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THE THERMODYNAMICS OF PROCESSES OF NEW-PHASE FORMATION

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1. INTRODUCTION

The theoretical and experimental study of processes of new-phase formation and the associated metastable states has been the subject of many papers, to which extensive reference has been made in a number of books, reviews, and symposia[1-12]. The great majority of these papers contain a discussion of the kinetics of the phase change, but all necessarily deal with the thermodynamics of the process, usually employed to estimate the work of forming a nucleus and its magnitude. This part of the theory has seemed most straightforward and has been based on the relationships given by Gibbs[13] and Kelvin[14], used in unchanged form by Volmer[3] and Becker and Döring[15], and transferred continuously from one paper to another, strengthening belief in their general applicability and triviality.

Studies carried out in the 1950's on the thermodynamics of microheterogeneous systems[16-30] showed, however, that the question is not so simple. The efforts of thermodynamicists were turned first towards a thorough analysis and correct interpretation of Gibbs' theory of surface phenomena and second to the development of this theory with the aim of deriving thermodynamic relationships for curved surfaces. Most of the results obtained concerned the dependence of surface tension on the curvature of the surface[17-27].

It was found that despite agreement with experiment[8,31-34] (theories of) the kinetics of phase changes include a number of unjustifiably crude assumptions which make no allowance for the properties of objects as small as the nuclei of new phases. The error involved in equating the properties of a nucleus to the properties of a macroscopic phase was pointed out at an early date by a number of authors, including Frenkel'[35], who continued, however, to assume that the surface tension and density of a nucleus were constant. After rigorous thermodynamic formulae describing the dependence of surface tension on the size of the nucleus[17] had been obtained, attempts were made[8,32] to introduce this dependence into the Becker–Döring kinetic equation[15]. The results obtained showed less satisfactory agreement with experiment than the original equation, and certain authors[8,10,36] preferred to continue within the framework of the "classical" theory making no allowance for the thermodynamic corrections.

This lack of success should not arouse scepticism towards rigorous thermodynamic relationships. As pointed out correctly by Buff and Kirkwood[20], unilateral allowance for the dependence of the surface tension on the curvature of the surface in equations based on the assumption that this quantity is constant may lead not to improvement but to worsening of the theory. To obtain a correct result it is necessary to make a systematic reexamination of the entire theory allowing not only for the dependence of surface tension on the size of the nucleus but also for the corresponding dependences of other thermodynamic parameters (density, composition, etc.).

Thus one of the problems in the thermodynamics of new-phase formation concerns the rigorous thermodynamic relationships characterising the equilibrium properties of small objects.

Another problem raised by the success of the thermodynamics of curved surfaces concerns more rigorous allowance for the physical conditions under which the process takes place, in calculating the work of formation of a nucleus. The result obtained by Gibbs is strictly applicable only to an infinitely large system, when the conditions under which the process takes place have no significance. When applied to real finite systems, this result becomes approximate and it is necessary to consider the corrections, whose magnitude depends on the conditions under which the process takes place.

In the present paper we shall have both of these problems in mind when discussing processes of new-phase formation.

The following symbols are used:

A = area of interface,
F = free energy,
H = enthalpy,
m_i = number of moles of the i-th component,
P = pressure,
R = the gas constant,
r = radius of curvature of the interface,
S = entropy,
s_i = partial molar entropy of the i-th component,
T = absolute temperature,
U = total internal energy,
V = volume,
v = molar volume,
v_i = partial molar volume of the i-th component,
W = work of formation of a new phase,
μ_i = chemical potential of the i-th component,
σ = surface tension,
Φ = Gibbs thermodynamic potential.

The superscript (1) indicates that the quantity belongs to the internal phase (nucleus) and the superscript (2) the external phase (medium).

2. TWO THERMODYNAMIC TREATMENTS OF METASTABLE STATES

Stable equilibrium in a multicomponent system is characterised by a minimum total internal energy U of the system at constant entropy S, volume V, and mass of the com-

ponents m_i ($i = 1, 2, \ldots$), so that when the system departs from the equilibrium state the condition

$$(\Delta U)_{S,V,m_1,m_2\ldots} > 0 \qquad (1)$$

should be satisfied.

According to Gibbs, it is necessary to distinguish two types of stability in homogeneous systems: stability relative to continuous changes in the given phase and stability relative to the formation of new phases (in the macroscopic sense). In the first case condition (1) applies to infinitely small changes and in the second case to finite changes.

Phases which are unstable with respect to infinitely small changes cannot exist, so that the term "stable state" is usually understood to mean a state stable relative to continuous changes. In a detailed treatment of condition (1), Gibbs obtained an inequality characterising the stability of a homogeneous system:

$$dTdS - dPdV + \sum_i d\mu_i\, dm_i > 0. \qquad (2)$$

This inequality leads to the familiar particular stability conditions characterising the mutual change in temperature and entropy, pressure and volume, and chemical potentials and masses of the components.

While completely stable relative to continuous changes and satisfying inequality (2), a phase of large dimensions may be unstable with respect to the formation of another macroscopic phase, so that inequality (1) is not fulfilled for certain finite changes. If, however, condition (1) is fulfilled for any finite changes, the phase is also completely stable with respect to the formation of new phases. In the first case we speak of the metastable state and in the second of the stable state of the phase.

When the energies of the phases are equal, the left-hand side of (1) becomes zero, with the production of an indifferent equilibrium corresponding to the boundary of stability relative to finite changes. Since these phases may coexist, the two-phase equilibrium curve or surface on the equilibrium diagram of the system (binodal) is also the curve or surface bounding the stable and metastable states (curve *AKB* in Fig. 1, phases *A* and *B* coexist).

The boundary of stability relative to continuous changes is reached when the left-hand side of (2) becomes zero and the curve or surface (spinodal) corresponding to this condition defines the stable and unstable states on the equilibrium diagram of the system (curve *CKD* in Fig. 1). At the critical point the stability boundaries of both types are reached and the binodal and spinodal touch one another. It follows from the thermodynamic theory of critical phenomena [37,38] that the curvature of the spinodal at the critical point is greater (by a factor of 3 in the case of binary systems, and of 1–3 in the case of ternary systems) than that of the binodal, so that the former lies inside the latter. With this mutual disposition of binodal and spinodal, the region between them corresponds to metastable states, from the definition of the latter.

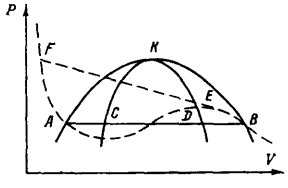


Fig. 1. Two-phase equilibrium in a one-component system: *AKB*-binodal, *CKD*-spinodal.

Thus the thermodynamics of macroheterogeneous equilibria leads logically to the existence of stable, metastable, and unstable states, establishes the position of the metastable range on the equilibrium diagram of a system, and defines the relative part played by the metastable and unstable regions in the neighbourhood of the critical point. In the general case, at a distance from the critical point, the thermodynamics of macroheterogeneous systems give no information on the width of the metastable range, apart from the fact that it is finite.

In this case another approach, provided by the thermodynamics of microheterogeneous systems, is extremely useful. Since the conditions of equilibrium for a finely-divided substance require that allowance be made for surface phenomena and curvature of the surface and hence differ from the corresponding conditions for macroscopic phases, it may be assumed that to each metastable state there corresponds an equilibrium with a particle of new phase, of definite dimensions. A characteristic feature of this equilibrium is that one of the phases lies in the metastable range and the other in the stable range, whereas in equilibrium between large masses the figurative points of the phases lie on the binodal. Thus isothermal compression of the equilibrium vapour *B* (Fig. 1) leads to the production of a metastable state *E*, which can be regarded as existing in equilibrium with a small drop of liquid in the state *F*, exhibiting an increased vapour pressure. The pressure inside the drop should exceed this pressure and the node *FE* will not now be horizontal.

In this treatment the width of the metastable range should be determined by the change in the dimensions of the equilibrium nucleus of the new phase from zero to macroscopic values and by the corresponding increase in the work *W* of formation of the nucleus on going from the spinodal to the binodal; this would correspond to complete consistency in the theories of macro- and micro-heterogeneous equilibria.

The theoretical results obtained in this field for binary systems are somewhat contradictory. According to Becker [39], *W* increases markedly as the binodal is approached; this indicates an increase in the stability of the system and agrees completely with the thermodynamics of macro-phases. Cahn and Hilliard [29] concluded that *W* becomes zero when the spinodal is reached, but they also extended this result to the unstable range. Some authors [8,40] postulate the existence of an energy barrier on the spinodal, *i.e.* they consider that *W* differs from zero.

In Section 5 we shall show that the use of rigorous thermodynamic formulae leads to complete consistency between the thermodynamics of microheterogeneous systems and general thermodynamic concepts. Before proceeding to a discussion of this question, however, it is necessary to become familiar with the thermodynamic properties of the nuclei of new phases and methods for calculating the work of their formation.

3. THE CONCEPT OF THE NUCLEUS OF A NEW PHASE

Volmer [3] gave two definitions of the nucleus of a new phase. According to the first, the nucleus is a region in the new phase, in chemical equilibrium with the medium

and hence satisfying the condition that the chemical potentials of the nucleus and medium are equal. The second definition, given by Volmer in an examination of drops of liquid in a vapour, relates the concept of the nucleus to the maximum work of its formation from the molecules of the old phase. Volmer considered that the equilibrium condition determines completely the dimensions of the new phase, but this is not always so. The two definitions become equivalent if the term "nucleus" is understood to mean the *minimal* accumulation of new phase in equilibrium with the medium [41].

