A reexamination of the equilibrium conditions in the theory of water drop nucleation

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ABSTRACT

The thermodynamic equations necessary to describe the conditions for equilibrium between a highly curved surface of a liquid and its vapour are re-examined. The complete equilibrium behaviour is reduced to one single differential equation for each component in an arbitrary c-component system. It is shown that this general formulation can be specialized to describe the conditions for equilibrium between water vapour and a pure water drop, the drop carrying an electric charge, containing a water soluble substance and/or containing a water insoluble nucleus. In the light of the present formulation, some incorrect physical statements of treatments by various authors reported in literature are pointed out.

In an added note, the energy of homogeneous water drop formation is discussed and some erroneous conclusions which commonly are drawn in the literature from formulations on the energy of nucleus formation are mentioned.

I. Introduction

A quantitative formulation of the process of homogeneous or heterogeneous nucleation, such as the process of cloud drop formation in the atmosphere or the process of drop formation in various types of cloud chambers, requires as an integral part, a formulation for the conditions of equilibrium between the formed drop and its vapour environment.

If the system consists of one component only, say water substance, the problem involves the derivation of the well-known Kelvin equation relating the saturation vapour pressure over a drop to the curvature of the drop surface. If a drop consists of an aqueous solution containing water-insoluble substances, and in addition, is electrically charged, the equilibrium condition becomes somewhat more complicated although the general principle of its derivation remains the same as that of the simple Kelvin law.

Nevertheless, numerous misconceptions and shortcomings are found in the literature with regard to this problem. Abraham (1968) and Bónis (1971), for example, use an incorrect Gibbs–Duhem equation to derive the Kelvin relationship. In order to arrive at the desired result he was therefore forced to neglect the functional dependence of the surface tension, in particular its radius dependence. Abraham's treatment also violates the phase rule which leads to an insufficient number of degrees of freedom. Other authors (Byers, 1965; Fletcher, 1962; Low, 1969; Mason, 1971; Lothe & Pound, 1969) use the Gibbs free enthalpy as thermodynamic function rather than the Helmholtz free energy for describing the nucleation process. In so doing, they assume that the nucleation process can be described by a constant temperature–pressure process while correctly it must be described by a constant temperature–volume process. Furthermore for the equilibrium condition of an aqueous solution drop, they introduce the density of the solution or the partial specific water volume in the solution, whereas it turns out that the specific volume of water is the correct quantity. In order to clear up these misconceptions and shortcomings we shall briefly re-derive the equilibrium conditions for the most general case of a water drop containing water-soluble substances, a water-insoluble nucleus, and carrying an electric charge on its surface. Various special cases are considered and the crucial steps where errors

appear in the literature are pointed out in passing.

II. The system and its thermodynamic description

Field experiments have shown that the atmospheric aerosol particles are composed of water-soluble as well as water-insoluble substances. Such experiments also show that from the very early stages of cloud development, electric charges reside on the water drops as well as on the aerosol particles entering with the cloud air.

Simulating atmospheric conditions as generally as possible we shall consider the equilibrium state in a c-component system between humid air and a very small and thus highly curved aqueous solution drop containing water-soluble components and a water-insoluble nucleus and carrying an electric charge on its surface.

Furthermore we shall make the reasonable assumption that the solutes are not surface active and thus molecularly uniformly distributed throughout the drop. Consequently we confine ourselves to that case where adsorptions in a small interphase are negligible.[1]

Thus the system to be examined consists of a gaseous phase of volume V' and mass M', a liquid phase of volume V'' and mass M'' and a solid phase of constant volume V''' and constant mass M'''. In principle, all of the c-components can exist in each phase.[2] The variances of the total volume V and the total mass M are then given by

$$dV = dV' + dV'',\ dM = dM' + dM''$$
$$(dV''' = 0 \quad \text{and} \quad dM''' = 0)$$

where

$$V = \sum_{j,i} V_i^j \text{ and } M = \sum_{j,i} M_i^j \quad (i = 1, 2, \ldots, c;\ j = ', '', ''') \tag{II-1}$$

