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Thermodynamic Investigations of Nucleation in Binary Finite Systems

A thermodynamic analysis of a two-phase system may lead to a deeper insight into the conditions of a first order phase transition /1/. The knowledge of the exact thermodynamic potential of the system allows us to calculate the critical and stable cluster size for a phase transition /2/, furthermore, critical thermodynamic constraints for a nucleation process in an one-component finite system are determined /2,3/.

Former investigations gave a general thermodynamic analysis of a heterogeneous k-component system considering the change of the initial matrix phase by the formation of the new phase /2, 4,5/. These results have been applied mainly to nucleation and cluster growth in one-component systems /6/, but also the kinetics of condensation in binary vapours /7/, the decomposition of solid solutions /6/, and Ostwald ripening of bubbles in liquid-gas solutions /8/ have been discussed based on a thermodynamic approach.

This paper continues the thermodynamic analysis. As done before, we consider the limitation of the total particle number of the system, that means a matrix depletion caused by the formation of clusters of a new phase.

1. Thermodynamics of a heterogeneous binary system

For a homogeneous binary system the inner energy is usually given by:

$$U_{hom} = TS - pV + \mu_1 n_1 + \mu_2 n_2 \tag{1.1}$$

In the heterogeneous state we have two phases α and β , which are divided by a boundary phase, indicated by the index o. The inner energy of the heterogeneous system is then given by /9/:

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$$U_{het} = U_\alpha + U_\beta + U_o \qquad (1.2)$$

with the contributions

$$U_\alpha = T_\alpha S_\alpha - p_\alpha V_\alpha + \mu_{1\alpha} n_{1\alpha} + \mu_{2\alpha} n_{2\alpha} \qquad (1.3)$$

$$U_\beta = T_\beta S_\beta - p_\beta V_\beta + \mu_{1\beta} n_{1\beta} + \mu_{2\beta} n_{2\beta} \qquad (1.4)$$

$$U_o = T_o S_o + \mu_{1o} n_{1o} + \mu_{2o} n_{2o} + \sigma A \qquad (1.5)$$

The boundary phase is here assumed to be the Gibbsian surface of tension /9/, σ being the surface tension and A the surface area. n_{io} and S_o denote excess values caused by deviations from additivity in the heterogeneous state:

$$n_{io} = n_i - n_{i\alpha} - n_{i\beta} \qquad i = 1,2 \qquad (1.6)$$

$$S_o = S - S_\alpha - S_\beta \qquad (1.7)$$

Formally n_{io}, S_o can be interpreted as thermodynamic values of the surface. For the surface energy U_o (eq. 1.5) the Gibbs-Duhem relation is valid:

$$S_o dT_o + A d\sigma + n_{1o} d\mu_{1o} + n_{2o} d\mu_{2o} = 0 \qquad (1.8)$$

For a former discussion of the surface part we use the condition of an internal equilibrium of both phases α and β /4,10/, that means an inner equilibrium and a quasi-stationary change of these states. Because a surface phase has no real autonomy in general/11/, we are allowed to replace the intensive variables of the surface by the corresponding values of one of the coexisting phases α or β . It seems to be reasonable that the phase with a larger density should determine the surface values T_o and μ_{io} /4/. We denote in the following the matrix phase by β and the evolving phase by α and assume further α to be the phase with a higher density (like in gas-liquid phase transitions).

Eq. (1.8) is then replaced by /4,12/:

$$-d\sigma = s_o dT_\alpha + \Gamma_{1o} d\mu_{1\alpha} + \Gamma_{2o} d\mu_2 \qquad (1.9)$$

with Γ_{io} being the surface particle densities and s_o the surface entropy density:

$$\Gamma_{io} = \frac{n_{io}}{A} \quad , \quad i = 1,2 \qquad s_o = \frac{S_o}{A} \qquad (1.10)$$

Considering a heterogeneous system established by a nucleation process eq. (1.9) means that the surface tension σ should be determined by the quantities describing the evolving phase α. In particular we find for the surface tension dependent on the temperature T_α and on the mole fraction x_α of the nucleus:

$$\frac{\partial \sigma}{\partial T_\alpha} = - s_o - \sum_{i=1}^{2} \Gamma_{io} \frac{\partial \mu_{i\alpha}}{\partial T_\alpha} \qquad (1.11)$$

$$\frac{\partial \sigma}{\partial x_\alpha} = - \sum_{i=1}^{2} \Gamma_{io} \frac{\partial \mu_{i\alpha}}{\partial x_\alpha} \qquad (1.12)$$

Consequently, the usual approximation $n_{io} \simeq 0$ results in a dependence of σ on the temperature only, but no longer on the molar fraction of the nucleus.