From Volmer's definitions, which have been adopted by most authors, it follows that he understood the term "nucleus" to mean a new formation of definite (critical) dimensions. A number of authors, however, following Frenkel' [35], use this term in a wider sense and understand by the term "nucleus" any (not necessarily equilibrium) formation consisting of new phase. The same term is sometimes used [42-44] to denote regions of the new phase which have not yet reached critical dimensions. Subsequently, therefore, we shall speak of "equilibrium nuclei" if we are dealing with Gibbs–Volmer nuclei and simply "nuclei" if the dimensions of the region of new phase are not of fundamental importance.

Having become familiar with the terminology, we must decide upon a method for the thermodynamic description of regions of new phases and particularly a method for defining their dimensions. Since the nucleus may be very small, it is necessary, for an accurate characterisation of its extent, to define a closed geometric surface whose dimensions change regularly with change in the physical state of the system under equilibrium conditions. The choice of this surface is not unique. Following Gibbs, we can take it to be the surface whose tension satisfies the condition (for spherical surfaces):

$$P^{(1)} - P^{(2)} = \frac{2\sigma}{r}. \qquad (3)$$

Having defined the geometric surface and mentally extended to this surface the external phase with all its macroscopic properties, we obtain certain excesses (from the side of the external phase) of extensive properties and relate these to the separating surface. If we now combine the separating surface with the total mass inside it, we obtain a complex which can be called the nucleus of the new phase (in the broad sense). Thus the mental operation involves the replacement of a real system consisting of two phases and a surface layer, or of a surface layer and an external phase (if an internal phase as such does not exist), by two substances — a nucleus and a medium — with a clearly-defined boundary between them.

As already noted, macro-phase properties were originally attributed to the nuclei. While rejecting this mechanistic viewpoint, we can retain its rational core and assume that the nucleus exists in equilibrium within itself. This makes it possible to use (possibly in a quasi-thermodynamic sense) the fundamental equation characterising the state of internal equilibrium for the complex being considered:

$$A d\sigma - V^{(1)} dP^{(1)} + S^{(1)} dT^{(1)} + \sum_i m_i^{(1)} d\mu_i^{(1)} = 0, \qquad (4)$$

where A is the area of the tension surface and the superscript (1) indicates that the quantity refers to the nucleus. It should be remembered that the quantities $S^{(1)}$ and $m_i^{(1)}$ by definition, include not only the entropy and masses of the components inside the volume $V^{(1)}$ but also the excesses of these quantities from the external phase side. Thus when $V^{(1)}$ and A become zero, $S^{(1)}$ and $m_i^{(1)}$ still retain finite values.

Eqn. (4) does not include any assumptions regarding the equilibrium between the nucleus and the medium, and can be used to characterise nuclei of any dimensions. For crystalline nuclei the quantities σ and r should be understood in accordance with the expressions

$$\sigma \equiv \frac{1}{A}\left(\sum_j \sigma_j A_j + \sum_k \tau_k l_k\right) \qquad (5)$$

and

$$r \equiv \frac{3V^{(1)}}{A}, \qquad (6)$$

where σ_j and A_j are the surface tension and area of the j-th face, and τ_k and l_k the linear tension and length of the k-th edge. The concept of a surface of tension also retains its meaning in this case [45].

4. CALCULATION OF THE WORK OF FORMATION OF A NEW PHASE BY MEANS OF THERMODYNAMIC POTENTIALS

The calculation of the work of formation of new phases plays an extremely important part in the theory of phase processes. In the first place, a knowledge of this quantity makes it possible to reach conclusions regarding the statistical distribution with respect to dimensions of nuclei, produced by fluctuations:

$$n = n_0 e^{-\frac{W}{kT}}, \qquad (7)$$

where n is the number of nuclei of given dimensions and n_0 is a slowly-changing function of W. In the second place, a knowledge of the maximal work of formation of the nucleus is necessary in order to establish the kinetics of the phase change. This quantity, together with the activation energy of the diffusion process Q, appears in the familiar kinetic equation

$$J = Ne^{-\frac{W+Q}{kT}}, \qquad (8)$$

where J is the rate of production of new phase and N a slight function of W.

The magnitude of the work of formation of the new phase depends on the mechanism of the process and the conditions under which it takes place. Two mechanisms are usually distinguished: homogeneous (spontaneous), when the nucleation of the new phase takes place in the bulk of the old phase, and heterogeneous, when this process takes place at the phase boundary.

Thermodynamic calculation [3,13] has shown that the work expended in the formation of an equilibrium nucleus by a heterogeneous mechanism is less than that for a homogeneous mechanism, and on this basis Volmer [3] concluded that heterogeneous processes predominate greatly in natural and laboratory conditions. Later studies showed that the homogeneous formation of new phases also plays an important part. In particular, it was found that not all heterogeneous impurities can act as centres for condensation or crystallisation [9,34], so that the presence of foreign particles in a system does not provide proof of a heterogeneous phase-change mechanism.

Moreover, observation of the crystallisation of small drops established the existence of supersaturations much greater than those for large masses. Thus drops of water with dimensions of 1–20 μm could be supercooled to

-40°,[11,46-50] whereas supercooling in a large mass of water did not even reach -20°. High supersaturations were observed for drops of organic liquids[50] and, more particularly, for metals[8,51,52]. For example, drops of Au with dimensions 10–15 μm can be supercooled by 230 deg, whereas the supercooling for a large mass amounts to only 2–3 deg; drops of Pt can be supercooled by 370 deg, etc. On the basis of these data it was concluded that the nucleation of new phases in finely-divided substances takes place by a homogeneous mechanism[8,11,52,53]. Thus it must be assumed that both phase-change mechanisms are of practical importance and thus deserve detailed study.

An extremely convenient (but not unique) method for finding the work of formation of new phases under different conditions involves the use of thermodynamic potentials. Of these, the five most familiar are: the energy U, enthalpy H, free energy F, Gibbs thermodynamic potential Φ, and potential Ω. For homogeneous systems the change in each of these potentials under definite conditions gives the magnitude of the "useful" work W:

$$W = \Delta U \text{ for constant } S,\ V,\ m_1,\ m_2,\ \ldots. \quad (9)$$
$$W = \Delta H \text{ for constant } S,\ P,\ m_1,\ m_2,\ \ldots. \quad (10)$$
$$W = \Delta F \text{ for constant } T,\ V,\ m_1,\ m_2,\ \ldots. \quad (11)$$
$$W = \Delta\Phi \text{ for constant } T,\ P,\ m_1,\ m_2,\ \ldots. \quad (12)$$
$$W = \Delta\Omega \text{ for constant } T,\ V,\ \mu_1,\ \mu_2,\ \ldots. \quad (13)$$

Since U, F, and Ω are defined in similar fashion for homogeneous and heterogeneous systems, expressions (9), (11), and (13) can also be applied without reservation to the processes of new-phase formation. Expressions (10) and (12) are applicable with the condition that the pressure in the system is constant, and it is known that this condition is not fulfilled for microheterogeneous systems. These expressions can also be used to calculate the work of formation of a nucleus, however, only if the external pressure is assumed to be constant and the corresponding thermodynamic functions for heterogeneous systems are defined in the same way as those used for homogeneous masses (see Section 5 for details).

Gibbs[13] considered the formation of an equilibrium nucleus in an infinite system and showed that the work necessary for this is equal to one-third of the surface energy of the nucleus. In the particular case of a homogeneous process

$$W = \frac{1}{3}\sigma A. \quad (14)$$

In the case of an infinite system, the conditions under which the process takes place are of no importance and any of the expressions (9)–(13) can be used to obtain (14). A difference appears only when the system is assumed to be finite. In practice this means that the volume and mass of the system per nucleus are not too large.

The effect of the conditions under which the process takes place on the work of formation of a new phase are almost independent of its mechanism and we shall examine this effect first of all for the case of homogeneous processes.

5. THE FORMATION OF A NEW PHASE UNDER ISOBARIC-ISOTHERMAL CONDITIONS

Let us consider the particular case of the homogeneous formation of a new phase under conditions of constant external pressure and temperature. In order to calculate the work of the process by Eqn. (12), it is necessary to find the values of the Gibbs potential for the original state, consisting of a homogeneous (metastable or unstable) medium, and the final state, which includes the nucleus and a metastable phase which generally speaking are not in equilibrium with one another. The energies of these two states are determined by the fundamental equations

$$U_{\text{hom}} = TS - PV + \sum_i \mu_i m_i \quad (15)$$

and

$$U_{\text{het}} = TS - P^{(1)}V^{(1)} - P^{(2)}V^{(2)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}. \quad (16)$$

The Gibbs potential for the initial stage is by definition

$$\Phi_{\text{hom}} \equiv U_{\text{hom}} - TS + PV = \sum_i \mu_i m_i. \quad (17)$$

In exactly the same way it is necessary to determine this potential for the final state by putting P equal to the pressure of the external phase $P^{(2)}$:

$$\Phi_{\text{het}} \equiv U_{\text{het}} - TS + P^{(2)}V = (P^{(2)} - P^{(1)})V^{(1)} + \sigma A + \sum_i m_i^{(1)}\mu_i^{(1)} + \sum_i m_i^{(2)}\mu_i^{(2)}. \quad (18)$$

This definition is contrary to that generally accepted ($\Phi = \sum_i \mu_i m_i$), but without it expression (12) cannot be used.