Assuming that the drop is spherical we have

$$\left.\begin{aligned} \Omega'' &= 4\pi r^2 & d\Omega'' &= 8\pi r\, dr \\ V'' &= \frac{4}{3}\pi r^3 - V''' & dV'' &= 4\pi r^2 dr = \frac{r}{2} d\Omega'' \end{aligned}\right\} \tag{II-2}$$

[1] In determining the equilibrium conditions the lack of autonomy of a surface active interphase does not even play a part (Dufour & Defay, 1963; Defay et al., 1966).

[2] For identifying the symbols used in the text below the reader is referred to the list of symbols at the end of this report.

In order to formulate the conditions for equilibrium processes we shall, for convenience, require constant temperature and volume in each possible system stage. It shall be emphasized at this point that for this reason the Helmholtz free energy F, but not the Gibbs free enthalpy G, is the correct thermodynamic equilibrium function to use. The function G is only allowed as long as confining to chemical and phase equilibrium only but not additionally also to mechanical equilibrium. Considering coordinates of work, as in the situation of surface equilibrium, G is unsuitable. While G would be the proper function for a system in which the pressure and temperature are uniform, in equilibrium it can readily be seen that in a system consisting of a bulk mother phase which contains an amount of new phase of very small dimensions, the pressure requirement is not fulfilled since the pressure inside the new phase is larger than that in the mother phase. On the other hand we may justifiably assume that the total volume $V = V' + V''$ is constant.

If at each location of the system at a time t all components and phases have the same temperature T then $F = F(T, V', V'', M_1' \ldots M_c', M_1'' \ldots M_c'')$ and the total differential dF equals:

$$dF = -SdT + \delta W + \sum u_i^j dM_i^j \tag{II-3}$$

The function S denotes the entropy of the system and the inexact differential δW the reversible work done by the system. It consists of the volume works $-p'dV'$ and $-p''dV''$ and the surface work $\sigma d\Omega''$ of phase $''$. We further assume that the drop consists of an aqueous salt solution which behaves as an electric conductor. Then the potential difference $\varphi(r) - \varphi(r = \infty)$ is represented by the voltage U of a spherical condenser where the vapour phase air is the dielectric medium. The energy of the condenser is given by $W_e = \frac{1}{2}QU = -\frac{1}{2}Q\int_\infty^r \frac{Q}{\varepsilon \varrho^2} d\varrho$ where Q denotes the electric charge and ε the dielectric constant of air. By differentiation we obtain immediately $\delta W_e = -\frac{Q^2}{2\varepsilon r^2} dr$ which also contributes to the reversible work. Thus

$$\delta W = -p'dV' - p''dV'' + \sigma d\Omega'' - \frac{Q^2}{2\varepsilon r^2} dr \tag{II-4}$$

Using eqs. (1) to (4) we find

$$dF = -SdT - p'dV' - \left(p'' - \frac{2\sigma}{r} + \frac{Q^2}{8\pi\varepsilon r^4}\right) dV'' + \sum \mu_i' dM_i' + \sum \mu_i'' dM_i'' \qquad \text{(II-5)}$$

This relationship denotes the Gibbs fundamental equation for the described c-component system containing a liquid surface phase. It represents the analytical formulation for the second law of thermodynamics and thus holds good in equilibrium as well as in non-equilibrium.

III. Equilibrium conditions

Before formulating the equilibrium conditions we first determine the variance of the system in equilibrium. This is found from the phase rule for systems with curved surfaces (Defay, 1932; Defay et al., 1966; Dufour & Defay, 1963) by:

$$w = 1 + (c - r') - (\phi - s) \qquad \text{(III-1)}$$

where c = components, r' = chemical reactions, ϕ = surface phases with ϕ radii of curvature and s = types of surfaces. This law includes also the Gibbs phase rule for plane surfaces as one easily can verify.

