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Critical Composition for Nucleation in Quasi-Binary Finite Systems

A first-order phase transition may proceed via homogeneous nucleation only in a certain range of the thermodynamic parameters /1/. From classical nucleation theory, e.g., the existence of a critical supersaturation is known, which must be reached, at least, in an infinite system, to observe the formation of drops /2/.

As was shown in recent investigations in infinite systems we find, in addition, critical system volumes, critical total particle numbers or critical values of the temperatures, different from macroscopic ones, which determine the boundaries in the parameter space, for which homogeneous nucleation may occur /3/. These preceding investigations of critical thermodynamic parameters have been carried out mainly for one-component systems /3, 4/. But also for nucleation in a quasi-binary system the existence of a critical system volume /5/ and a critical temperature (in the foregoing paper /6/) have been discussed.

The investigations are extended now to the calculation of a critical initial composition of the quasi-binary system in dependence on temperature which must be reached at least to allow the formation of supercritical clusters.

1. The free enthalpy of cluster formation in dependence on the molar fraction

The system considered here is a supersaturated solid solution with two components under the thermodynamic constraints

$$n = \text{const.}, p = \text{const.}, T = \text{const.} \quad (1.1)$$

Taking into account  $n = n_1 + n_2$ , we define the molar fraction of the initially homogeneous supersaturated system by  $x = n_2/n$ ,  $n$  being the total mole number of the finite system,  $p$  the ex-

ternal pressure and  $T$  the temperature. The formation of clusters of a new phase results in the evolution of a heterogeneous system, consisting of clusters in the otherwise homogeneous matrix. Parameters, describing the cluster phase are specified further by  $\alpha$ , parameters of the matrix by  $\beta$ .

Assuming, now, in addition, that the cluster is formed only by particles of component 2 (quasi-binary system) ( $x_\alpha = 1$ ) and considering the cluster phase as incompressible ( $v_{2\alpha}^0 = \text{constant}$ ) and of spherical shape, the number of particles in a cluster  $\tilde{n}_{2\alpha}$  can be expressed through the radius  $r_\alpha$  and the molar volume by  $\tilde{n}_{2\alpha} = \frac{4\pi}{3} r_\alpha^3 / v_{2\alpha}^0$ . The medium is considered as an ideal mixture of both components, the molar fraction being defined as

$$x_\beta = \frac{n_{2\beta}}{n_\beta} = \frac{n_2 - \tilde{n}_\alpha}{n - \tilde{n}_\alpha} = \frac{nx - \tilde{n}_\alpha}{n - \tilde{n}_\alpha} \quad (1.2)$$

The work of cluster formation is then given by the change of the free enthalpy connected with the transition from the initially homogeneous to the heterogeneous state. It has been derived in the foregoing paper /6/ as

$$\frac{\Delta G}{RT} = (-\ln \frac{c_{2\beta}}{c_{2\text{eq}}} + \frac{3\sigma}{r_\alpha} v_{2\alpha}^0) \tilde{n}_{2\alpha} + (x \ln \frac{x_\beta}{x} + (1-x) \ln \frac{(1-x_\beta)}{(1-x)}) n \quad (1.3)$$

Here  $c$  is the initial concentration of the total mole number,  $c_{2\text{eq}}$  the saturation concentration of component 2 in the matrix,  $v_{2\alpha}^0$  the molar density of the particles in the cluster,  $\sigma$  the surface tension. The existence of elastic strains resulting from the formation of the cluster in the matrix is not considered here, it leads to an additional contribution to  $\Delta G$  /6,7/.

Fig. 1 presents  $\Delta G$  vs. the cluster radius  $r_\alpha$  for different values of the initial molar fraction  $x$  of the binary system. First we note the existence of a critical cluster size given by a maximum of  $\Delta G$ , and a stable cluster size where the free enthalpy has got a minimum. This stable state is caused by the depletion of the medium due to the cluster formation, because of  $n = \text{const}$ .

