

On the Kinetic Description of Condensation in Binary Vapours

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Abstract. Based on a thermodynamic analysis and an earlier developed general growth equation for clusters of a new phase, the kinetics of growth of droplets in a binary gaseous mixture under isothermal and isobaric conditions is described. Differential equations for the time development of the mean radius of the droplets, the number of droplets, and the overall mass concentrated in the droplets are obtained. These equations describe the evolution of the system of droplets beginning after the nucleation period has finished. The equations can be easily solved numerically. For long times analytic solutions are derived. It is shown that the growth of droplets proceeds accordingly to the mechanism of Ostwald ripening.

Zur kinetischen Beschreibung der Kondensation binärer Dämpfe

Inhaltsübersicht. Basierend auf einer thermodynamischen Analyse und unter Verwendung einer früher entwickelten allgemeinen Wachstumsgleichung für Keime einer neuen Phase wird die Kinetik des Wachstums von Tropfen in einer binären Gasmischung unter isobar-isothermen Bedingungen mathematisch beschrieben. Es werden Ausdrücke für die zeitliche Entwicklung des mittleren Tropfenradius, der Tropfenzahl und der Gesamtmenge der flüssigen Phase erhalten. Diese Gleichungen beschreiben die zeitliche Entwicklung des Systems von Tropfen, beginnend unmittelbar nach Abschluß der Keimbildungsphase. Sie sind relativ einfach numerisch lösbar, für große Zeiten können analytische Lösungen angegeben werden. Es wird gezeigt, daß das Wachstum von Tropfen in der Gasphase nach dem Mechanismus der Ostwaldreifung erfolgt.

1. Introduction

Thermodynamic phase transitions of first order frequently proceed in two stages. In the first stage of nucleation a big number of relatively small clusters appear. The second stage is characterized by the growth of these clusters connected especially in the later periods of growth with a decrease of their number. The evolution of the system is qualitatively determined by the thermodynamic constraints [1–5].

Based on a thermodynamic analysis and a recently developed growth equation for clusters of a new phase [4–6] in preceding papers [5] the growth of droplets in a one-component vapour under isochoric and isothermal conditions was described mathematically. It was shown that the growth of the droplets under the mentioned conditions can be considered as a special case of Ostwald ripening and a method of kinetic description of this process including the initial stage has been proposed.

Condensation processes in real systems, e.g., the condensation of water in the atmosphere, do not proceed under isochoric but isobaric conditions. For this reason in the present paper the investigations are extended to multicomponent systems under isothermal and isobaric constraints.

First some general thermodynamic conclusions concerning the properties of ensembles of clusters under these conditions are derived. After then a model for the condensation process is developed and analyzed in detail. On the basis of this model the growth of droplets is described using the method proposed in preceding papers [4, 5].

It is shown that the depletion of the surrounding medium as a result of the evolution of the new phase leads to qualitatively the same behaviour as it has been noticed in the investigation of condensation under isothermal and isochoric conditions in one-component systems.

We restrict ourselves here to the kinetic description of the growth of the clusters of the new phase and do not consider nucleation processes [13, 14, 15]. The influence of the depletion of the surrounding medium on the nucleation stage, the conclusions which can be drawn from the outlined thermodynamic analysis for a description of the whole process of the phase transition [16, 17] will be discussed later.

The thermodynamic properties of the vapour are assumed here to be as simple as possible. The outlined method is also applicable to systems with a more complex thermodynamic behaviour.

2. Description the Model

We consider a mixture of gases. The thermodynamic constraints are given by

$$T = \text{const.}, \quad p_{\alpha} = \text{const.}, \quad n_i = \text{const.}, \quad i = 1, 2, \dots, k. \quad (2.1)$$

T is the temperature, p the pressure and n_i the number of moles of the i -th component of the gas. Chemical reactions do not proceed.

The characteristic thermodynamic potential is the free enthalpy G .

For the homogeneous initial state the free enthalpy G_{hom} can be written in the following form:

$$G_{\text{hom}} = \sum_{i=1}^k \mu_i n_i, \quad (2.2)$$

μ_i is the chemical potential of the i -th component.

The homogeneous initial state is assumed to be metastable. The formation of droplets can lead therefore to a phase transition of first order.

The free enthalpy G_{het} of the heterogeneous state consisting of s droplets in the gaseous medium can be approximately expressed by [2, 7]:

$$G_{\text{het}} = \sum_{j=1}^s \left\{ (p - p_{\alpha}^{(j)}) V_{\alpha}^{(j)} + \sigma_{\alpha}^{(j)} O_{\alpha}^{(j)} + \sum_{i=1}^k \mu_{i\alpha}^{(j)} n_{i\alpha}^{(j)} \right\} + \sum_{i=1}^k \mu_{i\beta} n_{i\beta}, \quad (2.3)$$

$\sigma_{\alpha}^{(j)}$ is the surface tension, $O_{\alpha}^{(j)}$ the surface area of the j -th droplet, V is the volume of the whole system. The subscripts α and β specify the thermodynamic parameters of the clusters (α) and the medium (β). Parameters without such a subscript refer to the homogeneous initial state.

The formation of droplets is connected with a change of the free enthalpy $\Delta G = G_{\text{het}} - G_{\text{hom}}$ of the system.

$$\Delta G = \sum_{j=1}^s \left\{ (p - p_{\alpha}^{(j)}) V_{\alpha}^{(j)} + \sum_{i=1}^k (\mu_{i\alpha}^{(j)} - \mu_{i\beta}) n_{i\alpha}^{(j)} + \sigma_{\alpha}^{(j)} O_{\alpha}^{(j)} \right\} + \sum_{i=1}^k (\mu_{i\beta} - \mu_i) n_i. \quad (2.4)$$

Under the assumed constraints (2.1) ΔG is equal to the work of formation of the ensemble of clusters [8].