Secondly, we recall that in equilibrium the entropy production vanishes. Correspondingly this leads at constant T, V and M to a minimum of the Helmholtz free energy F. To simplify the treatment we shall ignore chemical reactions and only consider transfers between the components of the gaseous and liquid state. The equilibrium requirement is then expressed by

$$(dF)_{T,V,M_i} = 0 \quad (i = 1, 2, \ldots, c) \qquad \text{(III-2)}$$

which denotes $dF = 0$ at the secondary conditions $dT = 0$, $dV = dV' + dV'' = 0$ and $dM_i = dM_i' + dM_i'' = 0$. With eq. (2) we get from (II-5) the equilibrium conditions of the intensive variables

$$\left.\begin{aligned} &p'' - p' - \frac{2\sigma}{r} + \frac{Q^2}{8\pi\varepsilon r^4} \equiv 0 \\ &\qquad \text{(mechanical equilibrium)} \\ &\mu_i' - \mu_i'' = \Delta\mu_i \equiv 0 \quad (i = 1, 2, \ldots, c) \\ &\qquad \text{(physico-chemical equilbrium)} \end{aligned}\right\} \qquad \text{(III-3)}$$

With respect to equilibrium displacements between two neighbouring equilibrium states, these conditions can be extended to

$$\left.\begin{aligned} &dp'' - dp' = d\left(\frac{2\sigma}{r}\right) + \frac{Q^2}{2\pi\varepsilon r^5} dr \\ &d\left(\frac{\Delta\mu_i}{T}\right) = 0 \quad (i = 1, 2, \ldots, c) \end{aligned}\right\} \qquad \text{(III-4)}$$

In the most general case $\Delta\mu_i$ is a function of the independant coordinates of state T, p_i', p'' and n_i''

$$\Delta\mu_i = \mu_i'[T, p_i^*(T, p_i')] - \mu_i''(T, p'', n_2'', \ldots, n_c'')$$

where

$$\mu_i' = \overset{+}{\mu}_i(T) + R_i T \ln p_i^* \text{ and } n_1'' = 1 - \sum_{i=2}^{c} n_i'' \qquad \text{(III-5)}$$

By means of this equation arbitrary real phases and components in a real mixture are admitted.

Developing $d(\Delta\mu_i/T)$ in terms of differentials of the independent variables given by (5) and correlating the two equations (4) we see that the equilibrium requirements of each component are finally reduced to the single differential equation

$$-\frac{\Delta h_i}{T} dT + R_i T d\ln p_i^* - v_i'' dp' - v_i'' d\left(\frac{2\sigma}{r}\right) - \frac{v_i'' Q^2}{2\pi\varepsilon} \frac{dr}{r^5} - \sum_{j=2}^{c} \frac{\partial \mu_i''}{\partial n_j''} dn_j'' = 0 \quad (i = 1, 2, \ldots, c) \qquad \text{(III-6)}$$

To obtain this form we made use of the fundamental thermodynamic relations $v_k^j = \partial\mu_k^j/\partial p^j$ and $h_k^j = -T^2(\partial/\partial T)(\mu_k^j/T)$. By the enthalpy difference $\Delta h_i = h_i' - h_i''$ we denote the latent heat of phase change of component i.

Eq. (6) connects the $(c+3)$-intensive variables T, p_i', p', r, n_2'', ..., n_c'' which completely describe the equilibrium state of component i. From the phase rule, eq. (1) follows that for the case of no chemical reactions ($r' = 0$) and for $s = \phi$ the system has $w = 1 + c$ degrees of freedom. Thus two of the $(c+3)$-variables in eq. (6) are, in general, dependent quantities.

[1] The electric term was merely introduced for completeness' sake as it turns out that it will contribute to the equilibrium condition only at very small drop size.

IV. Applications

We shall now test the general relation eq. (III-6) by considering several well known special cases.

