostwald–Freundlich equation very much higher values have been obtained for calcium and barium sulphates (cf. Jones, *Z. physikal. Chem.*, 1913, **82**, 448; Dundon and Mack, *J. Amer. Chem. Soc.*, 1923, **45**, 485). It may be stressed that the above calculations are correct, subject to the limitations of the theory which uses the concept of quasi-equilibrium.

Computed values of interfacial free energy (solute, naphthalene).

Solvent	$\Delta u/k$ (cal.)	L_s (cal. mole^{-1})	x (obs.)	α (ergs)
Chlorobenzene	2390	4557	1·0133	43·35
Benzene	2672	4421	1·017	58·84
Toluene	2184	4270	1·02	63·14
Hexane	1864	4557	1·0266	82·90
Aniline	4352	4731	1·03	127·00

CHEMISTRY DEPARTMENT, LUCKNOW UNIVERSITY,
LUCKNOW, INDIA.

[*Received, May 28th,* 1954.]