The extreme values of ΔG , which are especially important for the process of nucleation and growth of the clusters, are given by:

$$dG = \sum_{j=1}^s \left\{ \left(p - p_{\alpha}^{(j)} + \sigma_{\alpha}^{(j)} \frac{dO_{\alpha}^{(j)}}{dV_{\alpha}^{(j)}} \right) dV_{\alpha}^{(j)} + \sum_{i=1}^k (\mu_{i\alpha}^{(j)} - \mu_{i\beta}) dn_{i\alpha}^{(j)} \right\} = 0. \quad (2.5)$$

From (2.5) the following necessary conditions for extreme values of ΔG can be obtained:

$$p - p_{\alpha}^{(j)} = \frac{2\sigma_{\alpha}^{(j)}}{r_{\alpha}^{(j)}}, \quad \mu_{i\alpha}^{(j)} = \mu_{i\beta}, \quad j = 1, 2, \dots, s. \quad (2.6)$$

Generally it can be shown (appendix), that states of the heterogeneous system defined by the equations (2.5) or (2.6) correspond either to minimum values of the thermodynamic potential G_{het} (thermodynamically stable states) or to unstable states of saddle-point type (critical states). Maxima of G_{het} are possible only if additional approximations concerning the thermodynamic properties of the considered system are assumed. Such additional approximation (for instance, incompressibility of the liquid) can lead to a reduction of the number of independent variables and therefore to the consideration of a cut through the surface of free enthalpy. In this case saddle points can degenerate to maxima.

Further it can be shown generally (appendix), that for one-component systems under the constraints (2.1) a thermodynamically stable state consisting of s clusters ($s \geq 1$) in the medium cannot exist. For a fixed number of clusters the equations (2.6) have only one solution. This solution corresponds to a saddle point or, if the liquid is assumed to be incompressible, to a maximum of the free enthalpy. In this extreme state all droplets have the same parameters independent of the number of droplets. Each droplet is formed and grows independently of the existence of other droplets. Therefore in this case a stage of nucleation and simultaneous independent growth of supercritical clusters succeeds to the first stage of nucleation. The rate of nucleation can be calculated by the classical nucleation theory [9] or their modifications [13, 15].

In the present paper binary systems are considered. It is assumed that a closed system with the volume V contains n_1 and n_2 moles of two different gases (Fig. 1). The thermodynamic constraints are chosen in such a way that the gas n_2 by nucleation and growth can undergo a transition to the liquid state. It is assumed further, that the liquid consists only of particles of the second component.

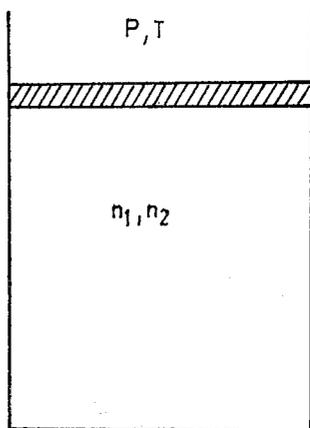


Fig. 1. Model for the description of a condensation process under isobaric and isothermal constraints. The pressure is kept constant by the moveable piston

Independent from the thermodynamic properties of the gases and the liquid it can be shown (appendix) that the extremum conditions can be fulfilled only if all s droplets have the same parameters, the parameters of the clusters depend on the number of clusters. States consisting of s clusters ($s > 1$) cannot be thermodynamically stable.

For the considered model equation (2.4) can be transformed into the following expression:

$$\Delta G = \sum_{j=1}^s \{ (p - p_{\alpha}^{(j)}) V_{\alpha}^{(j)} + (\mu_{2\alpha}^{(j)} - \mu_{2\beta}) n_{2\alpha}^{(j)} + \sigma_{\alpha}^{(j)} O_{\alpha}^{(j)} \} + \sum_{i=1}^2 (\mu_{i\beta} - \mu_i) n_i. \quad (2.7)$$

Assuming further that the liquid is incompressible and the mixture is an ideal one, we get:

$$\begin{aligned} \mu_{2\alpha} &= \mu_0 + \frac{1}{\varrho_{\alpha}} (p_{\alpha} - p_0), \quad \varrho_{\alpha} = \frac{n_{\alpha}}{V_{\alpha}}, \\ \mu_{1\beta} &= \mu_{10} + RT \ln \left[\frac{p}{p_0} (1 - x_{\beta}) \right], \quad \mu_1 = \mu_{10} + RT \ln \left[\frac{p}{p_0} (1 - x) \right], \\ \mu_{2\beta} &= \mu_0 + RT \ln \left[\frac{p}{p_0} x_{\beta} \right], \quad \mu_2 = \mu_0 + RT \ln \left[\frac{p}{p_0} x \right]. \end{aligned} \quad (2.8)$$

The change of the free enthalpy connected with the development of s identical droplets is given by

$$\begin{aligned} \Delta G &= s V_{\alpha} (p - p_0) - s \varrho_{\alpha} V_{\alpha} RT \ln \frac{px_{\beta}}{x} + s \sigma_{\alpha} O_{\alpha} \\ &+ n_1 RT \ln \frac{1 - x_{\beta}}{1 - x} + n_2 RT \ln \frac{x_{\beta}}{x}. \end{aligned} \quad (2.9)$$

Here the following abbreviations are used:

- p_0, μ_0 — pressure and chemical potential of the pure gas n_2 in equilibrium with the liquid at a plane surface,
- x, x_{β} — molefraction of the second component in the homogeneous initial state and during the condensation process,
- μ_{10} — chemical potential of the pure gas n_1 at the pressure p_0 .