In the most simple case we shall examine an uncharged one-component system consisting, e.g., of water vapour and a pure water drop. Formally we denote the component water by $i = 2$. For these conditions the total vapour pressure p' is identical with p_2' and eq. (III-6) becomes

$$-\frac{\Delta h_{2,0}}{T}dT + R_2 T d\ln p_2^* - v_{2,0}'' dp_2' - v_{2,0}'' d\left(\frac{2\sigma_2}{r}\right) = 0 \tag{IV-1}$$

where $\Delta h_{2,0}$ denotes the specific condensation heat of water in pure phases, $v_{2,0}''$ the specific water volume in pure liquid phase and σ_2 the surface tension of water depending in general on all parameters of state, in particular on T and r. From the phase rule we find that for $c = 1$ the number of degrees of freedom is $w = 2$. Choosing as the two independent variables r and T we may study the functional dependence of r on $p_2' \equiv p'$ during equilibrium.

At a given temperature, and assuming that water vapour is a perfect gas ($p_2^* \equiv p_2'$) and $v_{2,0}'' \simeq$ const., i.e. neglecting the compressibility of water, we obtain after integrating eq. (1) from $r = \infty$ to r and $p_{2,\infty}'$ to p_2'

$$\ln\frac{p_2'}{p_{2,\infty}'} = \frac{2\sigma_2 v_{2,0}''}{R_2 T r} + \frac{(p_2' - p_{2,\infty}')v_{2,0}''}{R_2 T} \tag{IV-2}$$

This is the well known Kelvin equation for the case of a one-component system, such as water drop in equilibrium with surrounding water vapour.

In a second application the curvature influence on the partial fugacities p_i^* (or the partial pressures p_i') at constant temperature and at a given composition of the liquid in an arbitrary c-component system will be briefly discussed. According to these conditions we specify the $(c+1)$-degrees of freedom by the variables T, r, n_2'', ..., n_c'' where T and n_2'', ..., n_c'' are given and r is the independent variable. The dependent variables are p_i^* (or p_i') and p'. Thus eq. (III-6) becomes

$$\left.\begin{aligned} &R_i T d\ln p_i^* - v_i'' d\left(\frac{2\sigma}{r}\right) - \frac{Q^2 v_i''}{2\pi\varepsilon r^5}dr = 0 \\ &(i = 1, 2, \ldots c) \end{aligned}\right\} \tag{IV-3}$$

If the vapour of component i behaves like a perfect gas, p_i^* can be replaced by p_i'. So we integrate while supposing incompressibility (v_i'' = const.) this differential equation from $r = \infty$ to r and get

$$\ln\frac{p_i'}{p_{i,\infty}'} = \frac{2\sigma v_i''}{R_i T r} - \frac{Q^2 v_i''}{8\pi\varepsilon R_i T r^4} + \frac{(p' - p_\infty')v_i''}{R_i T} \tag{IV-4}$$

The quantity p_∞' is the total external gas pressure at plane liquid surface. We wish to emphasize that the last term in eq. (4) only results from the fact that p' is a dependent variable. Thus p' is not identical with p_∞'.

Now we study in this connection the interesting case where the liquid phase does not contain one component, for example $(c-k)$ except i, but which exists in the gaseous phase. With regard to the variance of the system the total pressure p' can take the place of the mole fraction of the missing component, thus completing the number of degrees of freedom. If more than one component do not undergo any reaction we may treat them thermodynamically like a single component. Consequently the $(c+1)$-degrees of freedom are T, r, n_2'', ..., n_{c-k-1}'', n_{c-k+1}'', ..., n_c'' and p', where the total pressure is now a given variable. With $dp' = 0$ we find from eq. (3) by integrating over r the simplified relationship

$$\left.\begin{aligned} &\ln\frac{p_i'}{p_{i,\infty}'} = \frac{2\sigma v_i''}{R_i T r} - \frac{Q^2 v_i''}{8\pi\varepsilon R_i T r^4} \\ &(i = 1, 2, \ldots, c, \text{ except } c-k) \end{aligned}\right\} \tag{IV-5}$$

It must be stressed that under the above specified conditions this equation is exact. It does not represent any approximation of eq. (4) as is sometimes stated in literature.