In the following we restrict ourselves to isothermal systems, that means $T_\alpha = T_\beta = T$, and fix the thermodynamic constraints as follows:

$$n = \text{const.}, \; V = \text{const.}, \; T = \text{const.} \qquad (1.13)$$

Now the free energy $F = U - TS$ is the thermodynamic potential to describe the heterogeneous system. We calculate the change of the free energy for a transition from the initial homogeneous to the final heterogeneous system:

$$\Delta F = F_{het} - F_{hom} \qquad (1.14)$$

With the restrictions

$$\begin{aligned} n_i &= n_{i\alpha} + n_{i\beta} + n_{io} \quad , \quad i = 1,2 \\ V &= V_\alpha + V_\beta \end{aligned} \qquad (1.15)$$

and the notation $\tilde{n}_{i\alpha} = n_{i\alpha} + n_{io}$ we find for ΔF using eqs. (1.1)-(1.5) /4,5/:

$$\Delta F = (p_\beta - p_\alpha) V_\alpha + \sigma A + \sum_{i=1}^{2} (\mu_{i\alpha} - \mu_{i\beta}) \tilde{n}_{i\alpha}$$

$$+ (p - p_\beta) V + \sum_{i=1}^{2} (\mu_{i\beta} - \mu_i) n_i \qquad (1.16)$$

ΔF (eq. 1.16) is known to be the reversible work of formation of a nucleus in a initially homogeneous binary system. The terms $(p-p_\beta)$ and $(\mu_{i\beta}-\mu_i)$ consider the change of the medium by the formation of the nucleus which is a typical effect for finite systems /2,4/.

The consistency with Gibbs' thermodynamics requires that the surface area of the nucleus is unambiguously defined by the volume of the α-phase: $A = A(V_\alpha)$. Calculating the equilibrium states from the extremum condition $d\Delta F = 0$ we find therefore the three conditions:

$$\mu_{i\alpha} = \mu_{i\beta} \qquad i = 1,2 \tag{1.17}$$

$$p_\alpha - p_\beta = \sigma \frac{dA}{dV_\alpha} \tag{1.18}$$

It has been shown in a general thermodynamic analysis /5,13/ that the equilibrium states, determined by eqs. (1.17), (1.18), should be either states corresponding to a stable coexistence of the nucleus and the surrounding matrix phase leading to a minimum of the free energy, or unstable equilibrium states of a saddle-point type.

2. Work of formation for an incompressible binary cluster

In order to calculate the work of formation of the cluster and the equilibrium conditions we now make use of the common approximation of an incompressible spherical cluster /14/. For this case an additional relation between the volume and the mole numbers of the nucleus exists:

$$V_\alpha = \frac{4\pi}{3} r_\alpha^3 = v_{1\alpha} n_{1\alpha} + v_{2\alpha} n_{2\alpha} \tag{2.1}$$

Since we assume an nearly ideal mixture of both components (no volume mixing effects), the specific molar volumes $v_{i\alpha}$ of the two components in the nucleus are expressed by the values for the pure components $v^0_{i\alpha}$. Furthermore, for spherical clusters it yields $\partial A / \partial V_\alpha = 2\sigma / r_\alpha$, r_α being the cluster radius.

The chemical potential of the α-phase generally depends on the pressure p_α , the molar fraction $x_{i\alpha}$ of the i-th component in the nucleus and the temperature. A Taylor expansion of $\mu_{i\alpha}$

valid for sufficiently large clusters leads to:

$$\mu_{i\alpha}(p_\alpha,x_\alpha,T) = \mu_{i\alpha}(p_\beta,x_\alpha,T) + \left.\frac{\partial\mu_{i\alpha}}{\partial p_\alpha}\right|_{p_\alpha=p_\beta}[p_\alpha - p_\beta]+\dots \qquad (2.2)$$