The quantities $\mu_i^{(1)}$ and $\mu_i^{(2)}$ are equal in the case of equilibrium, but in any case they relate to different pressures $P^{(1)}$ and $P^{(2)}$. If we reduce $\mu_i^{(1)}$ to the value at $P^{(2)}$ using the formula

$$\mu_i^{(1)}(P^{(1)}) \simeq \mu_i^{(1)}(P^{(2)}) + v_i^{(1)}(P^{(1)} - P^{(2)}), \quad (19)$$

where $v_i^{(1)}$ is the partial molar volume of the i-th component in the new phase, Eqn. (18) acquires the shorter form

$$\Phi_{\text{het}} \simeq \sigma A + \sum_i m_i^{(1)}\mu_i^{(1)}(P^{(2)}) + \sum_i m_i^{(2)}\mu_i^{(2)}, \quad (20)$$

which has been used by Frenkel'[35] and many others. The disadvantages of this form are its approximate character and the fact that it contains the arbitrary quantity $\mu_i^{(1)}(P^{(2)})$.

Subtracting (17) from (18) and taking account of the conservation of mass ($m_i = m_i^{(1)} + m_i^{(2)}$), we obtain the work of formation of a nucleus under isobaric-isothermal conditions:

$$\Delta\Phi = (P^{(2)} - P^{(1)})V^{(1)} + \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \quad (21)$$

In order to study the dependence of $\Delta\Phi$ on the size of the nucleus, we differentiate the expression for $\Delta\Phi$, using the Gibbs–Duhem equation and Eqn. (4):

$$d\Delta\Phi = (P^{(2)} - P^{(1)})dV^{(1)} + \sigma dA + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) dm_i^{(1)}. \quad (22)$$

Assuming that $V^{(1)} = \frac{4}{3}\pi r^3$ and $A = 4\pi r^2$, we can readily show that when equilibrium conditions are established — chemical potentials equal and condition (3) satisfied — the expression (22) becomes zero. Substituting the same conditions in (21), we obtain the limiting value of $\Delta\Phi$, corresponding to the formation of a nucleus in equilibrium with the medium:

$$\Delta\Phi_0 = \frac{1}{3}\sigma A + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \quad (23)$$

The difference $\mu_i^{(2)} - \mu_i$ shows the change in the chemical potentials during the formation of the nucleus. For an infinite system this difference is equal to zero and (23) reduces to the Gibbs formula (14).

In order to establish the type of extremum, we evaluate the second differential of $\Delta\Phi$, again taking account of (4):

$$(d^2\Delta\Phi)_0 = -8\pi\sigma(dr)^2 + \left[d\sigma\, dA - dP^{(1)}dV^{(1)} + \sum_i d\mu_i^{(1)}dm_i^{(1)}\right] + \left[\sum_i d\mu_i^{(2)}dm_i^{(2)}\right]. \quad (24)$$

The result obtained does not lead so obviously to a maximum as is generally assumed. Since allowance is made for the individual properties of the nucleus and the finite dimensions of the system, expression (24) contains, in addition to the first term, which is clearly negative, two further terms, in square brackets. The second of these, in accordance with condition (2) for constant T and P, is always positive, since the phase in equilibrium with the nucleus is stable (metastable). In analogous fashion the sign of the first term in square brackets characterises the internal stability of the nucleus: if the nucleus is stable, this term is positive, otherwise it is negative.

If the system is sufficiently large, so that the formation of a nucleus has almost no influence on its state, the second term in (23) and the third in (24) are very small. The fact that a maximum value of $\Delta\Phi$ exists then follows from Eqn. (23) itself, so that expression (24) should be negative and hence if the second term in (24) is also positive it should have an absolute magnitude which does not exceed that of the first term.

Thus analysis of (24) shows that the possibility of a positive sign for this expression and of a corresponding minimum value for $\Delta\Phi$ arises only when the absolute magnitude of the third term is sufficiently high. This is conceivable, in the first place, for relatively small systems, and in the second place only for multicomponent systems.

In the case of a one-component system, constant values of the external pressure and temperature correspond at the same time to a constant value for the chemical potential of the substance in the two phases, and (23) acquires the simpler form:

$$\Delta\Phi_0 = \frac{1}{3}\sigma A. \quad (25)$$

According to (25), the work of formation of an equilibrium nucleus is always positive and increases with increase in its dimensions. The upper limit of $\Delta\Phi_0$ is reached for almost complete conversion of the original mass into the new phase (if the quantity σ is to retain its significance, it may be assumed that the maximal amount of new phase formed is still surrounded by a film of the old phase, necessary for equilibrium). If the system is infinite, there is no upper limit for $\Delta\Phi_0$ ($\Delta\Phi_0 \to \infty$ as $r \to \infty$). The lower limit is reached when A becomes zero, so that the work of formation of the equilibrium nucleus also becomes equal to zero ($\Delta\Phi_0 \to 0$ as $r \to 0$). This should evidently correspond to limiting supersaturation.

6. LIMITING SUPERSATURATION

In the literature on the formation of new phases, extensive use is made of the Kelvin, Thomson, and Ostwald–Freundlich relationships which characterise the equilibrium between small particles and a medium. Kelvin's formula describes the change in vapour pressure for isothermal curvature of the surface:

$$\ln\frac{P^{(2)}}{P_\infty^{(2)}} = \frac{2\sigma v^{(1)}}{rRT}, \quad (26)$$

where $P_\infty^{(2)}$ and $P^{(2)}$ are the pressures above planar and curved surfaces respectively and $v^{(1)}$ is the molar volume of the internal phase.

The Ostwald–Freundlich equation gives an analogous relationship for the change in solubility:

$$\ln\frac{x^{(2)}}{x_\infty^{(2)}} = \frac{2\sigma v^{(1)}}{rRT}, \quad (27)$$

where $x_\infty^{(2)}$ and $x^{(2)}$ are the solubilities of the substance in solution above planar and curved surfaces respectively.

Thomson's equation for isobaric superheating or supercooling ΔT with curvature of a planar surface has a slightly different form

$$\frac{\Delta T}{T} = \frac{2\sigma v^{(1)}}{rL}, \quad (28)$$

where L is the heat of the phase change.

All three equations are used to examine the phenomena of condensation and crystallisation in order to calculate the dimensions of the equilibrium nucleus for a given supersaturation and, in the final analysis, to calculate the work of formation of the nucleus. It follows from Eqns. (26)–(28) that the limiting supersaturation, corresponding to the condition $r = 0$, is infinite and hence unattainable. This conclusion clearly contradicts general thermodynamic theories of the finite nature of the metastable range and also experimental data, according to which a phase change is observed when a certain finite supersaturation is reached.

Several suggestions have been made in order to explain this contradiction. In the first place, Ostwald pointed out that the experimentally observed critical supersaturation is not the limiting supersaturation, but corresponds to an increase in the rate of phase transformation to an experimentally-observable value, which does not provide proof for the finite character of the limiting supersaturation. Nevertheless at the present time it is assumed that the limiting supersaturation is finite. Some authors suggest that the limiting supersaturation corresponds to the minimal possible dimensions of the new phase (elementary crystallites [54,55], minimal molecular associates [35]) and, on the basis of these minimal dimensions, they calculate the magnitude of the limiting supersaturation from Eqns. (26)–(28). [35,56,57] On the other hand, it is pointed out that Eqns. (26)–(28) lose their validity when the values of r reached are so small that thermodynamic consideration of the particle becomes unjustified. On the basis of this viewpoint, it is assumed that the limit of applicability of the Ostwald–Freundlich equation corresponds to the dimensions of colloidal particles (50 mμm), which also correspond to limiting supersaturation [58]. According to Rodebush [59,60], Kelvin's equation can have a meaning only when $r > 10^{-7}$ cm, not only because the surface tension for smaller dimensions is not constant, but also because, for smaller dimensions of the molecular aggregates, the vapour pressure of the drop as such does not exist, since these very small molecular aggregates themselves begin to play a significant part in the establishment of the equilibrium pressure.

Thus most authors relate the limiting supersaturation to a finite value of r. In some cases, it is true, this value is assumed to be very small, and it is usually considered that the dimensions of the minimal nucleus coincide with the dimensions of a single molecule [61]. Calculations carried out from formulae (26)–(28) lead to a higher value of r, corresponding to the presence of several [56] or several dozen [62,63] molecules in the nucleus.

The conclusion regarding a finite minimum value of r, although contrary to general thermodynamic theories of the limit of stability to continuous changes, is quite understandable from the molecular viewpoint. Moreover, this conclusion agrees with experimental data on the finite nature of limiting supersaturation and in principle does not contradict Eqns. (26)–(28). When these equations are used, however, two features are generally overlooked.

In the first place, Eqns. (26)–(28) are approximate relationships, applicable only for large values of r (strictly, for a low degree of curvature of the planar surface). When the surface is curved, the limit of applicability of these equations is reached earlier than the limit of applicability of thermodynamics in general, so that the limit of applicability of Eqns. (26)–(28) must be determined not from general molecular considerations but from an analysis of the equations themselves and the assumptions on which their derivation is based.