Next we shall consider the equilibrium condition between a cloud droplet in humid air while supposing that the components of dry air (oxygen, nitrogen etc.) are chemically inactive substances. Hence their mass ratios remain constant. This means with regard to the variance of the system that dry air behaves as one single component. Consequently we can specify the system by a gaseous phase which consists of dry air (= component 1) and water

vapour (= component 2), the liquid phase which consists of water (= component 2) and a dissolved salt (= component 3), and the solid phase which consists of an insoluble nucleus (= component 4). In addition the solution drop is assumed to carry an electric charge at the surface.

The mole fraction obeys then the simple relation $n_2'' + n_3'' = 1$. Thus eq. (III-6), for $i = 2$, reduces to

$$-\frac{\Delta h_2}{T}dT + R_2 T d\ln p_2^* - v_2'' dp' - v_2'' d\left(\frac{2\sigma}{r}\right) - \frac{v_2'' Q^2}{2\pi\varepsilon r^5}dr - \frac{\partial \mu_2''}{\partial n_2''}dn_2'' = 0 \qquad \text{(IV-6)}$$

We see from this equation that the system now has five intensive variables. From the phase rule (eq. III-1) we find that as consequence of $c = 4$ the system has five degrees of freedom. Because of the secondary condition $M_4''' = \text{const.}$ the number of intensive variables to be freely chosen reduces to $w = 4$. These are the coordinates T, p', r and n_2'' if we choose p_2^* or p_2' as the dependent variable.

Since during a condensation process in the atmosphere one is justified in assuming that the mass of the dissolved salt in the droplet is constant, the mole fractions n_3'' and n_2'' become unambiguous functions of the droplet size: $n_3'' = n_3''(r) \to n_2'' = 1 - n_3'' = n_2''(r)$. Thus, the total number of intensive variables reduces to four while $w = 3$, the three parameters T, p' and r. The number of intensive variables only exceeds the number of degrees of freedom by one, for component 1 (= dry air) is non-existent in the liquid phase, as we assumed.

In order to determine the effect of curvature on the vapour pressure over the drop, specified above, we consider the temperature and the total gas pressure p' to be given and constant. Thus, the independent variable is the radius and the dependent variable is p_2^*, i.e. p_2'. With these conditions, eq. (IV-6) becomes

$T = \text{const.}, p' = \text{const.}$

$$R_2 T d\ln p_2^* - v_2'' d\left(\frac{2\sigma}{r}\right) - \frac{v_2'' Q^2}{2\pi\varepsilon}\frac{dr}{r^5} - \frac{\partial \mu_2''}{\partial n_2''}dn_2'' = 0 \qquad \text{(IV-7)}$$

If we assume that the aqueous solution is a real mixture the chemical potential of the solvent in the mixture is given by

$$\mu_2'' = \overset{+}{\mu}{}_2''(T, p'') + R_2 T \ln n_2'' \gamma_2'' \qquad \text{(IV-8)}$$

where γ_2'' denotes the activity coefficient of water in the solution and $\overset{+}{\mu}{}_2''$ the chemical standard potential of water. Using well known thermodynamic relations we find from (8)

$$v_2'' = \overset{+}{v}{}_2'' + R_2 T\left(\frac{\partial \ln \gamma_2''}{\partial p''}\right)_{T, n_2''} \qquad \text{(IV-9)}$$

where v_2'' is the partial specific volume of water in the solution and $\overset{+}{v}{}_2''$ is that in the standard state. With eq. (9) we obtain for eq. (7) the more useful equilibrium equation with regard to integration

$$R_2 T d\ln p_2^* - \overset{+}{v}{}_2'' d\left(\frac{2\sigma}{r}\right) - \frac{\overset{+}{v}{}_2'' Q^2}{2\pi\varepsilon r^5}dr - R_2 T d\ln(n_2'' \gamma_2'') = 0 \qquad \text{(IV-10)}$$

where for temperature constancy the total differential of $n_2'' \gamma_2''$ is given by

$$d\ln(n_2'' \gamma_2'') = \frac{\partial \ln n_2'' \gamma_2''}{\partial n_2''}dn_2'' + \frac{\partial \ln n_2'' \gamma_2''}{\partial p''}dp''.$$