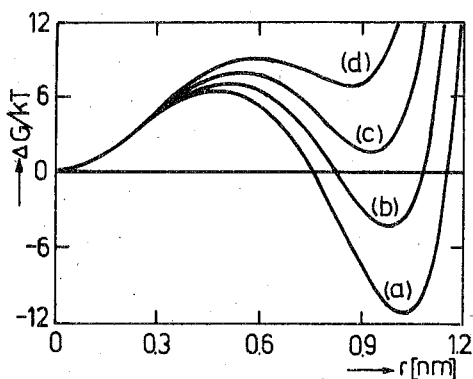


Fig. 1: Free enthalpy  $\Delta G/k_B T$  (eq. 1.3) vs. cluster radius  $r_d$  (nm) (a)  $x = 0.02$ , (b)  $x = 0.019$ , (c)  $x = 0.018$ , (d)  $x = 0.017$ , the calculation was carried out for a silver halogenide/natrium borate solution,  $x = x(\text{AgCl})$ ,  $T = 820 \text{ K}$ ,  $c = 3.48 \cdot 10^4 \text{ mol/m}^3$ , total particle number  $N = 10^4$

The values of the extrema of  $\Delta G$  and the equilibrium cluster sizes both depend on the value of  $x$ . As shown in Fig. 1 we find a critical initial molar fraction  $x_c$  where  $\Delta G$  has no extrema but only a point of inflexion. That means physically that for  $x < x_c$  no supercritical resp. no stable cluster can exist in the system, and a phase separation by nucleation should be impossible from a thermodynamic point of view.

## 2. Equilibrium cluster sizes and critical molar fraction

The dependence of the extremum states on the initial composition  $x$  can be discussed in more detail calculating the equilibrium condition. We find for the first derivative of  $\Delta G$ :

$$\left. \frac{\partial \Delta G}{\partial r_d} \right|_x = -4\pi r_d^2 \left[ \frac{RT}{v_0} \ln \frac{c x_B}{c_{2eq}} - \frac{2\sigma}{r_d} \right] = 0 \quad (2.1)$$

The first solution of eq. (2.1) is given by  $r_d = 0$ , that means we have a stable matrix phase  $\beta$  where no cluster exists.

The critical and the stable cluster sizes can be obtained from the following equilibrium condition:

$$\ln \frac{cx_p}{c_{2eq}} = \frac{2\sigma}{r_d} - \frac{v_2^0}{RT} \quad (2.2)$$

Here the value  $y = cx_p/c_{2eq}$  gives a measure of the actual supersaturation of component 2 in the system. Because  $x_p$  depends on  $r_d$ , eq. (2.2) possesses two solutions for a certain range of thermodynamic constraints. This is demonstrated in Fig. 2 obtained from an iteration of eq. (2.2). For a given value of  $x$  the smaller value for the radius corresponds to the critical cluster size and the larger value to the stable cluster size /2,3/. It is shown that for a critical value  $x_c$  both solutions coincide, and for  $x < x_c$  no solution of the equilibrium condition (2.2) exists. As can be seen from the figure this critical composition itself depends on temperature: for a larger temperature  $x_c$  also has got a larger value. The existence of a lower boundary of  $x$ , for which a decomposition may occur, is known from macroscopic phase diagrams. The important point, which is

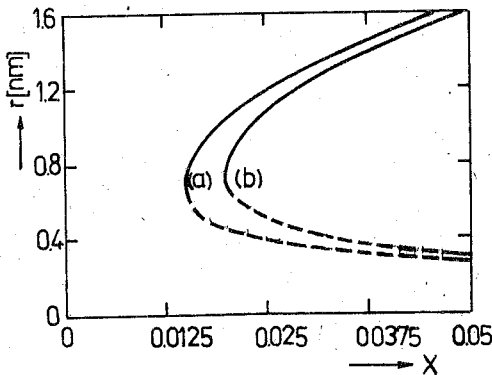


Fig. 2: Critical (---) and stable (—) cluster radius  $r_d$  (nm) vs. initial mole fraction  $x$   
 (a)  $T = 800$  K, (b)  $T = 880$  K  
 $x_c$  is obtained as (a)  $x_c = 0.0148$ , (b)  $x_c = 0.01995$   
 For the parameters see Fig. 1.