In the second place, the quantity r in Eqns. (26)–(28) characterises not the actual dimensions of the new phase but the dimensions of a geometric figure bounded on all sides by a surface of tension. At high values of r, the difference between the positions of the physical and geometric surfaces is negligibly small, since the surface of tension lies inside the surface layer. At small values of r, comparable with the thickness of the surface layer, this difference becomes appreciable and cannot be neglected. At the moment when the surface of tension disappears ($r = 0$), there still exists a microheterogeneity corresponding to a definite molecular complex. Thus the condition $r = 0$ is quite conceivable and physically real, so that rigorous thermodynamic equations should include this limiting case.

Rigorous thermodynamic analysis of curved surfaces [30] shows that for precise equations describing the dependence of the parameters of thermodynamic equilibrium on the curvature of the surface, two limiting cases can be considered: for large and small values of r. In the first case ($r \to \infty$) the precise thermodynamic equations become the Kelvin, Thomson, and Ostwald–Freundlich relationships, and in the second case ($r \to 0$) they acquire a different form.

Let us consider as an example the differential thermodynamic equation [30] describing the change in the vapour pressure for drops having very small dimensions:

$$\left(\frac{dp^{(2)}}{dr}\right)_T \simeq -\frac{\sigma A}{m^{(A)} r\,(v^{(2)} - v^{(A)})}, \qquad (29)$$

where $m^{(A)}$ and $v^{(A)}$ are the mass and molar volumes of the surface layer, $v^{(2)}$ is the molar volume of the vapour, and $A = 4\pi r^2$. The surface tension approaches zero proportionately with the radius of curvature [30], so that with decrease in r the numerator of the right-hand side of (29) approaches zero as a quantity of the third order of smallness. Since the mass of the surface layer at the moment when the surface of tension disappears is not yet zero, the denominator of the right-hand side of (29) approaches zero as a quantity of the first order of smallness. Thus from (29) we have

$$\lim_{r \to 0} \left(\frac{dp^{(2)}}{dr}\right)_T = 0. \qquad (30)$$

The same result is obtained if we assume that the surface tension is constant and equal to its value at the boundary of the macro-phases.

Condition (30) implies that the state where r becomes zero corresponds to a finite limiting supersaturation P_0/P_∞ (Fig. 2), and this agrees completely with experiment and with the thermodynamic theory of the boundary of stability. It can be seen from Fig. 2 that the increase in vapour pressure with decrease in the radius of curvature is described satisfactorily by Kelvin's equation up to a certain limit, after which the curves corresponding to Kelvin's equation and the precise thermodynamic equation diverge sharply. This takes place when the quantity r becomes commensurate with the thickness of the surface layer.

An interesting feature is that the dimensions of the physical heterogeneity at the moment when the surface of tension disappears ($r = 0$) are also close to the thickness of the surface layer, so that the calculations of the size of the minimal nucleus, carried out from Kelvin's formula [56,63], may sometimes give a result close to the true value. In actual fact, use of the value of the limiting supersaturation P_0/P_∞ and Kelvin's equation gives the radius r_0 (Fig. 2). If this radius is close to the limit where the continuous and broken curves in Fig. 2 diverge (in other words, if the continuous curve approximates sufficiently accurately to the broken curve when $r > r_0$ and to the horizontal line when $r < r_0$), r_0 is close to the thickness of the surface layer and hence close to the dimensions of the microheterogeneity corresponding to the condition $r = 0$. We cannot, however, be sure that the value of r_0 calculated from Eqns. (26)–(28) will always give a correct value for the minimal critical dimensions of the nucleus, for when this occurs a correct result will be due to "mutual cancellation" of two errors: the assumption that Eqns. (26)–(28) are applicable in the range of small values of r and the assumption that the quantity r coincides with the dimensions of the physical heterogeneity.

Since the surface of tension disappears with retention of the microheterogeneity, it is of interest to examine the result obtained using another geometric surface, which was also derived by Gibbs and corresponds to the case where the surface excess Γ of a substance in a one-component system becomes zero. This surface exists so long as the smallest heterogeneity is present [30].

Using the symbols σ' and r' to denote the surface tension and radius of curvature corresponding to the surface $\Gamma = 0$, we can write an expression for the work of formation of an equilibrium nucleus as follows [20,21]:

$$W = \frac{4}{3}\pi (r')^2 \left(\sigma' - r' \frac{d\sigma'}{dr'}\right). \qquad (31)$$

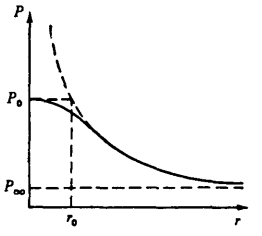


Fig. 2. Dependence of the equilibrium vapour pressure on the radius of curvature of the surface of tension according to Kelvin's equation and the precise thermodynamic equation.

From expression (31) it was concluded[64,65] that zero work of formation of a nucleus corresponds to the condition

$$\frac{\sigma'}{r'} = \frac{d\sigma'}{dr'}, \qquad (32)$$

and to a nucleus of finite dimensions. This conclusion was contrasted[65] with Gibbs' theory, which leads to formula (14). If, however, we bear in mind the difference between the geometric surfaces used in the derivation of relationships (31) and (14), it can readily be seen that the latter are quite adequate. The quantity σ' should in actual fact satisfy Kondo's equation

$$\sigma' = \frac{\sigma r^2}{3(r')^2} + \frac{1}{3} r' (P^{(1)} - P^{(2)}), \qquad (33)$$

where the quantities without primes, as before, relate to the surface of tension. From (33) we obtain

$$\frac{\sigma'}{r'} - \frac{d\sigma'}{dr'} = \frac{\sigma r^2}{(r')^3} > 0, \qquad (34)$$

from which it follows that condition (32) cannot be satisfied at finite values of r and is observed only when $r = 0$, in complete agreement with Gibbs' theory. Finally, substitution of (34) in (31) leads to the Gibbs formula (14).

Thus the work of formation of an equilibrium nucleus is found to be independent of the choice of geometric surface and equal, under the conditions considered, to one-third of the product of the area of the surface of tension and its surface tension. The fact that the work of formation of a nucleus becomes equal to zero when the surface of tension, and not any other surface, disappears, emphasises once again the physical significance of this important concept.

We have still to determine whether the use of the surface $\Gamma = 0$ is necessary in the range of small values of r', when the surface of tension no longer exists. Formally, the surface $\Gamma = 0$ can be found for molecular aggregates of any degree of smallness: even dimers, in which the distances between the molecules are less than the average distance between the molecules in a large mass, should exhibit definite "surface excesses" of substance. The use of these concepts in the range of very small values of r' is questionable, however. In addition to the fact that the thermodynamic method is here crossing the boundary of its applicability, we are also faced with the question of whether these systems can be regarded as heterogeneous. Any homogeneous phase is characterised by the presence of a whole series of molecular complexes in equilibrium with one another (monomers, dimers, trimers, etc.) and it is generally assumed[35,59] that there exists a definite minimal dimension for a new formation, at which it can be regarded as a deviation from homogeneity. If we define this minimal dimension as that corresponding to the disappearance of the surface of tension, it becomes unnecessary to consider the formation of new phases beyond the limit of existence of the surface of tension.

From all that has been said in the present Section, it follows that the limiting supersaturation is finite and corresponds to the state where the radius of curvature of the surface of tension becomes zero; the use of the surface of tension in the thermodynamics of microheterogeneous systems makes it possible to combine the theories of macro- and micro-heterogeneous equilibria into a single logical system and to define clearly the boundary between homogeneous and heterogeneous states.

7. THE FORMATION OF A NEW PHASE UNDER ISOCHORIC-ISOTHERMAL CONDITIONS

The isobaric-isothermal process conditions examined above assume that the formation of a new phase does not lead to a change in the mechanical state of the surrounding medium, although it may be accompanied by a change in composition. In practice this means that the whole system is under a constant external pressure (for example, atmospheric) and that the rate of attainment of mechanical equilibrium between the external part of the system and the immediate surroundings of the nucleus is very much greater than the rate of formation of the nucleus. These two conditions are not always satisfied. As pointed out by Frenkel'[35], the formation of a nucleus of liquid in a crystal may be accompanied by an increase in pressure and deformation of the crystal in the region adjoining the nucleus. The condensation of vapour in a closed vessel is also accompanied by a change in pressure.

In order to allow for the change in the mechanical state of the medium when a new phase is formed, we shall assume, as before, that the process takes place isothermally, but we shall replace the constant-pressure condition by the constant-volume condition. The work of formation of a new phase under isochoric-isothermal conditions is found from (11) as the difference in the free energies of the final and initial states of the process. For the initial state we have

$$F_{\text{hom}} = -PV + \sum_i \mu_i m_i \qquad (35)$$

and for the final state

$$F_{\text{het}} = -P^{(1)}V^{(1)} - P^{(2)}V^{(2)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}, \qquad (36)$$

where $V^{(1)} + V^{(2)} = V$ and $m_i^{(1)} + m_i^{(2)} = m_i$.