Consequently it is possible to write

$$x = \frac{n_2}{n_1 + n_2}, \quad x_{\beta} = \frac{n_2 - sn_{\alpha}}{n_1 + n_2 - sn_{\alpha}}. \quad (2.10)$$

In the following the notation $n = n_1 + n_2$ will be used.

3. Thermodynamic Analysis of the Model

The necessary condition for the possibility of a condensation process to appear is given by

$$\mu_{2\alpha}(p) - \mu_{2\beta}(p) < 0 \quad (3.1)$$

or

$$(p - p_0) - \varrho_{\alpha} RT \ln \left[\frac{px}{p_0} \right] < 0. \quad (3.2)$$

Therefore, the quantity Θ defined by (3.3)

$$\Theta = \ln \frac{px}{p_0} - \frac{p - p_0}{\rho_\alpha RT}, \quad (3.3)$$

can be considered as an appropriate measure of the initial supersaturation. For given values of p_0 and x , Θ is uniquely connected with the quantity $y = p/p_0$ which is used as another measure of supersaturation.

For not too high fixed values of s the function $\Delta G = \Delta G(r_\alpha)$ has a behaviour qualitatively presented in Fig. 2. There exists a critical radius of the droplets $r_{\alpha k}$. This radius corresponds to a relative maximum of the characteristic thermodynamic potential supposing the number of droplets is fixed. The finiteness of the system, here due to the condition $n_2 = \text{const.}$, leads to a relative minimum of ΔG for $r_\alpha = r_{\alpha s}$.

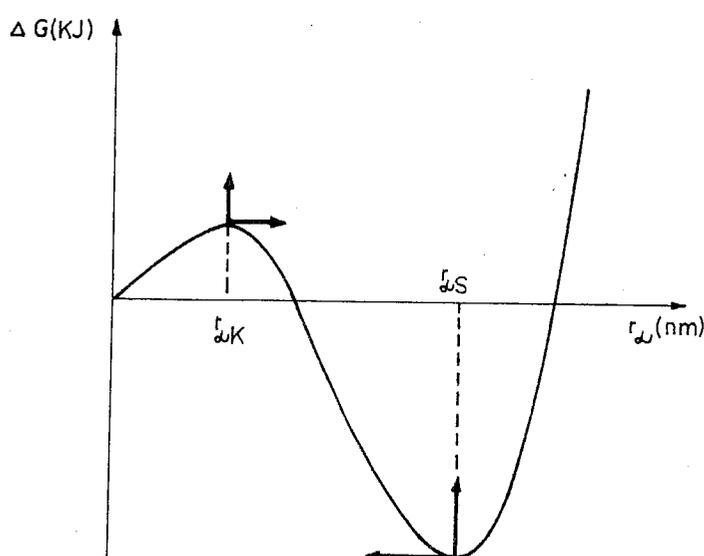


Fig. 2. Qualitative behaviour of the function $\Delta G = \Delta G(r_\alpha)$ for fixed not too high values of the number of droplets. The arrows indicate the variation of the position of the extremes with an increase of the number of droplets

The extremes of the function ΔG are determined by

$$\left(\frac{\partial \Delta G}{\partial r_\alpha}\right)_s = -4\pi r_\alpha^2 s \rho_\alpha RT \left\{ \ln \left[\frac{p}{p_0} \frac{(n_2 - sn_\alpha)}{(n - sn_\alpha)} \right] - \frac{p - p_0}{\rho_\alpha RT} - \frac{2\sigma}{\rho_\alpha RT r_\alpha} \right\} = 0. \quad (3.4)$$

The equation (3.4) leads to a generalized Gibbs-Thomson equation:

$$\ln \left[\frac{p}{p_0} \frac{(n_2 - sn_\alpha)}{(n - sn_\alpha)} \right] - \frac{p - p_0}{\rho_\alpha RT} - \frac{2\sigma}{\rho_\alpha RT r_\alpha} = 0. \quad (3.5)$$

This equation gives for the extreme values of ΔG a relation between the number of clusters and their radius. The first derivative of equation (3.5) with respect to s leads to the following equation:

$$\frac{dr_\alpha}{ds} = - \frac{r_\alpha}{3s} \frac{1}{1 + Z^{-1}}. \quad (3.6)$$

Here Z is determined by

$$Z = -3RT \frac{Q_\alpha r_\alpha s n_\alpha n_1}{2\sigma(n_2 - s n_\alpha)(n - s n_\alpha)} \quad (3.7)$$

Z is always smaller than zero. Further information about Z can be obtained from the extreme conditions.

The second partial derivative of ΔG can be expressed by

$$\left(\frac{\partial^2 \Delta G}{\partial r_\alpha^2}\right)_s = -8\pi\sigma s(1 + Z), \quad (3.8)$$

and consequently the following equations are valid:

$$\begin{aligned} \left(\frac{\partial^2 \Delta G}{\partial r_\alpha^2}\right)_s < 0, \quad 1 + Z > 0, \quad \frac{dr_\alpha}{ds} > 0 & \text{ for } r_\alpha = r_{\alpha k}, \\ \left(\frac{\partial^2 \Delta G}{\partial r_\alpha^2}\right)_s > 0, \quad 1 + Z < 0, \quad \frac{dr_\alpha}{ds} < 0 & \text{ for } r_\alpha = r_{\alpha s}. \end{aligned} \quad (3.9)$$

