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Rate of Nucleation in Condensed Systems

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On the basis of the nucleation theory developed by Volmer, Becker, and co-workers, and the theory of absolute reaction rates, an expression is derived for the absolute rate of nucleation in condensed systems.

BECKER¹ has proposed the following type of expression for the rate of nucleation in condensed systems (i.e., liquid-solid or solid-solid transformations)

$$r^* = K \exp[-(\Delta F_i^* + q)/kT], \quad (1)$$

where ΔF_i^* is the maximum free energy necessary for nucleus formation, q is the energy of activation for diffusion across the phase boundary (or within the solid solution when the transformation involves the separation of a phase having a different composition), and K is an undetermined constant. Although Becker and Döring² were able to evaluate semiquantitatively the factor corresponding to K for the rate of nucleation of a liquid from a supersaturated vapor, to the authors' knowledge no theory has been proposed for nucleation in condensed systems from which K can be specified.

It is the purpose of the present paper to derive an expression for r^* , applying to condensed systems, on the basis of the theory of absolute reaction rates.

Nucleation theory frequently leads to an expression of the form

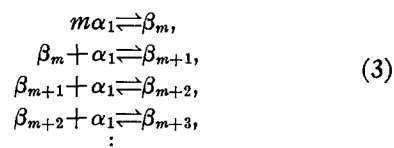
$$\Delta F_i/kT = Ai^3 - Bi \quad (2)$$

for the local free energy change associated with the formation of a region of a new phase β in a parent phase α . In this equation i is the number of atoms or molecules in the transformed region. A is proportional to the interfacial free energy per unit area of α - β -interface, and B is proportional to the bulk free energy difference between β and α in the absence of surfaces.

The curve of $\Delta F_i/kT$ versus i passes through a

maximum $\Delta F_i^*/kT = 4A^3/27B^2$ at $i^* = (2A/3B)$. then decreases without limit as shown in Fig. 1³ Subcritical nuclei containing fewer than i^* atoms require free energy for further growth, while those containing more than i^* grow freely with decreasing free energy. Since nuclei generally grow one atom at a time as the result of statistical thermal fluctuations, it is evident that small nuclei with fewer than i^* atoms will usually disappear without reaching critical size. Only occasionally will a long chain of favorable energy fluctuations produce a nucleus exceeding the critical size.

The steady state rate of nucleation for a given transformation corresponds to constant equal net forward rates for the following set of reactions

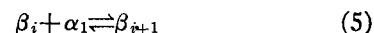


where α_1 represents an atom of phase α , β_i a nucleus of phase β containing i atoms, and where β_m is the smallest nucleus of phase β . Further, the concentration of β -nuclei must decrease to zero as the nucleus size increases,

$$\lim_{i \rightarrow \infty} [\beta_i] = 0, \quad (4)$$

since otherwise the percentage of untransformed α will not differ from zero.

Consider the reaction



at steady state. Referred to phase α as the standard state, the free energy of $\beta_i + \alpha_1$ is ΔF_i , while that of β_{i+1} is ΔF_{i+1} . Assuming that the intermediate configurations between $\beta_i + \alpha_1$ and β_{i+1} correspond to free energies greater than either ΔF_i or ΔF_{i+1} , each path by which β_i and

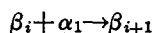
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¹ R. Becker, Ann. Physik, 32, 128 (1938).

² R. Becker and W. Döring, Ann. d. Physik [5] 24, 719 (1935).

α_1 can be combined to give β_{i+1} will have an intermediate configuration of maximum free energy. For one of these paths there will be a particular intermediate configuration corresponding to the least maximum free energy. This configuration may be called an activated complex. The free energy difference between the activated complex and the mean of ΔF_i and ΔF_{i+1} will be denoted by Δf^* .

Figure 2 indicates schematically the free energy variation associated with the combination of β_i and α_1 to give β_{i+1} (or the decomposition of β_{i+1} to give $\beta_i + \alpha_1$) by a path having the least possible maximum free energy. If n_i represents the steady state concentration of β_i nuclei, the rate of the forward reaction



can be written as

$$r^+ = n_i a_1 i^{\frac{1}{2}} (kT/h) \exp(-\Delta f_1^*/kT) \quad (6)$$

according to the theory of absolute reaction rates.³ Here $a_1 i^{\frac{1}{2}}$ is the number of α -atoms in contact with each β_i nucleus, and $n_i a_1 i^{\frac{1}{2}}$ is therefore the concentration of α -atoms available for the reaction. $(kT/h) \exp(-\Delta f_1^*/kT)$ is the specific reaction rate for the formation of the activated complex with free energy increment Δf_1^* as shown in Fig. 2.

The rate of the reverse reaction $\beta_{i+1} \rightarrow \beta_i + \alpha_1$ can be written as

$$r^- = n_{i+1} a_2 i^{\frac{1}{2}} (kT/h) \exp(-\Delta f_2^*/kT), \quad (7)$$

where $a_2 i^{\frac{1}{2}}$ is the number of β -atoms in contact with α per β_{i+1} nucleus. The net forward rate of the reaction is therefore

$$r^* = r^+ - r^- = (kT/h) i^{\frac{1}{2}} [n_i a_1 \exp(-\Delta f_1^*/kT) - n_{i+1} a_2 \exp(-\Delta f_2^*/kT)]. \quad (8)$$

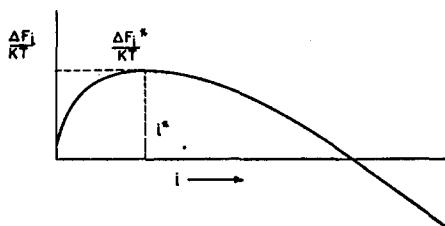


FIG. 1. $(\Delta F_i/KT) = Ai^{\frac{1}{2}} - Bi$ versus i .