Thus

$$\Delta F = F_{\text{het}} - F_{\text{hom}} =$$
$$= (P^{(2)} - P^{(1)}) V^{(1)} + (P - P^{(2)}) V +$$
$$+ \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \qquad (37)$$

It is interesting to compare the work of the isobaric-isothermal and isochoric-isothermal processes leading to the same final state. From (21) and (37) we have

$$\Delta\Phi - \Delta F = -(P - P^{(2)}) V + \sum_i \left[\mu_i (P) - \mu_i (P^{(2)})\right] m_i. \qquad (38)$$

If we make use of the expansion

$$\mu_i (P^{(2)}) = \mu_i (P) + v_i (P^{(2)} - P) + \frac{1}{2} \frac{\partial v_i}{\partial P} (P^{(2)} - P)^2 + \ldots, \qquad (39)$$

where v_i is the partial molar volume of the i-th component, we can writen (38) in the form

$$\Delta\Phi - \Delta F \simeq -\frac{1}{2} \left(\frac{\partial V}{\partial P}\right)_T (P^{(2)} - P)^2 > 0, \qquad (40)$$

from which it follows that $\Delta\Phi > \Delta F$, irrespective of the sign of the difference $P^{(2)} - P$. Thus allowance for the change in the mechanical state of the medium during the formation of a nucleus of the new phase leads to a decrease in the work of formation of a nucleus of given dimensions.

By differentiating (37), taking account of the fundamental equation for the nucleus (4), we can readily show that the condition for equilibrium between the medium and the nucleus corresponds to an extremal value of ΔF:

$$\Delta F_0 = \frac{1}{3} \sigma A + (P - P^{(2)}) V + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \qquad (41)$$

The nature of the extremum is determined by the sign of the second differential

$$(d^2\Delta F)_0 = -8\pi\sigma\,(dr)^2 + \left[d\sigma\,dA - dP^{(1)}\,dV^{(1)} + \sum_i d\mu_i^{(1)} dm_i^{(1)}\right] + \left[-dP^{(2)}\,dV^{(2)} + \sum_i d\mu_i^{(2)}\,dm_i^{(2)}\right]. \quad (42)$$

As in the case of isobaric-isothermal conditions, the expression for the second differential of the work of formation of the new phase contains, in addition to the first term, which is clearly negative, two positive terms in square brackets. The first of these characterises the internal stability of the nucleus and the second the internal stability of the medium (metastable phase). The magnitude of the second term in the square brackets is higher, the greater the changes in the state of the medium as a result of growth of the new phase. Under certain conditions, therefore, expression (42) as a whole may become positive and the quantity (41) will correspond not to a maximum but to a minimum of ΔF (that this is in fact the case will be demonstrated in the next Section for the case of the condensation of a vapour). However, if the growth of the nucleus is accompanied by a small change in the state of the medium, expression (42) is negative and (41) corresponds to the maximal work.

Unlike Eqn. (23), expression (41) does not become the Gibbs formula (14), even for one-component systems. It cannot therefore be concluded on the basis of expression (41) that the work of formation of the equilibrium nucleus is always positive and always increases with increase in its dimensions. Only for very large systems, when the change in pressure and chemical potentials can be neglected, does expression (41) approximate to the Gibbs formula (14).

Thus examination of the isochoric-isothermal conditions for a phase change in the general form shows that this case exhibits a number of unique features. For greater clarity we shall reexamine these in the next Section for the case of the condensation of a single-component gas.

8. THE ISOCHORIC-ISOTHERMAL CONDENSATION OF A VAPOUR

One of the characteristic features of an isochoric-isothermal process is that all the substance necessary for the formation of a heterogeneous system of a given volume is from the very beginning concentrated in this volume in the form of a homogeneous mass (in the case of the isobaric process the substance enters the given volume as formation of the new phase proceeds). Thus the initial state of the system may correspond to such a marked degree of supersaturation that it will lie not in the metastable but in the unstable range. It is clear that the use of the ideal-gas and ideal-solution equations in this case is impossible in principle, since these equations relate to stable phases. The final state of the system always corresponds to a metastable state of the medium and is not necessarily characterised by high supersaturation. The use of the ideal-gas and ideal-solution equations here becomes possible in principle, and we can consider merely the corrections, if these are sufficiently large.

To take a specific example, let us consider the isochoric-isothermal condensation of a vapour and estimate firstly the magnitude of the third term in (42), which characterises the stability of the final (metastable) state of the vapour in equilibrium with drops of liquid. In the solution of this problem we can assume that the vapour is ideal.

For a one-component ideal gas, this term is equal to

$$-dP^{(2)}\,dV^{(2)} + d\mu^{(2)}\,dm^{(2)} = m^{(2)}RT\,(d\ln P^{(2)})^2 = m^{(2)}RT\left(\frac{d\ln P^{(2)}}{dr}\right)^2 (dr)^2, \quad (43)$$

and its relative role in (42) depends on the way in which the coefficient preceding $(dr)^2$ changes with growth of the new phase. Using the relationships $P^{(2)} = m^{(2)}RT/V^{(2)}$, $m = m^{(1)} + m^{(2)}$, and $V = V^{(1)} + V^{(2)}$, we obtain

$$m^{(2)}RT\left(\frac{d\ln P^{(2)}}{dr}\right)^2 = m^{(2)}RT\left(\frac{4\pi r^2}{V^{(2)}} - \frac{1}{m^{(2)}}\frac{dm^{(1)}}{dr}\right)^2. \quad (44)$$

The value of r cannot exceed a certain maximal possible value r_{max} corresponding to total conversion of the material into the liquid state. It is evident that as $r \to r_{max}$, $m^{(2)}$ approaches zero and the coefficient preceding $(dr)^2$ increases without limit. If the dimensions of the new phase are sufficiently large, this coefficient becomes greater than $8\pi\sigma$ and stable equilibrium will be observed.

The change from unstable to stable equilibrium between the drop and vapour should be accompanied by a decrease in the work of its formation and hence the curve giving the dependence of ΔF_0 on r should show a maximal value of ΔF_0 which is positive (Fig. 3). The curve in Fig. 3 should not be confused with the usual curves giving the dependence of the work of formation of a non-equilibrium nucleus on its size, where the maximum corresponds to the formation of an equilibrium nucleus: in this case only equilibrium quantities are plotted on the axes.

The form of the dependence of ΔF_0 on r (Fig. 3) can readily be explained by a graphical method. To determine the points on the graph corresponding to equilibrium between the drop and the vapour, two relationships must be known: (1) the dependence of the equilibrium vapour pressure on the drop size (this relationship is shown in Fig. 2) and (2) the dependence of the vapour pressure on the drop size in a given system with mechanical transfer of substance from the vapour to the liquid. The second relationship is not concerned with the equilibrium but is related to the fact that since the total volume of the system and the difference between the densities of the phases are constant, the change in the volume $V^{(2)}$ associated with the vapour and the change in the mass of the vapour $m^{(2)}$ with growth of the liquid phase occur at different rates.

Let us assume that the gas obeys the van der Waals' equation and occupies a certain volume V. As the gas is converted into liquid its pressure P will change as follows:

$$\frac{dP^{(2)}}{dr} = \left[-\frac{RT}{(v^{(2)}-b)^2} + \frac{2a}{(v^{(2)})^3}\right]\frac{dv^{(2)}}{dr}, \quad (45)$$

where the molar volume of the vapour $v^{(2)} \equiv V^{(2)}/m^{(2)} = (V - V^{(1)})/(m - m^{(1)})$ also depends on the value of r:

$$\frac{dv^{(2)}}{dr} = -\frac{4\pi r^2}{m^{(2)}} - \frac{V^{(2)}}{(m^{(2)})^2}\frac{dm^{(1)}}{dr}. \quad (46)$$

To establish the shape of the $P^{(2)}(r)$ curve, it is sufficient to consider two limiting cases. In the first, when

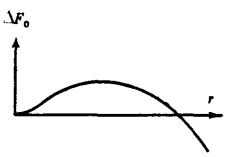


Fig. 3. Influence of the equilibrium dimensions of the new phase on the work of the isochoric-isothermal process.

$r \to 0$, the right-hand side of (46), and with it the right-hand side of (45), approach zero. At the same time $P^{(2)}$ becomes equal to the initial pressure P. The other limiting case corresponds to complete conversion of vapour into liquid, when $m^{(1)}$, $V^{(1)}$, and r reach their maximal values, and $m^{(2)}$ and $P^{(2)}$ become zero. In this case $v^{(2)}$ and the right-hand side of (46) increase without limit, but the right-hand side of (45) remains a finite negative quantity. From this it follows that the curve describing the change in pressure when the substance is converted from vapour into liquid should be concave towards the r axis (Fig. 4). The limiting slope α of this curve is greater, the higher the initial pressure P.

With the curves given in Figs. 2 and 4 we can consider all possible cases of equilibrium, since they are defined on the graph giving the dependence of $P^{(2)}$ on r by the points of intersection of these curves. Fig. 5 gives examples of their mutual disposition.

The case a ($P \leq P_\infty$) corresponds to unsaturated or, in the limit, saturated vapour. The curves do not intersect and equilibrium (if the liquid is conceived as a spherical drop) is impossible.

The case c ($P_0 > P > P_\infty$) corresponds to initial supersaturation of the vapour within the limits of the metastable range. Since the curve in Fig. 2 for a great part of its length is concave, and the curve in Fig. 4 convex towards the r axis, they must intersect in two points (A and B). It can readily be seen that one of these points (point A) corresponds to unstable equilibrium and the other (point B) to stable equilibrium. In actual fact, if it is assumed that the radius of a drop existing initially in state A increased accidentally, the equilibrium vapour pressure of the drop, in accordance with Fig. 5, curve c, will be less than the pressure in the surrounding medium and the drop will continue to grow. On the other hand, with an accidental decrease in the dimensions of the drop, its equilibrium pressure increases to a greater extent than the pressure in the surrounding medium and the drop will volatilise — the equilibrium is unstable. At the point B on the other hand, an accidental change in the dimensions of the drop leads to a ratio between the equilibrium vapour pressure and the pressure in the surrounding medium which restores the drop to its original dimensions — the equilibrium is completely stable.