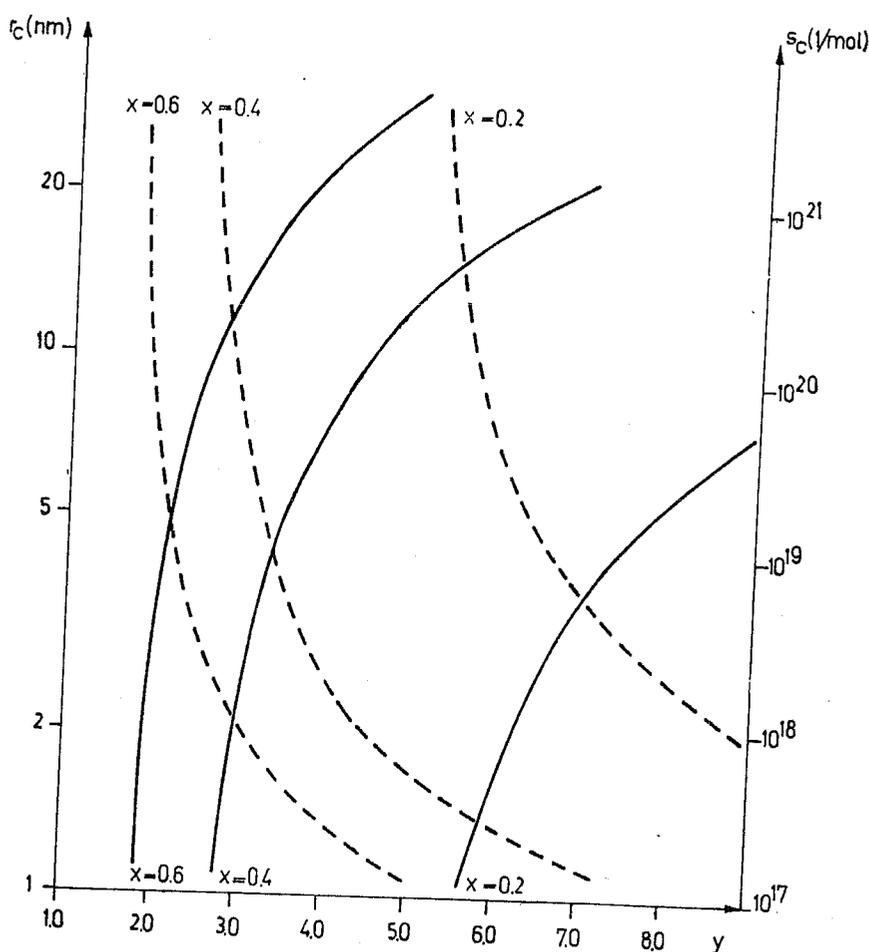


Fig. 3. Molar critical number of cluster s_c (—) and the corresponding critical radius $r_{\alpha c}$ (---) as a function of the initial supersaturation expressed by $y = p/p_0$ for different values of the initial mole fraction x (ethanol, $T = 312.35$ K)

The change of the extremes of ΔG in dependence on the number of clusters s is given by

$$\frac{d}{ds} \Delta G = \frac{1}{3} \sigma O. \quad (3.10)$$

This variation is indicated in Fig. 2 by arrows. There exists a critical value s_c of the number of clusters. For $s > s_c$ ΔG is a monotonically increasing function of the common radius of the clusters r_α .

The critical number of clusters s_c and the corresponding critical radius $r_{\alpha c}$ are presented in Fig. 3. $r_{\alpha c}$ corresponds to the point of inflexion of the function ΔG , it is determined by

$$\left(\frac{\partial \Delta G}{\partial r_\alpha}\right)_s = \left(\frac{\partial^2 \Delta G}{\partial r_\alpha^2}\right)_s = 0 \quad (3.11)$$

With an increase of the initial supersaturation, the critical number of the droplets increases and the critical radius $r_{\alpha c}$ decreases.

The same results were obtained in the earlier analysis of condensation in one-component closed isochoric systems [5]. A further analogy consists in the existence of a lowest possible critical value V_c of the volume of the whole system. For $V < V_c$ the system cannot occur a phase transition by the mechanism of homogeneous nucleation.

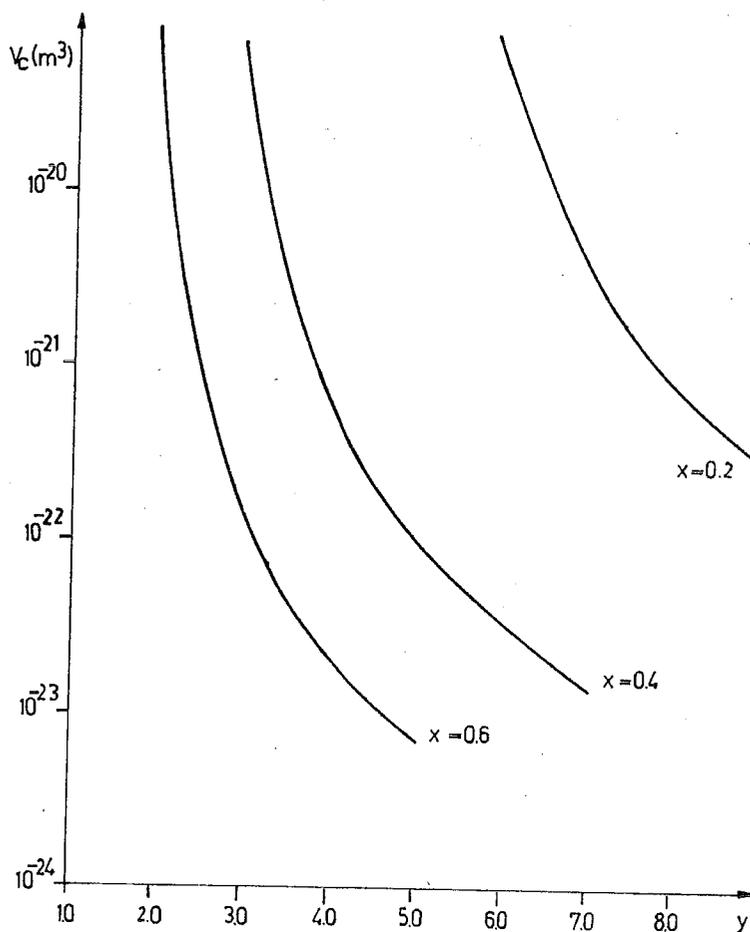


Fig. 4. Critical volume V_c of the whole system as a function of the initial supersaturation y for different values of x (ethanol, $T = 312.35$ K)