At this point it must be stressed that in the literature various authors identify the specific volume appearing in eq. (10) with the partial specific volume of water in solution v_2'', or even with $1/\varrho = v$ where ϱ is the density and v the specific volume of the solution. Such identification would be incorrect, as it can be seen from eq. (10) that the quantity to be dealt with is the specific standard volume $\overset{+}{v}{}_2''$ of water in the solution which equals the specific volume of pure water (Robinson & Stokes 1970). Thus, we shall set $\overset{+}{v}{}_2'' = v_{2,0}''$.

Neglecting the small compressibility of water and considering that for a plane surface

$$\lim_{r\to\infty} n_2'' = n_{2,\infty}'' = 1; \lim_{r\to\infty} \gamma_2'' = \gamma_{2,\infty}'' = 1; \lim_{r\to\infty} p_2^* = p_{2,\infty}^*$$

where $p_{2,\infty}^*$ is the fugacity of water vapour over a plane surface of liquid, and $\lim_{r\to\infty} p_2' = p_{2,\infty}'$ which is the water vapour pressure over a plane surface of liquid we derive by integrating eq. (10) from $r = \infty$ to r if we treat water vapour for simplicity as an ideal gas

$$\ln \frac{p_2'}{p_{2,\infty}'} = \frac{2\sigma v_{2,0}''}{R_2 T r} + \ln n_2'' \gamma_2'' - \frac{Q^2 v_{2,0}''}{8\pi\varepsilon R_2 T r^4} \qquad \text{(IV-11)}$$

From this equation we find for an electrically uncharged aqueous solution drop

$$\ln \frac{p_2'}{p_{2,\infty}'} = \frac{2\sigma v_{2,0}''}{R_2 T r} + \ln n_2'' \gamma_2'' \qquad \text{(IV-12)}$$

from which the well known Köhler equation for equilibrium between humid air and an aqueous solution drop readily follows.

If the liquid does not contain any solute but is an electrically charged pure water drop eq. (11) becomes

$$\ln \frac{p_2'}{p_{2,\infty}'} = \frac{2\sigma_2 v_{2,0}''}{R_2 T r} - \frac{Q^2 v_{2,0}''}{8\pi\varepsilon R_2 T r^4} \qquad \text{(IV-13)}$$

an equation first derived by J. J. Thomson.

If the drop consists of pure water and is not electrically charged, eq. (11) becomes

$$\ln \frac{p_2'}{p_{2,\infty}'} = \frac{2\sigma_2 v_{2,0}''}{R_2 T r} \qquad \text{(IV-14)}$$

This is the Kelvin equation for the case of equilibrium between a pure water drop and humid air. The difference to the Kelvin equation (2) which applies to pure water vapour as gaseous phase should be noted.

At this point we wish to emphasize that during the integration of eqs. (1) and (10) leading to the results eqs. (2), (11), (12), (13) and (14) we have by no means supposed that the surface tension remains constant. The values of σ and σ_2 in the above relationships are those of the final state characterized by T, r, n_2'' and T, r respectively.

V. Energy of nucleus formation and equilibrium state

We shall now add to the preceding discussion on the equilibrium conditions for a small drop coexisting with a homogeneous gaseous phase a brief note on the energy necessary to form a drop embryo. In so doing we shall point out some rather widespread misconceptions appearing in the literature on being justified to deduce equilibrium conditions such as the Kelvin law from expressions for the energy of nucleus formation.