Thus a given value of P corresponds not to one but to two equilibrium states: the first of these is unstable and corresponds to the Gibbs–Volmer nuclei, while the second is stable and corresponds to particles of large dimensions.

An intermediate case between a and c is case b, where the curves merely touch. The equilibrium corresponding to this case is stable with respect to condensation and unstable with respect to volatilisation. An interesting feature is that on going from a to c the dimensions of the Gibbs–Volmer nuclei and the stable new formations may be as close to one another as desired. Case b corresponds to the maximal work of formation of the equilibrium nucleus (maximum in Fig. 3). With increase in the initial supersaturation, the work of formation of both the unstable and stable drops decreases.

Case e in Fig. 5 corresponds to a high initial supersaturation, which brings the vapour into an unstable state. The curves intersect only once, corresponding to the formation of a fairly large stable drop. When the initial state becomes unstable, the shape of the initial section (at small values of r) of the curve in Fig. 4 may change in such a way that a maximum value of $P^{(2)}$ is produced. This cannot, however, influence the conclusion that the final state is unique and stable. The work of formation of a new phase in case e is negative and the process of phase change takes place at a high rate.

An intermediate case between c and e is case d, where the initial supersaturation of the vapour corresponds to the boundary of stability relative to continuous changes. In case d the dimensions of the unstable equilibrium nucleus and its work of formation are equal to zero.

This examination confirms the relationships shown in Fig. 3. To make the picture of the change in ΔF during the formation of a new phase more complete, we have given curves (Fig. 6) describing the formation of non-equilibrium nuclei and larger drops for different initial conditions (for cases a, b, c, d, and e examined above). The extremal points on these curves correspond to equilibrium states.

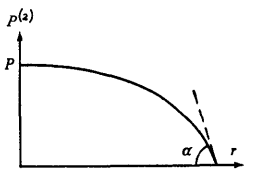


Fig. 4. Change in vapour pressure as the substance is converted from the vapour into the condensed phase under isochoric conditions.

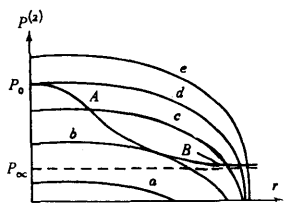


Fig. 5. Possible cases of equilibrium for the isochoric-isothermal condensation of vapour.

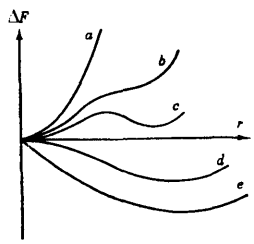


Fig. 6. Change in ΔF with change in the dimensions of the new phase for different initial supersaturations.

From Fig. 6, as from Fig. 3, it can be seen that in a certain range of dimensions the formation of stable drops takes place with expenditure of work (as does the formation of unstable equilibrium nuclei) so that the state of these drops is metastable with respect to the initial state. The probability of volatilisation of these drops is still fairly high. True stable states will correspond to greater supersaturation, which need not reach the boundaries of stability of the vapour.

The qualitative examination carried out in the present section can readily be extended to subliming crystals, by taking account of relationships (5) and (6). Since the shape of the solubility curve is the same as that of the curve in Fig. 2, an analogous discussion can be extended to the processes of crystallisation from solutions.

9. THE FORMATION OF A NEW PHASE UNDER ISOBARIC-ISENTROPIC CONDITIONS

Up to the present, in accordance with the general pattern, we have assumed that the process of new-phase formation is isothermal. In other words, we have assumed that the whole system is immersed in a thermostat at constant temperature and that the rates of attainment of thermal equilibrium between the system and thermostat, and between the nucleus and the medium, are very much greater than the rate of formation of the new phase. It cannot be assumed that these conditions are always satisfied[66] and it is necessary to discuss the changes in the thermodynamic formulae, introduced by departure from these conditions in finite systems.

If the system is thermally isolated, the process of new-phase formation will take place adiabatically. Thermodynamically, however, it is more convenient to deal with the isentropic process, since this makes it possible to use expressions (9) and (10) to calculate the work of formation of the new phase. The two types of process coincide only for reversible changes and the assumption that the entropy is constant generally assumes some heat exchange between the system and external bodies. It is possible that this assumption corresponds more closely to actual conditions than the assumption that thermal isolation is complete.

Let us assume in the present section that the formation of a new phase takes place at constant total entropy of the system S and external pressure $P^{(2)}$. The work of formation of the new phase under these conditions is found from formula (10). For the initial state we have

$$H_{\text{hom}} = TS + \sum_i \mu_i m_i, \tag{47}$$

and for the final state

$$H_{\text{het}} = T^{(1)} S^{(1)} + T^{(2)} S^{(2)} + (P^{(2)} - P^{(1)}) V^{(1)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}, \tag{48}$$

where T is the initial temperature of the system and $T^{(1)}$, $S^{(1)}$ and $T^{(2)}$, $S^{(2)}$ are the final temperatures and entropies of the nucleus and medium respectively.

Subtracting (47) from (48) and making allowance for the fact that the total entropy and masses of the components are constant, we obtain

$$\Delta H = (T^{(1)} - T^{(2)}) S^{(1)} + (T^{(2)} - T) S + (P^{(2)} - P^{(1)}) V^{(1)} + \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \tag{49}$$

Expression (49) gives the work of formation of a new phase with volume $V^{(1)}$, component masses $m_i^{(1)}$, and entropy $S^{(1)}$ for an isobaric-isentropic process. It can readily be shown that the first differential of this expression becomes zero when equilibrium conditions are reached, namely, equality of temperatures and chemical potentials and fulfilment of condition (3). Substituting the same conditions in (49), we find the extremal value of the work of formation of the new phase:

$$\Delta H_0 = \frac{1}{3}\sigma A + (T^{(2)} - T) S + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \tag{50}$$

This relationship differs from the Gibbs relationship (14) in that it contains additional terms which take account of the change in the thermal and chemical states of the system during the formation of the new phase. For a very large system these terms are small and the two relationships almost coincide.

It is of interest to compare the work of formation of an equilibrium nucleus of given dimensions, carried out isentropically with change in the temperature of the system from T to $T^{(2)}$, with the corresponding quantity for the isothermal process at temperature $T^{(2)}$. From (50) and (23) we have

$$\Delta\Phi_0 - \Delta H_0 = -(T^{(2)} - T) S - \sum_i \left[\mu_i (T^{(2)}) - \mu_i (T)\right] m_i. \tag{51}$$

By making use of the expansion

$$\mu_i (T^{(2)}) = \mu_i (T) - s_i (T^{(2)} - T) - \frac{1}{2}\frac{\partial s_i}{\partial T}(T^{(2)} - T)^2 - \dots, \tag{52}$$

where s_i is the partial molar entropy of the i-th component in the initial state of the system, we can write (51) in the following approximate form:

$$\Delta\Phi_0 - \Delta H_0 \simeq \frac{1}{2}\left(\frac{\partial S}{\partial T}\right)_P (T^{(2)} - T)^2 > 0. \tag{53}$$

It follows from expression (53) that the correction for non-isothermal character in the process, like the correction for non-isobaric character, leads to a decrease in the magnitude of the work of formation of an equilibrium nucleus of given dimensions.

To study the nature of the extremal value of ΔH, corresponding to the equilibrium state of the new phase, we use Eqn. (4) and the equilibrium condition to find the second differential of ΔH:

$$(d^2\Delta H)_0 = -8\pi\sigma (dr)^2 + \left[dT^{(1)} dS^{(1)} - dP^{(1)} dV^{(1)} + d\sigma\, dA + \sum_i d\mu_i^{(1)} dm_i^{(1)}\right] + \left[dT^{(2)} dS^{(2)} + \sum_i d\mu_i^{(2)} dm_i^{(2)}\right]. \tag{54}$$

This relationship differs from the analogous relationships (24) and (42) in that it contains additions terms $dT^{(1)} dS^{(1)}$ and $dT^{(2)} dS^{(2)}$ which take account of the possibility of change in the thermal state of the nucleus and medium. The term $dP^{(2)} dV^{(2)}$, as in the case of (24), does not appear, since the pressure $P^{(2)}$ is assumed to be constant. We have represented the right-hand side of (54) in the form of three terms, the first of which is clearly negative, while the other two in the square brackets are positive for stable states. The first of the terms in the square brackets characterises the internal stability of the nucleus of the new phase and the second the internal stability of the metastable phase. For the case where growth of the nucleus is not reflected in the state of the medium, the second term is equal to zero — like the additional terms on the right-hand side of (50) — and there is a maximum value of ΔH for the formation of the equilibrium nucleus, in complete

accordance with Volmer's theory. If, however, growth of the nucleus is accompanied by a marked change in the state of the medium, the second term may acquire sufficiently high positive values to make the whole of the right-hand side of (54) positive. This corresponds to stable equilibrium between the new phase and the medium, characterised by a minimum value of ΔH.