The critical value V_c is presented as a function of the ratio $y = p/p_0$ in Fig. 4. With an increase of the initial supersaturation the critical volume decreases.

The results of the thermodynamic investigations are summarized in Fig. 5. They lead to the following conclusions concerning the proceeding of the phase transition.

In a first stage of nucleation a big number of small clusters appears and a state in the neighbourhood of the critical state $(s_c, r_{\alpha c})$ develops. The broken line in Fig. 5 represents the expected path of further evolution of the system of droplets (see also [1, 3]).

The evolution of the system is characterized by a growth of the mean radius of the droplets and a decrease of their number. These are the characteristic properties of the process of Ostwald ripening. In the next section a kinetic description of this process is given.

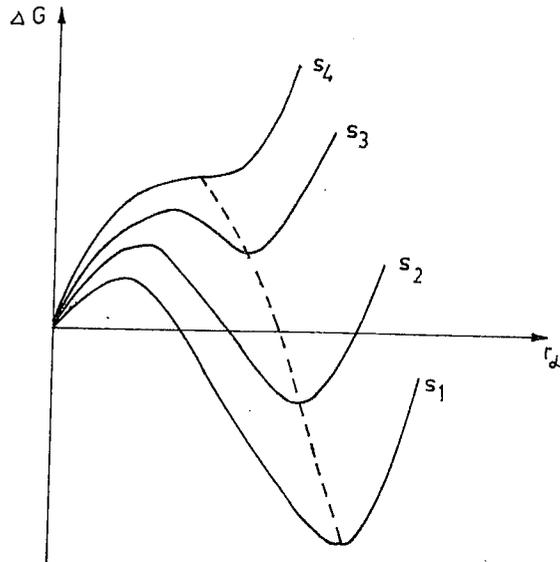


Fig. 5. Qualitative behaviour of the function $\Delta G = \Delta G(r_\alpha)$ for different values of the number of droplets ($s_1 < s_2 < s_3 < s_4$). With a broken line the expected path of development of the system of clusters is marked

4. Kinetic Description of the Growth of Droplets

Based on a general growth equation for clusters of a new phase proposed in preceding papers [4, 6] the time evolution of the volume of the j -th droplet $V_\alpha^{(j)}$ can be described in the following way:

$$\frac{dV_\alpha^{(j)}}{dt} = - \frac{\varrho_\beta}{\varrho_\alpha^2} \cdot \frac{D}{RT} \cdot \frac{1}{r_\alpha^{(j)}} \frac{\partial}{\partial r_\alpha^{(j)}} \Delta G^{(j)}, \quad (4.1)$$

ϱ_β is the molar density, D the diffusion coefficient of the condensing component in the gaseous phase, ϱ_α the molar density of the liquid. $\Delta G^{(j)}$ represents the change of the free enthalpy of the system due to the growth of the j -th droplet.

In particular the evolution of only one droplet in the medium is given by

$$\frac{dr_\alpha}{dt} = \frac{\varrho_\beta}{\varrho_\alpha} \frac{D}{r_\alpha} \left\{ \ln \left[\frac{p}{p_0} \frac{(n_2 - n_\alpha)}{(n - n_\alpha)} \right] - \frac{p - p_0}{\varrho_\alpha RT} - \frac{2\sigma}{\varrho_\alpha RT r_\alpha} \right\}, \quad (4.2)$$

or for not too high values of the radius of the cluster by

$$\frac{dr_\alpha}{dt} = \frac{2\varrho_\beta \sigma D}{\varrho_\alpha^2 RT} \frac{1}{r_\alpha} \left[\frac{1}{r_{\alpha k}} - \frac{1}{r_\alpha} \right]. \quad (4.3)$$

The critical droplet radius $r_{\alpha k}$ can be expressed approximately by

$$r_{\alpha k} = \frac{2\sigma}{\rho_{\alpha} RT \left[\ln\left(\frac{p}{p_0} x\right) - \frac{p - p_0}{\rho_{\alpha} RT} \right]} \quad (4.4)$$

In a real system there exists a big number of droplets of different size. To describe the time evolution of the system of clusters from this real distribution of clusters we go over to an idealized ensemble of s identical clusters with the same mean radius r_{α} . Summarizing equation (4.1) over all these droplets equation (4.5) is obtained as

$$s \frac{dV_{\alpha}}{dt} = - \frac{\rho_{\beta}}{\rho_{\alpha}^2} \frac{D}{RT} \frac{1}{r_{\alpha}} \frac{\partial}{\partial r_2} \Delta G. \quad (4.5)$$

In accordance with the thermodynamic investigations the thermodynamic driving force is the change of free enthalpy of the whole system due to the change of the number of droplets. Therefore we can write:

$$\frac{\partial \Delta G}{\partial r_{\alpha}} = \frac{d}{ds} \Delta G \frac{ds}{dr_{\alpha}}. \quad (4.6)$$