Neglecting derivatives of the second order and considering $\left(\frac{\partial\mu_{i\alpha}}{\partial p_\alpha}\right)_{T,x_\alpha}\approx v^0_{i\alpha}$ the work of cluster formation (eq. 1.16) with respect to eqs. (2.1), (2.2) is now obtained as follows:

$$\Delta F = \sum_{i=1}^{2} (\mu_{i\alpha}(p_\beta,x_{i\alpha},T)-\mu_{i\beta}(p_\beta,x_{i\beta},T)+\frac{3\sigma}{r_\alpha}v^0_{i\alpha})n_{i\alpha}$$

$$+ (p-p_\beta)V + \sum_{i=1}^{2} (\mu_{i\beta}(p_\beta,x_{i\beta},T)-\mu_i(p,x_i,T))n_i \qquad (2.3)$$

Because of the additional condition (eq. 2.1) we find now from the extremum condition $d\Delta F = 0$ two instead of three equilibrium conditions for the binary heterogeneous system, given by:

$$\mu_{i\alpha}(p_\beta,X_\alpha,T)-\mu_{i\beta}(p_\beta,x_\beta,T)+\frac{2\sigma}{r_\alpha}v^0_{i\alpha} = 0 \quad i=1,2 \qquad (2.4)$$

Finally, we want to specify the chemical potentials of both phases for a particular heterogeneous system. As mentioned before the nucleus should represent an incompressible binary liquid phase, while the surrounding matrix phase is given by a binary ideal vapour. Thus it yields /12/:

$$\mu_{i\alpha}(p_\alpha,X_{i\alpha},T) = \mu_{i\alpha}(p_{oi},T)+v^0_{i\alpha}(p_\beta-p_{oi})+RT\ln(x_{i\alpha}f_{i\alpha}) \qquad (2.5)$$

$$\mu_{i\beta}(p_\beta,x_{i\beta},T) = \mu_{i\beta}(p_{oi},T)+RT\ln\frac{p_\beta}{p_{oi}} + RT\ln x_{i\beta} \qquad (2.6)$$

p_{oi} is chosen to be the partial saturation pressure of component i over a flat binary liquid surface. $x_{i\alpha}$ and $x_{i\beta}$ are the molar fractions of components i in the α- or the β-phase. In a binary system it yields $x_{2\alpha} = 1 - x_{1\alpha}$. Moreover, due to the limitation of the total mole number $x_{i\beta}$ is a function of the variables of the nucleus:

$$x_{2\beta} = \frac{n_{2\beta}}{n_\beta} = \frac{nx_2-\tilde{n}_a x_{2\alpha}}{n-\tilde{n}_\alpha}, \quad x_{1\beta} = 1 - x_{2\beta} \qquad (2.7)$$

x_2 means the molar fraction of the initial homogeneous state: $x_2 = n_2/n$, $x_1 = 1-x_2$. The $f_{i\alpha}$ are corrections to the mole fraction $x_{i\alpha}$ caused by nonideality effects of the liquid mixture. For ideal mixtures we have $f_{i\alpha} = 1$, but it is easy to consider also symmetrical mixtures and mixtures of the Margules-type using special expressions for the $f_{i\alpha}$ /12/. p_β means the actual vapour pressure in the system. Assuming an ideal vapour we have

$$p_\beta = \frac{n_\beta}{V_\beta} RT = \frac{n-\tilde{n}_\alpha}{V-V_\alpha} RT \tag{2.8}$$

Inserting the expressions for the chemical potentials into eq. (2.4) the equilibrium conditions for a binary heterogeneous system read finally:

$$\ln\frac{p_\beta x_{i\beta}}{p_{oi} x_{i\alpha} f_{i\alpha}} - \frac{v^o_{i\alpha}}{RT}(p_\beta - p_{oi}) = \frac{2\sigma}{r_\alpha}\frac{v^o_{i\alpha}}{RT} \qquad i = 1,2 \tag{2.9}$$

The eqs.(2.9) represent a generalized form of the Kelvin equation known to be the equilibrium condition for an one-component vapour above a curved liquid surface /10,12/. But here the depletion of the vapour caused by the formation of the cluster in the finite system is considered. Because the vapour pressure p_β and the molar fraction x_β both depend on the cluster variables, more than one solution of the system of equations (2.9) should exist for the finite binary system. That means, in addition to the critical cluster state a stable coexistence between both phases should be possible, dependent on the thermodynamic constraints.