to be stressed here, is the deviation of the corresponding value for finite compared with macroscopic systems. This result should be of importance in practical situations, if phase transitions in relatively small cavities are investigated. In the following this effect is studied in more detail.

Inserting  $x_p$  (eq. 1.2) into the equilibrium condition we find:

$$\ln \frac{c}{c_{2eq}} \frac{(nx - \frac{4\pi}{3} \frac{1}{v_{2d}^0} r_d^3)}{(n - \frac{4\pi}{3} \frac{r_d^3}{v_{2d}^0})} - \frac{2\sigma v_{2d}^0}{r_d RT} = 0 \quad (2.3)$$

For the logarithm of eq. (2.3) we use a power expansion neglecting terms of higher than the first order. Then eq. (2.3) can be transformed into an algebraic equation for  $r_d$  /3,8/:

$$r_d^4 + A r_d + B = 0 \quad (2.4)$$

with

$$A = -n(4\pi/3 \cdot v_{2d}^0)^{-1} \left( \frac{x}{1-x} \right) \left( \ln \frac{cx}{c_{2eq}} \right) < 0 \quad (2.5)$$

$$B = n(4\pi/3 \cdot v_{2d}^0)^{-1} \left( \frac{1}{1-x} \right) \left( -\frac{2\sigma v_{2d}^0}{RT} \right) > 0 \quad (2.6)$$

It has been shown analytically /8/ that eq. (2.4) possesses only two positive solutions which depend on the values of the thermodynamic constraints (compare also Fig. 2). These solutions coincide if the relation (2.7) holds

$$\left( \frac{A}{4} \right)^4 = \left( \frac{B}{3} \right)^3 \quad (2.7)$$

Thus eq. (2.7) determines the boundaries in the space of the thermodynamic parameters between thermodynamically stable and metastable states. From eq. (2.7) we find with (2.5), (2.6):

$$n \left( \frac{x}{1-x} \right) \left( \ln \frac{cx}{c_{2eq}(T)} \right)^4 = 4 \left( \frac{4\pi}{3 v_{2d}^0} \right) \left( \frac{4\pi}{3} \frac{2\sigma v_{2d}^0}{RT} \right)^3 = \text{const.}(T) \quad (2.8)$$

Neglecting the dependence of  $\sigma$  on the composition of the matrix, the r.h.s. of eq. (2.8) is only a function of temperature. For a given total particle number  $n$  in the system and a given temperature we can calculate, now, the critical value of  $x$  determined by eq. (2.8) The results are given in Fig. 3 for different va-

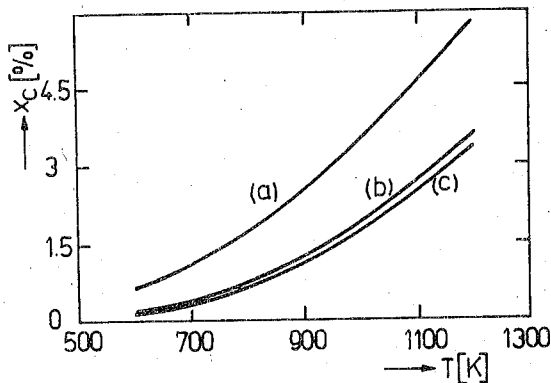


Fig. 3: Critical initial mole fraction  $x_C$  (%) vs. temperature (K), total particle number (a)  $N = 10^4$ , (b)  $N = 10^6$ , (c)  $N > 10^{20}$ .  
For the parameters see Fig. 1.

values of  $n$ . Only for  $x > x_C$  a phase transition via nucleation may occur. It is shown, that for finite systems  $x_C$  increases for a decreasing total mole number, but in the thermodynamic limit  $x_C$  converges into the constant value obtained for the infinite system.