Taking into account (3.6) and (3.10) equation (4.6) can be transformed into (4.7)

$$\frac{dr_{\alpha}}{dt} = \frac{\rho_{\beta}}{\rho_{\alpha}^2} \frac{D}{RT} \frac{\sigma}{r_{\alpha}^2} (1 + Z^{-1}). \quad (4.7)$$

The derivation of equation (3.5) with respect to time gives the following expression for the time-development of the overall mass of the liquid phase:

$$\frac{d}{dt} [\ln(sn_{\alpha})] = - \frac{1}{Z} \frac{d}{dt} [\ln(r_{\alpha}^3)]. \quad (4.8)$$

The equations (4.7), (4.8) can be easily solved numerically. As the result the mean droplet radius, the mass of the liquid phase, and the number of droplets can be calculated as a function of time.

For long times ($Z^{-1} \rightarrow 0$) the following analytic solutions can be derived (see also [4]):

$$\begin{aligned} sV_{\alpha} &= \frac{n \cdot n_2}{n_1 \rho_{\alpha}} \left[\ln \frac{px}{p_0} - \frac{p - p_0}{\rho_{\alpha} RT} \right], \quad r_{\alpha}^3 = 3 \frac{\rho_0}{\rho_{\alpha}^2} \frac{D\sigma}{RT} t, \\ s &= \left[n_2 \frac{\rho_{\alpha}}{\rho_0} \frac{RT}{4\pi D\sigma n_1} \left(\ln \frac{px}{p_0} - \frac{p - p_0}{\rho_2 RT} \right) \right] \frac{1}{t}, \\ O_{ov} &= \left(9 \frac{RT}{\rho_{\alpha} \rho_0 D\sigma} \right)^{1/3} \frac{n_2 n}{n_1} \left(\ln \frac{px}{p_0} - \frac{p - p_0}{\rho_{\alpha} RT} \right) \frac{1}{t^{1/3}}. \end{aligned} \quad (4.9)$$

Here ρ_0 is the saturation density of the pure condensing gas in contact with the liquid at a plane surface, O_{ov} the overall surface area of the s droplets.

In the asymptotic region the mass of the liquid phase is nearly constant, the overall surface area of the droplets decreases with time.

5. Discussion

Up to now the growth of droplets was described phenomenologically. Some additional information about the mechanism of growth of the system of droplets can be derived by the formulation of the growth equation for a $(s + 1)$ -th droplet with the radius r .

Based on (4.1) this equation can be written in the following form:

$$\frac{dr}{dt} = \frac{2\varrho_\beta D\sigma}{\varrho_\alpha^2 RT} \frac{1}{r} \left(\frac{1}{r_\alpha} - \frac{1}{r} \right). \quad (5.1)$$

Changes in the gaseous medium due to the growth of the additional droplet are neglected here.

The relative minimum of the free enthalpy assuming the existence of a fixed number of s identical droplets with the common radius r_α (idealized ensemble) corresponds therefore to a critical droplet radius for the real distribution of clusters. Droplets with a radius $r > r_\alpha$ grow, droplets with $r < r_\alpha$ vanish. The critical radius grows more rapidly than the radii of the single droplets and more and more droplets disappear.

The described mechanism of growth of the system of droplets represents the mechanism of Ostwald ripening. The analyzed here growth of droplets can be considered therefore as a special case of Ostwald ripening.

If in equation (4.3) ϱ_β is replaced by ϱ_0 the methods developed by LIFSHITZ and SLYOZOV [10] or MARQUSEE and ROSS [11] for the description of the process of Ostwald ripening can be used directly. Instead of (4.9) the following asymptotic solutions can be obtained then:

$$r_\alpha^3 = \frac{8}{9} \frac{D\sigma}{RT} \frac{\varrho_0}{\varrho_\alpha^2} t, \quad s = \left[n_2 \frac{\varrho_\alpha}{\varrho_0} \frac{27RT}{32\pi D\sigma} \left(\ln \frac{p_\alpha}{p_0} - \frac{p - p_0}{\varrho_\alpha RT} \right) \right] \frac{1}{t}. \quad (5.2)$$

In the asymptotic region these methods lead therefore qualitatively to the same results as derived by us. The rate of growth of the mean radius of droplets calculated by our method is greater by a factor of the order three. This is due firstly to the approximation $\varrho_\beta = \varrho_0$ used in [10, 11] and secondly to the assumption of an idealized ensemble of s identical clusters underlying our method.

Using, for instance, the method of LIFSHITZ and SLYOZOV it can be shown further that in the asymptotic region the distribution of droplets in reduced variables $r_\alpha/r_{\alpha k}$ is nearly constant.

The method applied here has the advantage that the thermodynamic origin of the growth process is demonstrated very clearly and that explicit expressions for the description of the initial stage of ripening are obtained.

Appendix: Necessary and Sufficient Conditions for the Thermodynamic Stability of Droplets in the Gaseous Phase

Assuming the thermodynamic constraints are given by

$$p = p_\beta = \text{const.}, \quad T = \text{const.}, \quad n_i = \text{const.}, \quad i = 1, 2, \dots, k, \quad (1)$$

the necessary (2) and sufficient conditions (3) for the thermodynamic stability of the heterogeneous system consisting of s clusters in the medium can be expressed in the following way:

$$\delta G_{\text{het}} = 0 \quad (2)$$

$$\delta^2 G_{\text{het}} > 0 \quad (3)$$

The condition (2) or (2.6) are assumed further to be fulfilled.