For the sake of simplicity we shall assume that the system consists of one component, say water substance (component 2), only. We have already justfied in the preceding sections that we must use the Hemholtz function F as the proper thermodynamic quantity for describing the process of formation of a new phase since this process can be considered to take place at constant volume and temperature. Denoting with F_0 the Helmholtz free energy of the system before the appearance of the new phase in volume V, at temperature T, and by F the Helmholtz free energy of the system containing mother phase and new phase in the same volume at the same temperature, the energy of nucleus formation is

$$(\Delta F)_{T,V} = F - F_0 \qquad \text{(V-1)}$$

where $F_0 = M_2 \mu_{2,0}' - p_0' V$ and $F = M_2' \mu_2' - p' V' + M_2'' \mu_2'' - p'' V'' + \sigma\Omega''$. If we use the approximations

$$\mu_2' \simeq \mu_{2,0}' \text{ and } p' \simeq p_0' \qquad \text{(IV-2)}$$

as well as the mechanical equilibrium condition $p'' = p' + (2\sigma/r)$ and consider further $V = V' + V''$ and $M_2 = M_2' + M_2''$ we find

$$(\Delta F)_{T,V} = M_2''(\mu_2'' - \mu_2') + \frac{1}{3}\sigma\Omega'' \qquad \text{(V-3)}$$

In the literature this expression is often erroneously identified with the Gibbs free enthalpy ΔG (Byers, 1965; Fletcher, 1962; Mason, 1971; Lothe & Pound, 1969). The error introduced in so doing may be shown readily by considering

$$\begin{aligned} \Delta G &= (\Delta F)_{T,V} + p' V' + p'' V'' - p_0' V \\ &\simeq (\Delta F)_{T,V} + (p'' - p') V'' \\ &= (\Delta F)_{T,V} + \tfrac{2}{3}\sigma\Omega \end{aligned} \qquad \text{(V-4)}$$

Thus we see that ΔG differs from $(\Delta F)_{T,V}$ by the quantity $(p'' - p') V''$ which is equal to $\frac{2}{3}\sigma\Omega$ supposing mechanical equilibrium. This quantity disappears only if one assumes a constant pressure process, i.e. if one replaces $(\Delta F)_{T,V}$ by $(\Delta G)_{T,p}$ where T, p denote the conjugate thermodynamic coordinates of G. However, as we remarked above, this clearly is not allowed since the pressure of the new phase p'' is not equal to the pressure of the

mother phase p'. For the case when the new phase is a drop, the overpressure $p''-p'$ becomes significant if the drop radius $r \leqslant 10^{-5}$ cm.

If eq. (3) is expressed in terms of the radius r of the new phase drop embryo and $(\Delta F)_{T,V}$ plotted as a function of r, schematically Fig. 1 is obtained.

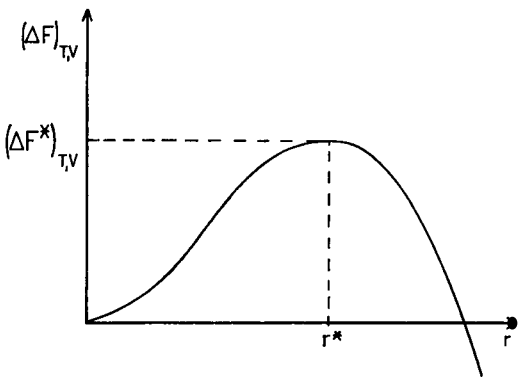

Fig. 1. Free energy of formation of an embryo of new phase in supersaturated air as a function of its radius r.