³ S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

Equation (8) can be solved approximately for n_i by making the following simplifications:

(a) The number of α -atoms in contact with a β_i nucleus is not strictly equal to the number of β atoms in contact with α at the surface of a β_{i+1} nucleus. However, the difference is negligible for all but the smallest nuclei, and $a_1 = a_2 = a$ will be assumed.

(b) n_i and ΔF_i will be assumed smooth functions of i although they have meaning only for integral values of i . The change in n_i as i changes by one unit will be approximated by $(dn_i/di)\Delta i = dn_i/di$; similarly the change in ΔF_i will be approximated by $d(\Delta F_i)/di$. The approximation is good for all but the smallest nuclei.

(3) The quantities $(1/kT)d(\Delta F_i)/di$ and $(1/n_i) \times (dn_i/di)$ will both be assumed small in comparison with unity. Again the approximation is poor only for the smallest nuclei.

Noting that

$$\begin{aligned} \Delta f_1^* &= \Delta f^* + \frac{1}{2}(\Delta F_i + \Delta F_{i+1}) - \Delta F_i \\ &= \Delta f^* + \frac{1}{2}(\Delta F_{i+1} - \Delta F_i) \\ &= \Delta f^* + \frac{1}{2}d(\Delta F_i)/di, \\ \Delta f_2^* &= \Delta f^* - \frac{1}{2}d(\Delta F_i)/di, \end{aligned}$$

$$r^* = (-akT/h) \exp(-\Delta f^*/kT) \times [n_i(\frac{2}{3}Ai^{\frac{1}{2}} - B) + dn_i/di]i^{\frac{1}{2}}. \quad (9)$$

Defining

$$R = r^* / \left(\frac{akT}{h} \right) \exp(-\Delta f^*/kT), \quad (10)$$

Eq. (9) reduces to the differential equation

$$dn_i/di + (\frac{2}{3}Ai^{\frac{1}{2}} - B)n_i = -Ri^{\frac{1}{2}}. \quad (11)$$

The solution to Eq. (11) is

$$\begin{aligned} n_i &= \exp[-(Ai^{\frac{1}{2}} - Bi)] \\ &\times \left[-R \int_{i_0}^i \exp(Ai^{\frac{1}{2}} - Bi) i^{\frac{1}{2}} di \right. \\ &\quad \left. + n_{i_0} \exp(Ai_0^{\frac{1}{2}} - Bi_0) \right], \quad (12) \end{aligned}$$

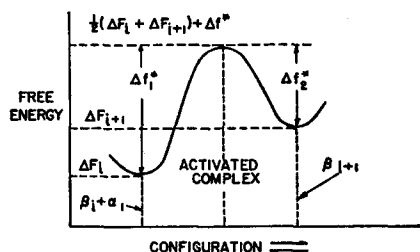


FIG. 2. Schematic representation of free energy of activation.

where n_{i_0} is the steady state number of β_{i_0} nuclei.

The steady state concentration of subcritical nuclei containing say one-third the critical number of atoms does not differ appreciably from the equilibrium concentration assuming no nucleation. Taking $i_0 = i^*/3$,

$$n_{i_0} = n \exp(-\Delta F_{i_0}/kT) = n \exp[-(Ai_0^3 - Bi_0)],$$

where n is the number of atoms of untransformed α . The expression for the steady state number of β_i nuclei reduces to

$$n_i = \exp(-\Delta F_i/kT) \times \left[-R \int_{i_0}^i \exp(\Delta F_i/kT) i^{-1} di + n \right]. \quad (13)$$

Since

$$\lim_{i \rightarrow \infty} \exp(-\Delta F_i/kT) = \infty,$$

and it is required that

$$\lim_{i \rightarrow \infty} n_i = 0,$$

it must follow that

$$\lim_{i \rightarrow \infty} \left[-R \int_{i_0}^i \exp(\Delta F_i/kT) i^{-1} di + n \right] = 0, \quad (14)$$

and hence that

$$R = n / \left[\int_{i_0}^{\infty} \exp(\Delta F_i/kT) i^{-1} di + n \right]. \quad (15)$$

The exact location of the lower limit of integration in Eq. (15) is unimportant, since for i_0 intermediate between zero and i^* practically all the contribution to the integral comes from values of i very near i^* . Replacing $\Delta F_i/kT$ by a Taylor's expansion about $i = i^*$ and neglecting all

terms after the third, the integral can be evaluated as

$$I = (9\pi/A)^{1/2} i^{*-1/2} \exp(\Delta F^*/kT). \quad (16)$$

The steady state rate of nucleation is, therefore,

$$r^* = n^* (A/9\pi)^{1/2} (NkT/h) \times \exp[-(\Delta f^* + \Delta F^*)/kT] \quad (17)$$

nuclei per second per mole of untransformed material, where n^* is the number of surface atoms in the critical size nucleus. The quantity $n^* (A/9\pi)^{1/2}$ proves to be within a factor of ten of unity for most nucleation problems of interest, giving

$$r^* \cong (NkT/h) \exp[-(\Delta f^* + \Delta F^*)/kT] \quad (18)$$

nuclei per mole per second to an order of magnitude.

Equation (18) was derived for nucleation processes that do not require long-range diffusion. Δf^* is the free energy of activation for the short-range diffusion of atoms or molecules moving a fraction of an atomic distance across an interface to join a new lattice. However, long-range diffusion is to be expected in phase transformations that involve more than one component, since the new phase and the old are generally of different composition. Equation (18) approximates the rate of nucleation in a two or more component system when Δf^* is taken as the activation energy for diffusion of the most slowly moving component and when the expression is multiplied by the mole fraction of the precipitating component.

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