### 3. Temperature dependence of the critical molar fraction

To obtain general analytical results concerning the temperature dependence of the critical value of the initial molar fraction  $x_C$  we apply, now, the theory of implicate functions in an analogous way, as it was done in an analysis of the size dependence of a critical temperature in one-component systems /10/.

As it was discussed in the preceding paragraphs (see, in particular, Fig. 1) the critical value of the molar fraction is given by the conditions (3.1)

$$\left. \frac{\partial \Delta G}{\partial r_2} \right|_{x_C} = \frac{\partial^2 \Delta G}{\partial r_2^2} = 0 \quad (3.1)$$

The first derivative of  $\Delta G$  is given by eq. (2.1). The second derivative can be calculated as follows:

$$\frac{\partial^2 \Delta G}{\partial r_d^2} = -8\pi r_d \left[ \frac{RT}{v_{2d}^0} \ln \frac{cx_B}{c_{2eq}} - \frac{2\sigma}{r_d} \right] - 4\pi r_d^2 \left[ \frac{RT}{v_{2d}^0} \frac{1-x_B}{n_B x_B} (-4\pi r_d^2 / v_{2d}^0) + \frac{2\sigma}{r_d} \right] \quad (3.2)$$

We obtain therefore the following system of equations for the determination of  $x_C$

$$f_1(r_d, n, x, T) = \ln \frac{cx_B}{c_{2eq}} - \frac{2\sigma}{r_d} \frac{v_{2d}^0}{RT} = 0$$

$$f_2(r_d, n, x, T) = -4\pi r_d^3 / v_{2d}^0 \frac{1-x_B}{n_B x_B} + \frac{2\sigma}{r_d} \frac{v_{2d}^0}{RT} = 0 \quad (3.3)$$

For a given value of  $n$  both equations define implicitly a function  $r_d(x, T)$ . Combining these two functions, we find an equation for  $x_C(T)$ . A numerical solution of the system of equations (3.3) is possible, it is equivalent to the results, given in Fig. 2, obtained based on eqs. (2,3) and (2.7).

Based on eqs. (3.3) and the theory of implicate functions we may obtain the following differential equations for the cluster size  $r_d^C$ , corresponding to the point of inflexion, and the critical molar fraction  $x_C$  in dependence on temperature.

$$\frac{dr_d^C}{dT} = -\frac{1}{\Delta} \begin{vmatrix} \frac{\partial f_1}{\partial T} & \frac{\partial f_1}{\partial x} \\ \frac{\partial f_2}{\partial T} & \frac{\partial f_2}{\partial x} \end{vmatrix} \quad (3.4)$$

$$\frac{dx_C}{dT} = -\frac{1}{\Delta} \begin{vmatrix} \frac{\partial f_1}{\partial r_d} & \frac{\partial f_1}{\partial T} \\ \frac{\partial f_2}{\partial r_d} & \frac{\partial f_2}{\partial T} \end{vmatrix} \quad (3.5)$$

with

$$\Delta = \begin{vmatrix} \frac{\partial f_1}{\partial r_d} & \frac{\partial f_1}{\partial x} \\ \frac{\partial f_2}{\partial r_d} & \frac{\partial f_2}{\partial x} \end{vmatrix} \quad (3.6)$$

The partial derivatives of the functions  $f_1$  and  $f_2$  (eqs. 3.3) are calculated approximately, retaining only the dominant terms. Consequently, the possible temperature dependence of  $\bar{v}_2^0$  is neglected,  $c_{2eq}$  is expressed through /11/

$$\frac{1}{c_{2eq}} \frac{\partial c_{2eq}}{\partial T} = \frac{q}{RT^2}$$

$q$  being the molar heat of solution.