The states of the heterogeneous system determined by (2) or (2.6) are thermodynamically

cally stable states if the following inequality is fulfilled (see also [3, 5]):

$$\begin{aligned} \delta^2 G_{\text{het}} = & \sum_{j=1}^s \left\{ \sum_{i,l}^k \left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}} + \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}} \right) \delta n_{i\alpha}^{(j)} \delta n_{l\alpha}^{(j)} - \sum_{l=1}^k \frac{\partial p_{\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}} \delta n_{l\alpha}^{(j)} \delta V_{\alpha}^{(j)} \right. \\ & + \sum_{i=1}^k \frac{\partial \mu_{i\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \delta n_{i\alpha}^{(j)} \delta V_{\alpha}^{(j)} - \left(\frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} - \sigma_{\alpha}^{(j)} \frac{\partial^2 O_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)2}} \right) \delta V_{\alpha}^{(j)2} \\ & \left. + \sum_{j'=1}^s (1 - \Theta_{jj'}) \sum_{i,l}^k \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}} \delta n_{i\alpha}^{(j)} \delta n_{l\alpha}^{(j')} \right\}. \end{aligned} \quad (4)$$

Here $\Theta_{jj'}$ is the Kronecker symbol and δ denotes infinitesimal deviations from the state given by (2).

If the state given by (2) is a thermodynamically stable state the quadratic matrices (5) are positive definite.

$$\left[\begin{array}{cccccc} \frac{\partial \mu_{1\alpha}^{(j)}}{\partial n_{1\alpha}^{(j)}} + \frac{\partial \mu_{1\beta}}{\partial n_{1\beta}} & \frac{\partial \mu_{1\alpha}^{(j)}}{\partial n_{2\alpha}^{(j)}} + \frac{\partial \mu_{1\beta}}{\partial n_{2\beta}} & \dots & \frac{\partial \mu_{1\alpha}^{(j)}}{\partial n_{k\alpha}^{(j)}} + \frac{\partial \mu_{1\beta}}{\partial n_{k\beta}} & \frac{\partial \mu_{1\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} & \\ \frac{\partial \mu_{2\alpha}^{(j)}}{\partial n_{1\alpha}^{(j)}} + \frac{\partial \mu_{2\beta}}{\partial n_{1\beta}} & \frac{\partial \mu_{2\alpha}^{(j)}}{\partial n_{2\alpha}^{(j)}} + \frac{\partial \mu_{2\beta}}{\partial n_{2\beta}} & \dots & \frac{\partial \mu_{2\alpha}^{(j)}}{\partial n_{k\alpha}^{(j)}} + \frac{\partial \mu_{2\beta}}{\partial n_{k\beta}} & \frac{\partial \mu_{2\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} & \\ \dots & \dots & \dots & \dots & \dots & \\ \frac{\partial \mu_{k\alpha}^{(j)}}{\partial n_{1\alpha}^{(j)}} + \frac{\partial \mu_{k\beta}}{\partial n_{1\beta}} & \frac{\partial \mu_{k\alpha}^{(j)}}{\partial n_{2\alpha}^{(j)}} + \frac{\partial \mu_{k\beta}}{\partial n_{2\beta}} & \dots & \frac{\partial \mu_{k\alpha}^{(j)}}{\partial n_{k\alpha}^{(j)}} + \frac{\partial \mu_{k\beta}}{\partial n_{k\beta}} & \frac{\partial \mu_{k\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} & \\ - \frac{\partial p_{\alpha}^{(j)}}{\partial n_{1\alpha}^{(j)}} & - \frac{\partial p_{\alpha}^{(j)}}{\partial n_{2\alpha}^{(j)}} & \dots & - \frac{\partial p_{\alpha}^{(j)}}{\partial n_{k\alpha}^{(j)}} & - \frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} - \frac{\sigma_{\alpha}^{(j)}}{2\pi r_{\alpha}^{(j)4}} & \end{array} \right] \quad (5)$$

Taking into account the condition of inner stability of the volume phases [2, 12], which underlies the thermodynamic description, the matrices (5) are positive definite if their determinants J are positive. The inequality $J > 0$ must be fulfilled for each of the s clusters. For the case $s = 1$ the condition $J > 0$ is necessary and sufficient for the thermodynamic stability.

The condition of inner stability of the volume phases leads further to the conclusion that states given by (2) cannot correspond to maxima of the thermodynamic potential (see also [3, 5]).

For one-component systems the necessary extreme conditions (2) lead to the equations (6):

$$p_{\alpha}^{(j)}(\varrho_{\alpha}^{(j)}) - p = \frac{2\sigma_{\alpha}^{(j)}}{r_{\alpha}^{(j)}}, \quad \mu_{\alpha}^{(j)}(\varrho_{\alpha}^{(j)}) - \mu_{\beta}(p) = 0. \quad (6)$$

For a given value of the pressure the second of these equations uniquely determines $\varrho_{\alpha}^{(j)}$. Therefore by the first of these equations $V_{\alpha}^{(j)}$ and $n_{\alpha}^{(j)}$ are determined uniquely, too. The equations (6) can be fulfilled consequently only if all clusters have the same parameters. These parameters do not depend on the number of clusters. The necessary condition for thermodynamic stability in the one-component case leads to the inequality

$$\frac{\sigma_{\alpha}^{(j)}}{2\pi r_{\alpha}^{(j)4}} < 0 \quad (7)$$

and cannot be fulfilled.

In one-component systems under the thermodynamic constraints (1) the states given by (2) are unstable states of saddle-point type.