3. Work of formation for a cluster in a quasi-binary solution with elastic straints

The given results should be applied, now, to a case of practical importance: the segregation of a pure component within a binary supersaturated solid solution /15,16/. Assuming that only component 2 segregates purely in clusters ($x_\alpha \equiv x_{2\alpha} = 1$) the molar fraction of the matrix is given by

$$x_\beta \equiv x_{2\beta} = \frac{n_{2\beta}}{n_\beta} = \frac{nx-\tilde{n}_\alpha}{n-\tilde{n}_\alpha}, \quad 1-x_\beta \equiv x_{1\beta} \tag{3.1}$$

with $x \equiv n_2/n$. Instead of the constraints (1.13), we consider in the following:

$$n = \text{const.},\ p = \text{const.},\ T = \text{const.} \qquad (3.2)$$

that means that the pressure p_β is always equal to the external pressure p. The thermodynamic potential for the given constraints (3.2) is the free enthalpy G. The work of cluster formation ΔG is found from eq. (2.3) considering $p_\beta = p$:

$$\Delta G = \left(\mu_{2\alpha}(p,x_\alpha,T)-\mu_{2\beta}(p,x_\beta,T)+\frac{3\sigma}{r_\alpha}v^0_{i\alpha}\right)\tilde{n}_{2\alpha} + \sum_{i=1}^{2}\left(\mu_{i\beta}(p,x_{i\beta},T)-\mu_i(p,x_i\ ,T)\right)n_i \qquad (3.3)$$

Replacing now the pressure p = const. by the concentration c = n/V = const. and neglecting a small term of the order $\sim v^0_{2\alpha}\cdot p$ the differences of the chemical potentials can be expressed in accordance with eqs. (2.5), (2.6) by:

$$\mu_{2\alpha} - \mu_{2\beta} \approx - RT \ln \frac{cx_\beta}{c_{2eq}} \qquad (3.4)$$

$$\mu_{1\beta} - \mu_1 = RT \ln \frac{1-x_\beta}{1-x},\quad \mu_{2\beta} - \mu_2 = RT \ln \left(\frac{x_\beta}{x}\right) \qquad (3.5)$$

c_{2eq} means the saturation concentration of component 2 in the matrix which depends on temperature as follows:

$$\frac{1}{c_{2eq}}\ \frac{dc_{2eq}}{dT} = \frac{q}{RT^2} \qquad (3.6)$$

q being the molar solution heat.
Inserting eqs. (3.4), (3.5) in eq. (3.3) we finally arrive at:

$$\frac{\Delta G}{RT} = \left(-\ln\frac{cx_\beta}{c_{2eq}} + \frac{3\sigma}{r_\alpha}v^0_{2\alpha}\right)\tilde{n}_{2\alpha} + \left(x \ln\frac{x_\beta}{x} + (1-x)\ln\frac{(1-x_\beta)}{(1-x)}\right)n \qquad (3.7)$$

Eq. (3.7) takes into account the depletion of component 2 in the matrix due to the cluster formation by the change of x_β compared with x. If this depletion could be neglected as was assumed in the classical approximations, $x_\beta = x$ results and only the first contribution to ΔG (eq. 3.7) remains.

We want to describe in the following the formation of AgCl-clusters in a silver halogenide /natrium borate solution. It should be realistic for this phase transition to consider also elastic strains /15,16/. These strains evolve when the matrix building units (components 1 and 2) change their places with these of the segregating units (component 2) which move to form the cluster, because the components 1 and 2 have a distinct mean molar volume. Assuming a spherical cluster phase α with an elastic modulus E and a Poisson number γ similar to the β-phase, the elastic strains can be described by equations of the Nabarro type /1/, that means the work of cluster formation eq. (3.7) is completed by an additional term

$$\Delta G^{e} = \varepsilon V_{\alpha} = \varepsilon v^{0}_{2\alpha} \tilde{n}_{2\alpha} \qquad (3.8)$$

which reflects the elastic energy, ε being

$$\varepsilon = \frac{E}{9(1-\gamma)} \delta^{2} \quad ; \quad \delta = \frac{\bar{v}_{\beta} - \bar{v}_{\alpha}}{\bar{v}_{\alpha}}$$

$\bar{v}$ stands for the mean molar volume of the considered phase. It yields:

$$\bar{v}_{\alpha} = v^{0}_{2\alpha}$$

$$\bar{v}_{\beta} = \frac{v_{1\beta} n_{1\beta} + v_{2\beta} n_{2\beta}}{n_{1\beta} + n_{2\beta}} = v_{1\beta}(1-x_{\beta}) + v_{2\beta} x_{\beta} \qquad (3.9)$$