It is seen from this figure that $(\Delta F)_{T,V}$ increases from zero to a maximum $(\Delta F^*)_{T,V}$ at $r=r^*$. At embryo sizes larger than r^*, $(\Delta F)_{T,V}$ decreases indefinitely with increasing r. At the maximum where

$$\left[\frac{\partial(\Delta F)_{T,V}}{\partial r}\right]_{r=r^*} = 0 \qquad \text{(V-5)}$$

also the Helmholtz function F of the system drop–vapour passes through a maximum at which $(dF)_{T,V}=0$, saying that the new phase is produced spontaneously if $r>r^*$, since F is decreasing with increasing r. Because $r=r^*$ at $(dF)_{T,V}=0$, which represents a condition for equilibrium, the new phase drop-embryo of radius r^* must be considered in a metastable equilibrium with its environment. An embryo of such a size r^* is called a germ, and its size shall therefore be denoted by r_g. The energy necessary for germ formation is then readily found by introducing the equilibrium conditions $\mu_i' = \mu_i''$ in eq. (3). With this, one obtains

$$(\Delta F^*)_{T,V} = (\Delta F)_g = \tfrac{1}{3}\sigma_g \Omega_g \qquad \text{(V-6)}$$

Note that this equation holds by means of the assumptions (2).

Many authors have erroneously used eq. (5) for deriving the Kelvin equation. Such an approach cannot be justified, for several reasons. First of all we see that only one relation follows from eq. (5), namely a relation between r^* and p'. If eq. (5) were to represent an equilibrium condition it would necessarily need to produce other relations such as the equilibrium dependency between T and p' at given r and T and r at given p', which it clearly does not. In contrast to this, eq. (III-6), which is indeed an equilibrium condition, produces all the required relationships.

Secondly, eq. (3) is not an exact equation since it includes the approximations eq. (2). Only on these conditions has ΔF the maximum at the same r as F itself, so that $r^*=r_g$. In that artificial system state $\Delta F^*, r^*$, the Kelvin equation follows from maximising $\Delta F(r)$, if in addition the r-dependency of σ is disregarded, which denotes a further restriction.

If the approximations eq. (2) are not made, ΔF is in principle not maximum at the same r as F and thus $(\Delta F^*)_{T,V} \neq (\Delta F)_g \neq \frac{1}{3}\sigma_g \Omega_g$. Consequently one is not a priori allowed to take eq. (5) as a condition for equilibrium, as many authors in the literature have done.

List of symbols

T	= absolute temperature
r	= drop radius
Ω^j	= surface area of phase j ($j='', '''$)
V^j	= volume of phase j ($j=', '', '''$)
M^j	= mass of phase j ($j=', '', '''$)
v_k''	= partial specific volume of liquid
$\overset{+}{v}_k''$	= specific standard volume of liquid component k
$v_{k,0}''$	= specific volume of pure liquid component k
v	= specific volume of mixture or solution
R_k	= individual gas constant of component k
p_k^*	= partial fugacity in vapour phase
p_k'	= partial vapour pressure
p'	= total pressure in gas phase
p''	= total pressure in liquid phase
n_k''	= mole fraction in liquid phase
σ	= surface tension of liquid solution
σ_k	= surface tension of pure liquid component
μ_k^j	= chemical potential of component k in phase j.

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ПЕРЕСМОТР УСЛОВИЙ РАВНОВЕСИЯ В ТЕОРИИ НУКЛЕАЦИИ ВОДЯНЫХ КАПЕЛЬ

Пересматриваются термодинамические уравнения для описания условий равновесия между сильно искривленной поверхностью жидкости и ее паром. Описание полного равновесия достигается с помощью одного дифференциального уравнения для каждой компоненты в произвольной с-компонентной системе. Показано, что эта общая формулировка может быть специализирована для описания условий равновесия между водяным паром и каплей чистой воды, каплей, несущей электрический заряд, каплей, содержащей растворимую в воде примесь или нерастворимое ядро. В свете данной формулировки отмечаются некоторые физически некорректные утверждения в трактовке проблемы, высказанные в литературе различными авторами. В качестве дополнительного замечания обсуждается энергия формирования однородной капли воды и упоминаются некоторые ошибочные заключения, обычно выводимые в литературе при трактовке энергии образования зародышей.