To illustrate this possibility, let us estimate the magnitude of the last term for an ideal gas. Using the expressions for the entropy and chemical potential of an ideal gas (assumed to be monatomic)

$$S^{(2)} = \frac{5}{2} m^{(2)} R \ln T^{(2)} + m^{(2)} f(P^{(2)}), \quad (55)$$

$$\mu^{(2)} = \frac{5}{2} RT^{(2)} - \frac{5}{2} RT^{(2)} \ln T^{(2)} - T^{(2)} f(P^{(2)}), \quad (56)$$

we obtain

$$dT^{(2)} dS^{(2)} + d\mu^{(2)} dm^{(2)} = \frac{5}{2} m^{(2)} RT^{(2)} (d \ln T^{(2)})^2 = \frac{5}{2} m^{(2)} RT^{(2)} \left(\frac{d \ln T^{(2)}}{dr}\right)^2 (dr)^2. \quad (57)$$

Using the equation of state for an ideal gas $m^{(2)} RT^{(2)} = P^{(2)} V^{(2)}$ and the condition that the mass of the system $m_i = m^{(1)} + m^{(2)}$ is constant, we can express the result obtained in the form

$$\frac{5}{2} m^{(2)} RT^{(2)} \left(\frac{d \ln T^{(2)}}{dr}\right)^2 = \frac{5}{2} m^{(2)} RT^{(2)} \left(\frac{d \ln V^{(2)}}{dr} + \frac{1}{m^{(2)}} \frac{dm^{(1)}}{dr}\right)^2. \quad (58)$$

The derivative $d \ln V^{(2)}/dr$ cannot be expressed in explicit form as was previously done for the derivative $d \ln P^{(2)}/dr$ in formula (44), since the total volume of the system in this case is variable. From expression (58), as from expression (44), however, it follows that the magnitude of the whole expression increases without limit with decrease in $m^{(2)}$. This result is physically understandable, since with a relative increase in the mass of the new phase its influence on the state of the medium will continue to increase. When the new-phase range reaches definite dimensions, the magnitude of (58) exceeds $8\pi\sigma$ and the equilibrium becomes stable.

Thus examination of isobaric-isentropic processes reveals qualitatively the same regular features as in the case of isochoric-isothermal conditions: the work of formation of a new phase becomes less than the work under isobaric-isothermal conditions; with increase in the equilibrium dimensions of the new phase, the work of its formation ΔH_0 at first increases and then decreases, entering the range of negative values; relatively small ranges of new phase (nuclei) correspond to unstable equilibria with the medium, whereas relatively large ranges correspond to stable equilibrium.

10. THE FORMATION OF A NEW PHASE UNDER ISOCHORIC-ISENTROPIC CONDITIONS

Abandoning conditions of constant temperature and pressure, let us assume that the process of new-phase formation takes place under isochoric-isentropic conditions. This is the most general of all the cases considered, since it assumes a change in the chemical, thermal, and mechanical state of the system during the formation and growth of the new phase.

The work of formation of a new phase under isochoric--isentropic conditions is found from formula (9). For the initial homogeneous state of the system we have

$$U_{\text{hom}} = TS - PV + \sum_i \mu_i m_i. \quad (59)$$

and for the final heterogeneous state

$$U_{\text{het}} = T^{(1)} S^{(1)} + T^{(2)} S^{(2)} - P^{(1)} V^{(1)} - P^{(2)} V^{(2)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}. \quad (60)$$

Taking account of the fact that the total entropy, total volume, and component masses are constant, we obtain from (60) and (59) an expression for the work of formation of the new phase

$$\Delta U = (T^{(1)} - T^{(2)}) S^{(1)} + (T^{(2)} - T) S + (P^{(2)} - P^{(1)}) V^{(1)} + (P - P^{(2)}) V + \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \quad (61)$$

For the equilibrium state of the heterogeneous system

$$\Delta U_0 = \frac{1}{3} \sigma A + (T^{(2)} - T) S + (P - P^{(2)}) V + \sum (\mu_i^{(2)} - \mu_i) m_i. \quad (62)$$

This result differs from the Gibbs formula (14) in that it contains additional terms which take account of the change in the thermal, mechanical, and chemical state of the system during the formation of the new phase. For an infinitely large system these terms are equal to zero and (62) becomes (14).

Allowance for the changes in the thermal and mechanical states of the system during the formation of the new phase was made separately in sections 9 and 7, and we saw that these two changes act in the same direction, decreasing the work of formation of the new phase with increase in its dimensions. We can therefore be sure that a simultaneous change in the thermal and mechanical state of the system will have an influence in the same direction, so that the dependence of ΔU_0 on the dimensions of the new phase will be characterised by the same qualitative relationships as the dependence of ΔF_0 and ΔH_0 on these dimensions. Moreover, the simultaneous action of factors decreasing the work of formation of the new phase will apparently cause the quantity ΔU_0 to be smaller than the corresponding quantities $\Delta \Phi_0$, ΔF_0, and ΔH_0.

11. THE HETEROGENEOUS FORMATION OF NEW PHASES

In examining the influence of the imposed conditions on the work of formation of a new phase, we have until now assumed that the formation of the new phase is brought about by a homogeneous mechanism. Let us now consider the heterogeneous mechanism.

Gibbs[13] obtained the following expression for the work of formation of an equilibrium lenticular mass (*1*) at the planar boundary between two infinitely-extended phases (*2*) and (*3*) (Fig. 7):

$$W = \frac{1}{3} (\sigma_{12} A_{12} + \sigma_{13} A_{13} - \sigma_{23} A_{23}), \quad (63)$$

where σ_{12}, σ_{13}, and σ_{23} are the surface tensions at the boundaries between the first and second, first and third,

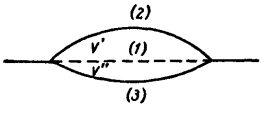


Fig. 7. Formation of a lenticular mass at a planar boundary between two phases.

and second and third phases respectively, A_{12} and A_{13} the areas of contact between the lens and the second and third phases respectively, and A_{23} is that part of the area of contact between the second and third phases which disappears when the lens is formed (broken line in Fig. 7). Gibbs' expression (63) is a generalisation of his formula (14) for the case of a heterogeneous process. This expression can be written in the slightly different form

$$W = \frac{\sigma_{12} V'}{r_{12}} + \frac{\sigma_{13} V''}{r_{13}}. \qquad (64)$$

where V' and V'' are the volumes of the second and third phases replaced by the new phase ($V' + V'' = V^{(1)}$), and r_{12} and r_{13} the radii of curvature of the surfaces of the lenticular mass.

If the formation of the new phase takes place on the planar surface of a solid (Fig. 8), the second term on the right-hand side of (64) disappears and the magnitude of the work will be determined by the relationship

$$W = \frac{\sigma_{12} V^{(1)}}{r_{12}}. \qquad (65)$$

It can readily be seen that formula (14) can be brought to exactly the same form, and we can equate directly the work of the heterogeneous process and the work of the homogeneous process, both for a given radius of curvature of the nucleus and for a given nucleus volume. For nuclei with identical radii of curvature (the surface tensions in this case will also be identical) with a contact angle of wetting $\theta < 180°$, the volume of the heterogeneous nucleus amounts to only a fraction of the volume of the homogeneous nucleus and hence the work of the heterogeneous process will be less than that of the homogeneous process. In the comparison of nuclei of equal volume, allowance must be made for the change in the surface tension with the radius of curvature of the surface. If it is assumed that at small values of r the surface tension depends linearly on r,[30] there is no difference between the work of the heterogeneous process and that of the homogeneous process in the range of small values of r and large values of θ. Since for equal volumes a heterogeneous nucleus has small curvature, however, the heterogeneous process will correspond to a lower supersaturation. With increase in the wettability of the surface of the solid, the work of the heterogeneous formation of the nucleus decreases, and at values of θ close to zero it is necessary to take account of the perimeter energy of the now almost two-dimensional nucleus.

For given values of the wetting angle θ and the curvature of the nucleus at its boundary with the liquid or gaseous phase, the change from a planar to a convex solid surface corresponds to an increase in the volume of the nucleus; the change from a planar to a concave surface corresponds to a decrease in the volume of the nucleus (Fig. 8). On the basis of expression (65) (although the latter is not now rigorous), it may be concluded that the change from a planar to a convex surface leads to an increase, and the change from a planar to a concave surface to a decrease, in the work of the heterogeneous formation of the new phase.

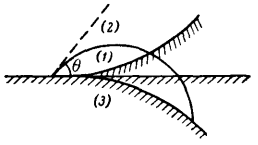


Fig. 8. Formation of a new phase on the surface of a solid.

A particular case is the heterogeneous formation of an equilibrium nucleus in the form of a closed layer on a condensation or crystallisation nucleus. The magnitude of the work of this process is given by the expression

$$W = \sigma_{12}\left(A_{12} - A_{13}\cos\theta - \frac{2V^{(1)}}{r_{12}}\right). \qquad (66)$$

If the equilibrium nucleus and the condensation or crystallisation nucleus are spherical, this expression becomes Krystanov's formula[67,68]:

$$W = \frac{1}{3}\sigma_{12} A_{12}\left[1 - 3\left(\frac{r_{13}}{r_{12}}\right)^2 \cos\theta + 2\left(\frac{r_{13}}{r_{12}}\right)^3\right]. \qquad (67)$$

Analysis of this formula shows[67] that in the range of wetting angles $0 \leqslant \theta \leqslant 48°12'$ the work of the heterogeneous formation of an equilibrium nucleus is always less than the work of the homogeneous process. In the range $48°12' < \theta < 90°$, there exists for each value of θ a critical magnitude of the condensation or crystallisation nucleus from which the work of the heterogeneous process exceeds the work of the homogeneous process. Finally, at $\theta \geqslant 90°$ the work of the heterogeneous formation of the nucleus is always greater than the work of the homogeneous process.