Assuming an ideal mixture, the partial molar volumes $v_{i\beta}$ of the β-phase are given by the corresponding values of the pure components, $v^{0}_{i\beta}$, in the β-phase. Further, we note, that the molar fraction of the segregating component is rather small in the considered case, x = 0.02. Therefore we can approximate:

$$\bar{v}_{\beta} \approx v^{0}_{1\beta} \quad ; \quad \delta \approx \frac{v^{0}_{1\beta} - v^{0}_{2\alpha}}{v^{0}_{2\alpha}} \qquad (3.10)$$

The influence of the elastic energy on the work of cluster formation is presented in Fig. 1 by the difference between the curves (b) and (c). It is shown that in the presence of elastic strains the nucleation barrier (maximum of ΔG) increases, fur-

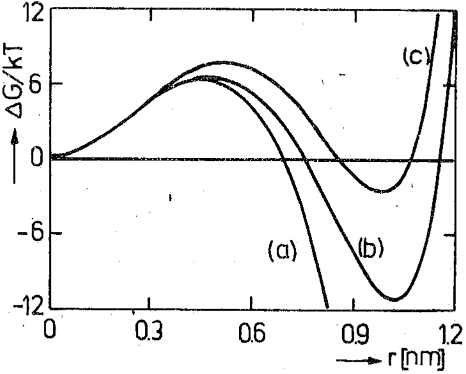

Fig. 1:
Free enthalpy ΔG ($k_B T$) (eq. 3.7) vs. cluster radius r (nm)
(a) neglecting depletion ($x_\beta = x$), (b) considering depletion, (c) considering depletion and elastic strains (eq. 3.8)

The calculation was carried out for a silver halogenide/natrium borate solution, x(AgCl) = 0.02, T = 820 K, $\varepsilon = 7 \cdot 10^7$ N/m^2, total particle number N = 10^4, c = $3{,}48 \cdot 10^4$ mol/m^3

thermore, the critical cluster size increases too, and the stable cluster size indicated by a minimum of ΔG, decreases. The difference between the curves (a) and (b) demonstrates that a stable state is obtained only if the depletion of the segregating particles is considered. In the case $x_\beta = x$ we find only a critical cluster size which is smaller than before, and a lower nucleation barrier.

The influence of the elastic strains on the equilibrium states of the cluster shall be further discussed. By means of the extremum condition $\partial \Delta G / \partial \tilde{n}_{2\alpha} = 0$ we find the equilibrium condition:

$$\ln \frac{c x_\beta}{c_{2eq}(T)} - \varepsilon \frac{v^0_{2\alpha}}{RT} - \frac{2\sigma}{r_\alpha} \frac{v^0_{2\alpha}}{RT} = 0 \qquad (3.11)$$

The value $y = c x_\beta / c_{2eq}$ gives a measure of the actual supersaturation of component 2 in the system. Because x_β depends on r_α (eq. 3.1), we find two solutions of the equilibrium condition in a certain range of the temperature. Fig. 2 demonstrates the influence of the elastic strains on these states. For a given temperature the smaller value of the radius corresponds to the cri-

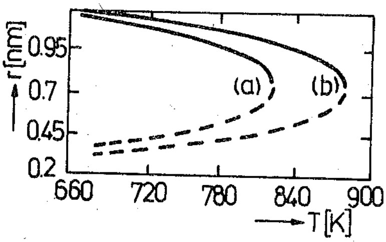

Fig. 2: Critical (---) and stable (——) cluster radius (nm) vs. temperature (K), (a) $\varepsilon = 7\cdot10^7$ N/m^2, (b) $\varepsilon = 0$
T_c is obtained as (a) 824 K, (b) 882 K
For the parameters see Fig. 1.

tical cluster size, while the larger value gives the stable cluster size. It is shown that the elastic strains decrease the stable cluster size and increase the critical cluster size. That means, in the presence of elastic strains the initial supersaturation in the system, given by the ratio cx/c_{2eq}, should be larger to form a cluster of the same critical size as in the case $\varepsilon = 0$.

The intersection of the stable and the critical cluster size for a certain temperature T_c indicates the smallest stable cluster in equilibrium with the surrounding phase. For $T > T_c$ a phase coexistence is thermodynamically impossible, that means for given constrains n = const., x = const., T_c is the upper limit of the temperature where a phase transition can occur in the system. This critical temperature for the phase transition depends on the value of the elastic strains as shown in Fig. 2. T_c becomes considerably smaller in the presence of elastic strains. This fact should be important for the determination of the appropriate values of the thermodynamic constraints for the phase transition in a binary solid solution.

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