This approach yields

$$\frac{\partial f_1}{\partial T} \approx -\frac{q}{RT^2} \quad \frac{\partial f_2}{\partial T} = -\frac{2\bar{v}_2^0}{RT^2} \frac{1}{r_d}$$

$$\frac{\partial f_1}{\partial x} = -\frac{1}{x_p} \frac{n}{n_p} \quad \frac{\partial f_2}{\partial x} = \frac{4\pi r_d^3}{v_{2d}^0 n_p x_p^2}$$

$$\frac{\partial f_1}{\partial r_d} \approx \frac{2\bar{v}_2^0}{RT} \frac{1}{r_d^2} \quad \frac{\partial f_2}{\partial r_d} \approx -\frac{2\bar{v}_2^0}{RT} \frac{1}{r_d}$$

Inserting these derivatives into eqs. (3.5), (3.6) the dependence of the critical molar fraction on temperature can be expressed by

$$\frac{dx^c}{dT} = \frac{n_p x_p^2 \left[ \frac{q}{RT^2} + \frac{2\bar{v}_2^0}{RT^2} \frac{1}{r_d} \right]}{4\pi r_d^3 / v_{2d}^0 + n x_p} \quad (3.7)$$

For a discussion of eq. (3.7) we approximate, finally, the derivative again by the largest terms of the numerator and the denominator and arrive at:

$$\frac{dx^c}{dT} \approx \frac{n_p x_p}{n} \frac{q}{RT^2} \quad (3.8)$$

In agreement with the numerical results presented in Fig. 3 we find that the critical initial molar fraction  $x_c$  increases with an increasing temperature or, in other words, with a decreasing initial supersaturation. The temperature dependence of  $x_c$  can be given also in an alternative form obtained from eq. (3.8)

$$\frac{dx_c}{dT} = \left( \frac{1}{c_{2eq}} \frac{\partial c_{2eq}}{\partial T} \right) \left( \frac{1}{x_p} \frac{\partial x_p}{\partial x} \right)^{-1} \quad (3.9)$$



It means that the most important contributions to the change of  $x_c$  with temperature are the temperature dependence of  $c_{2eq}$  and the dependence of  $x_p$  on  $x$  reflecting the influence of the total number of particles  $n$ .

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The Effect of Elastic Strains and Depletion on Nucleation and Growth in Binary Solutions

As discussed in preceding papers /1,2/ elastic strains quantitatively and qualitatively modify the kinetics of growth of the supercritical clusters and the cluster evolution in the late stage of Ostwald ripening.

In this paper we restrict ourselves mainly to the initial stage of the phase transition including the formation of clusters and their growth up to an overcritical size.

The investigations are based on a thermodynamic analysis presented in the foregoing papers /3,4,5/.

1. Rate equation

We consider a binary system with the thermodynamic constraints

$$n = n_1 + n_2 = \text{const.}, \quad p = \text{const.}, \quad T = \text{const.} \quad (1.1)$$

where  $n$  is the total mole number in the system consisting of two components,  $p$  the external pressure and  $T$  the temperature.

The molar fraction of the initial stage is introduced as  $x = n_2/n$ . In the heterogeneous state the total mole number is divided into the mole number of the cluster phase, denoted by  $n_\alpha$ , and the mole number of the matrix phase indicated by  $n_\beta$ . Assuming as before /4,6,7/, that the clusters are formed only by particles of component 2 it yields  $n_2 = n_{2\beta} + n_\alpha = \text{const.}$  and we may write for the molar fraction of the matrix:

$$x_\beta = \frac{n_{2\beta}}{n_\beta} = \frac{n_2 - n_\alpha}{n - n_\alpha} \quad (1.2)$$

The cluster phase shall be spatially distributed in clusters with the particle number  $j$  ( $j \geq 2$ )

$$n_\alpha = N_A^{-1} \sum_{j=2}^M j N_j, \quad (1.3)$$