Considering binary systems and assuming, that the liquid consists only of particles of the second component, equation (2) leads to

$$p_\alpha^{(j)} \left(\frac{n_\alpha^{(j)}}{V_\alpha^{(j)}} \right) - p = \frac{2\sigma_\alpha^{(j)}}{r_\alpha^{(j)}}, \quad \mu_\alpha^{(j)} \left(\frac{n_\alpha^{(j)}}{V_\alpha^{(j)}} \right) = \mu_{2\beta}(p, x_\beta). \tag{8}$$

For any given x_β the second of these equations uniquely determines $\rho_\alpha^{(j)}$ and, together with the first equation, $V_\alpha^{(j)}$ and $n_\alpha^{(j)}$. The equations (8) can be fulfilled again only if all clusters have the same parameters. x_β and therefore the parameters of the clusters depend on the number of clusters.

Assuming only one cluster in the system the equations (8) can be transformed into (9):

$$\begin{aligned} p_\alpha \left(\frac{n_\alpha}{V_\alpha} \right) - p - \frac{2\sigma_\alpha}{r_\alpha} &= 0, \\ \mu_\alpha \left(\frac{n_\alpha}{V_\alpha} \right) - \mu_{2\beta} \left(\frac{n_1}{V - V_\alpha}, \frac{n_2 - n_\alpha}{V - V_\alpha} \right) &= 0. \end{aligned} \tag{9}$$

These equations implicitly determine two functions $n_\alpha^{(l)} = n_\alpha^{(l)}(V_\alpha)$. The derivations of these functions are given by (10):

$$\frac{\partial n_\alpha^{(1)}}{\partial V_\alpha} = \frac{\frac{\rho_\alpha}{V_\alpha} \frac{\partial \mu_\alpha}{\partial \rho_\alpha}}{\frac{1}{V_\alpha} \frac{\partial \mu_\alpha}{\partial \rho_\alpha} + \frac{1}{V_\beta} \frac{\partial \mu_{2\beta}}{\partial \rho_{2\beta}}}, \quad \frac{\partial n_\alpha^{(2)}}{\partial V_\alpha} = \frac{\frac{\rho_\alpha^2}{V_\alpha} \frac{\partial \mu_\alpha}{\partial \rho_\alpha} - \frac{\sigma_\alpha}{2\pi r_\alpha^4}}{\frac{\rho_\alpha}{V_\alpha} \frac{\partial \mu_\alpha}{\partial \rho_\alpha}}. \tag{10}$$

The functions $n_\alpha^{(l)}$ have therefore qualitatively the form represented in Fig. 6. The points of intersection of these functions correspond to solutions of the equations (9).

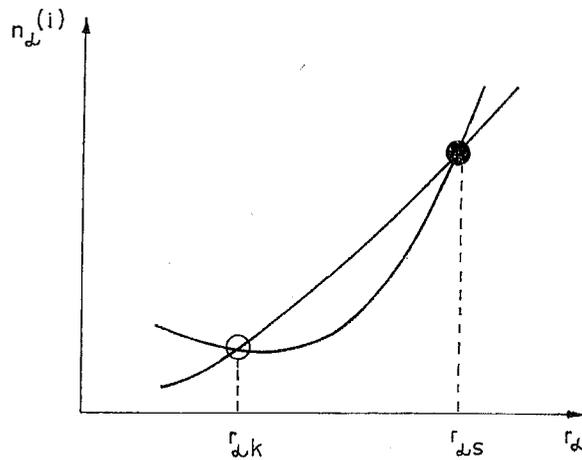


Fig. 6. Qualitative behaviour of the functions $n_\alpha^{(l)} = n_\alpha^{(l)}(r_\alpha)$

As a necessary and sufficient condition for stability from (4) the following inequality can be derived:

$$\frac{\sigma_\alpha}{2\pi r_\alpha^4} < \frac{\frac{1}{V_\beta} \frac{\partial \mu_{2\beta}}{\partial \rho_{2\beta}}}{\frac{1}{V_\alpha} \frac{\partial \mu_\alpha}{\partial \rho_\alpha} + \frac{1}{V_\beta} \frac{\partial \mu_{2\beta}}{\partial \rho_{2\beta}}} \frac{\rho_\alpha^2}{V_\alpha} \frac{\partial \mu_\alpha}{\partial \rho_\alpha}. \tag{11}$$

This condition is equivalent to the inequality (12):

$$\frac{\partial n_{\alpha}^{(1)}}{\partial V_{\alpha}} < \frac{\partial n_{\alpha}^{(2)}}{\partial V_{\alpha}}. \quad (12)$$

Therefore the state marked in Fig. 6 with a full point is a thermodynamically state, the state marked by a circle is an unstable state of saddle-point type.

A change of the number of clusters leads to a variation of the values $r_{\alpha k}$ and $r_{\alpha s}$. Since an increase of the number of clusters is equivalent to a decrease of the volume V for one cluster the variation of $r_{\alpha k}$ and $r_{\alpha s}$ can be calculated by (13) [3]:

$$\Delta V_{\alpha} = \frac{\Delta V}{\partial V_{\beta}} \frac{Q_{\alpha}^2}{V} \frac{\partial \mu_{\alpha}}{\partial Q_{\alpha}} \frac{\partial \mu_{2\beta}}{\partial Q_{2\beta}}. \quad (13)$$

An increase of the number of clusters or a decrease of the volume for one cluster ($\Delta V < 0$) leads to an decrease of $r_{\alpha s}$ ($J > 0$) and to an increase of $r_{\alpha k}$ ($J < 0$).

Further it can be shown starting with (4) that in the considered binary system a state consisting of more than one cluster cannot be thermodynamically stable. The conclusions derived by WARD et al. [18, 19] concerning the possibility of a stable coexistence of bubbles in finite closed systems of a liquidgas solution are, therefore, wrong (see also [20]).

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