Formulae (63)–(65) are applicable for finite systems only if the process of new-phase formation takes place at constant pressure, temperature, and chemical potentials and hence at constant surface tension. These formulae make no allowance for change in the thermal, mechanical, and chemical state of the system during the formation of the new phase and assume that these changes are compensated by the action of external forces. This does not always correspond to real conditions and it is necessary to discuss the corrections which must be introduced into formula (63) when different process conditions are considered.

Let us assume that the production of a new phase at a plane interface takes place under isochoric-isentropic conditions. A characteristic feature of a heterogeneous process is that the initial and final states of the system are heterogeneous and both exhibit surface energy. For the initial equilibrium state we can write

$$U'_{het} = TS - PV + \sigma'_{23} A'_{23} + \sum_i \mu_i m_i, \qquad (68)$$

where σ'_{23} and A'_{23} are the surface tension and area of the interface in the initial state (Fig. 7). For the final state, which does not necessarily correspond to equilibrium between the new phase and the rest of the system, we have

$$U''_{het} = T^{(1)}S^{(1)} + T^{(2)}(S - S^{(1)}) - P^{(1)}V^{(1)} - P^{2}(V - V^{(1)}) + \\ + \sigma_{12}A_{12} + \sigma_{13}A_{13} + \sigma''_{23}A''_{23} + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)}(m_i - m_i^{(1)}), \qquad (69)$$

where σ''_{23} and A''_{23} are the surface tension and area of the interface between the initial phases and the final state. By definition, $A_{23} = A'_{23} - A''_{23}$. Subtracting (68) from (69), we obtain

$$\Delta U = (T^{(1)} - T^{(2)})S^{(1)} + (T^{(2)} - T)S + (P^{(2)} - P^{(1)})V^{(1)} + (P - P^{(2)})V + \sigma_{12}A_{12} + \\ + \sigma_{13}A_{13} + \sigma''_{23}A''_{23} - \sigma'_{23}A'_{23} + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \qquad (70)$$

Expression (70) gives the work of formation of a new phase at the boundary between the two phases under isochoric-isentropic conditions. Comparison with Eqn. (61)

shows that the corrections for the change in pressure, temperature, and chemical potentials in the system with the formation of the new phase are of the same form as in the case of the homogeneous process.

For the equilibrium state, expression (70) can be converted into the form

$$\Delta U_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (T^{(2)} - T)S + \\ + (P - P^{(2)})V + (\sigma''_{23} - \sigma'_{23})A'_{23} + \sum_i (\mu_i^{(2)} - \mu_i)m_i. \quad (71)$$

Relationship (71) exhibits two characteristics which distinguish it from the analogous relationship (62) for the work of the homogeneous formation of a new phase. Firstly, on going from (62) to (71), the first term becomes more complicated, but this does not change in physical significance; as before, it is one-third of the work of formation and disappearance of the interface. Secondly, on going from (62) to (71) we have an additional term $(\sigma''_{23} - \sigma'_{23})A'_{23}$ characterising the change in the state of the initial interface, which unavoidably accompanies the change in state of the coexisting phases during the formation of the nucleus. The magnitude of this additional term is small and can be neglected in comparison with the other corrections, except for the case where the volumes of the phases are relatively small (for example, when nuclei are formed in films).

Both characteristic features shown by relationship (71) should be preserved for other process conditions, and it is possible to write, without derivation,

$$\Delta H_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (T^{(2)} - T)S + (\sigma'_{23} - \sigma'_{23})A'_{23} + \\ + \sum_i (\mu_i^{(2)} - \mu_i)m_i, \quad (72)$$

$$\Delta F_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (P - P^{(2)})V + (\sigma''_{23} - \sigma'_{23})A'_{23} + \\ + \sum_i (\mu_i^{(2)} - \mu_i)m_i, \quad (73)$$

$$\Delta\Phi_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (\sigma''_{23} - \sigma'_{23})A'_{23} + \sum_i (\mu_i^{(2)} - \mu_i)m_i. \quad (74)$$

The corrections distinguishing relationships (71)–(74) from the Gibbs formula (63), with the exception of the correction (usually small) for surface tension, are the same as those for homogeneous processes. Thus the conclusions regarding the influence of process conditions on the magnitude of the work of formation of a new phase, reached for the case of homogeneous processes, remain completely applicable to heterogeneous processes and special analysis of expressions (71)–(74) is unnecessary.

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It follows from the foregoing that the work of formation of new phases in real systems can be represented as the sum of two terms: the Gibbs work $W(r)$, determined by formula (14) or (63) depending on the mechanism of the process, and a correction $\Delta W(V)$, which depends on the dimensions of the system and the process conditions:

$$W = W(r) + \Delta W(V). \quad (75)$$

The introduction of the correction $\Delta W(V)$ makes it possible to follow not only the nucleation but also the growth of the new phase to macroscopic dimensions. This is convenient from the practical viewpoint, since it is then unnecessary to consider the dimensions of the nucleus to which a given formula is applicable. Analysis of relationship (75) leads to the conclusion that during growth, a bubble, drop, or crystallite of new phase passes first through a state of unstable equilibrium corresponding to the Gibbs–Volmer nuclei, after which, when sufficiently large dimensions are reached, it is converted into a state of stable equilibrium.

It should be noted that the conclusion regarding the stability of two-phase equilibrium under certain conditions is applicable for a system consisting of only two bodies, for example, a single drop and vapour. If it is assumed that two drops are present in the same volume, the result is altered significantly. In actual fact, if one of the drops volatilises with a decrease in its dimensions, it is found that although the vapour pressure in the system increases to a greater extent than the equilibrium vapour pressure of this drop (stable equilibrium condition), condensation takes place on the larger drop, leading finally to the disappearance of one of the drops. Thus the conclusion regarding the stability of the final state cannot be extended to systems consisting of many new-phase regions before these are converted into a single region, either by phase change (*via* vapour or solution) or by merging or collision. Nevertheless, this conclusion makes it possible to understand the reasons for the apparent stability of such systems; this stability, like that of polydisperse systems [69], is due to the low rate of attainment of equilibrium between the individual regions of new phase.

It is now of interest to discuss the part which may be played by the correction $\Delta W(V)$ strictly for the nuclei of the new phase. Usually the volume per nucleus in real systems is fairly large compared with the dimensions of the nucleus, and there is no doubt that Gibbs' assumption regarding the infinite nature of the system is applicable in this respect. Even if we make allowance for the change in surface tension for small radii of curvature and assume that $W(r)$ is a quantity not of the second but of the third order of smallness, the changes which may be produced by the formation of a nucleus in the fraction of the volume of the system corresponding to this nucleus lead only to a small correction $\Delta W(V)$.

These arguments, however, like the Gibbs theory, assume that in spite of the large magnitude of the system, equilibrium in it is established almost instantaneously, so that the whole system reacts with the nucleus formed. This is not always the case. In most cases the nucleus "succeeds" in reacting only with its immediate environment, so that the actual volume of the nucleus–medium system is much less than the volume per nucleus. The magnitude of the correction $\Delta W(V)$ in this case increases significantly.

The actual volume of the nucleus–medium system and the magnitude of the correction $\Delta W(V)$ depend on the rate of formation of the nucleus and the factors determining the rate of attainment of equilibrium, the coefficients of diffusion and self-diffusion, thermal conductivity, and the elastic properties of the medium. The relative part played by these factors differs for different processes. For example, the rate of diffusion plays an important part in condensation and crystallisation processes, particularly with mixtures. For processes involving fusion and the formation of drops of liquid in crystals, an important part is played by the mechanical factor associated with the deformation of the crystal in the region adjoining the drop. The correction $\Delta W(V)$ arising in this case may be fairly large and this possibly explains the almost complete absence of superheating in fusion processes.

Finally, one further important point should be noted. According to the above calculations, $\Delta W(V)$ is negative. In order to understand this result, it is necessary to remember that it is obtained by comparison of work values leading to the same final state. For infinite systems the initial and final supersaturations coincide. For finite systems the initial supersaturation is always greater than the final. Thus the formation of an equilibrium nucleus of given dimensions in a finite system requires a higher initial supersaturation than in the case of an infinite system, so that the process of new-phase formation in a finite system takes place more readily, with a lower expenditure of work.

If, however, we compare processes relating to the same initial state, the final states may correspond to a high activation energy, since for a given initial supersaturation the finite system corresponds to larger equilibrium-nucleus dimensions than does the infinite system. If the work of formation of a nucleus is calculated from the Gibbs formula for a given initial supersaturation, correction for the finite character of the system Q will give the expression

$$Q = W(r) + \Delta W(V) - W(r_0), \qquad (76)$$

where r_0 and r are determined from the equilibrium curve (for example, from the curve in Fig. 2) for the initial and final supersaturations respectively. For small values of $\Delta W(V)$, Q is always positive, since $r > r_0$.

Thus the thermodynamics of processes of new-phase formation leads to a kinetic equation having the form of (8), where Q involves not only diffusion but also the thermal conductivity and elastic properties of the medium.

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