

Bibliographie

- 1) R. Ducros, J. Wach et P. Le Goff, *Surface Science* 14 (1969) 181.
- 2) C. F. Robinson, *Rev. Sci. Instr.* 29 (1958) 250.
- 3) C. T. Sims, G. M. Graicehead et R. J. Jaffee, *J. Metals* 7 AIME Trans. 203 (1955) 168.
- 4) S. Tribalat, *Rhénium et Technétium* (Gauthier Villars, Paris, 1957).
- 5) J. E. Hughes, *J. Less Common Metals* 1 (1959) 377.
- 6) E. Fromm et U. Roy, *Phys. Status Solidi* 9 (1965) K 83.
- 7) J. Wach et P. Le Goff, *Revue des Hautes Températures et Réfractaires* 3 (1966) 165.
- 8) S. Dushman, *Scientific Foundations of Vacuum Technique* (Wiley, New York, 1965).
- 9) E. R. Plante et R. Szwarc, *J. Res. Develop. Natl. Bur. Std.* 70A (1966) 175.
- 10) R. Ducros et P. Le Goff, *Compt. Rend. (Paris)* (1968).
- 11) H. S. Carslaw et J. C. Jaeger, *Conduction of Heat in Solids* (Oxford Univ. Press, 1959).
- 12) R. Ducros et P. Le Goff, à paraître.

SOLUTION OF THE NON-STEADY STATE PROBLEM IN NUCLEATION KINETICS

D. KASHCHIEV

Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Received 13 August 1968

An approximate solution of the Zeldovich-Frenkel equation is obtained. Expressions are derived for the transient nucleation rate and for the time-lag. The analysis shows that the phenomena in the critical region play the decisive role during the establishment of the steady state. Finally, the possibility is indicated of comparing the theoretical results with experimental data.

1. Introduction

A central problem in the theory of the phase transformations is the derivation of the nucleation rate. The expression obtained by Volmer and Weber¹⁾, Farkas²⁾, Kaischew and Stranski³⁾, and Becker and Döring⁴⁾ represents, however, the steady state nucleation rate. Later Frenkel⁵⁾ and Zeldovich⁶⁾ considered nucleation as a non-steady state process and they arrived at a partial differential equation describing it. If its solution is known under defined initial and boundary conditions, subsequently one may easily find the transient nucleation rate $J_k(t)$ as a function of the time t .

Many papers⁶⁻¹²⁾ are devoted to the solution of the Zeldovich-Frenkel equation. In most of them, several more or less allowed assumptions and approximations are made as has been discussed in detail by Lyubov and Roitburd¹²⁾. The purpose of the present paper is to obtain an expression for $J_k(t)$, at the same time avoiding the assumptions which concern the physical picture of the process and which were hitherto made during the solution of the Zeldovich-Frenkel equation.

2. Formulation of the problem

Let us consider a thermodynamic system containing a constant number of atoms N , which occupy an invariable volume at a fixed absolute temperature T and a pressure $p \ll p_e$. At the moment $t=0$, let the pressure become $p > p_e$, where p_e is the equilibrium pressure. Then clusters of the daughter phase, stable under the new conditions, will begin to form in the system.

Let $Z(x, t)$ be the number of those clusters containing x atoms which exist in the mother phase at time t . If the supersaturation $s = \ln(p/p_e)$ remains invariable during the process, the distribution function $Z(x, t)$ satisfies, as is known⁶⁾, the Zeldovich-Frenkel equation

$$\frac{\partial Z(x, t)}{\partial t} = \frac{\partial}{\partial x} \left\{ D(x) Z_c(x) \frac{\partial}{\partial x} \left[\frac{Z(x, t)}{Z_c(x)} \right] \right\}, \quad (2.1)$$

subject to the initial and boundary conditions

$$\begin{aligned} Z(x, 0) &= 0 \quad (x > 1), \\ Z(1, t) &= Z_c(1), \\ Z(N, t) &= 0. \end{aligned} \quad (2.2)$$

In eq. (2.1), $D(x)$ is the probability per unit time of an atom joining to a cluster of size x and it is customarily assumed to be proportional to the surface area of the cluster, i.e.

$$D(x) = \alpha x^2, \quad (2.3)$$

where α is a frequency factor.

The equilibrium size distribution of clusters $Z_c(x)$ is obtained by Frenkel⁵⁾ in the form

$$Z_c(x) = N_1 \exp\left(-\frac{\Delta G(x)}{kT}\right), \quad (2.4)$$

where N_1 is the number of single atoms when the system is in equilibrium, k is the Boltzmann constant and $\Delta G(x)$ is the isothermal reversible work required for the formation of a cluster of size x . According to ref. 13,

$$\Delta G(x) = \Delta G_0 - kTsx + ax^{\frac{2}{3}}, \quad (2.5)$$

in which the constants a and ΔG_0 are known.

Finding the solution $Z(x, t)$ of (2.1) under conditions (2.2), we can obtain the transient nucleation rate $J_k(t)$ by means of the expression

$$J_k(t) = -D(x_k) Z_c(x_k) \left\{ \frac{\partial}{\partial x} \left[\frac{Z(x, t)}{Z_c(x)} \right] \right\}_{x=x_k}, \quad (2.6)$$

in which x_k is the size of the critical cluster, the so-called nucleus.

3. Solution of the equation

By introducing the function

$$F(x, t) = \frac{Z(x, t)}{Z_c(x)}, \quad (3.1)$$

eq. (2.1) and the initial and boundary conditions (2.2) become

$$\frac{\partial F(x, t)}{\partial t} = \frac{1}{Z_c(x)} \frac{\partial}{\partial x} \left[D(x) Z_c(x) \frac{\partial F(x, t)}{\partial x} \right], \quad (3.2)$$

$$\begin{aligned} F(x, 0) &= 0 \quad (x > 1), \\ F(1, t) &= 1, \\ F(N, t) &= 0. \end{aligned} \quad (3.3)$$

The boundary conditions become homogeneous if we write $F(x, t)$ in the form

$$F(x, t) = F_{st}(x) + \psi(x, t). \quad (3.4)$$

The time-independent function

$$F_{st}(x) = 1 - \left[\int_1^x \frac{dx}{D(x) Z_c(x)} \right]^{-1} \int_1^x \frac{d\xi}{D(\xi) Z_c(\xi)} \quad (3.5)$$

is a solution of the "steady state" equation

$$\frac{d}{dx} \left[D(x) Z_c(x) \frac{dF_{st}(x)}{dx} \right] = 0 \quad (3.6)$$

under the boundary conditions

$$F_{st}(1) = 1, \quad F_{st}(N) = 0. \quad (3.7)$$

Taking into account the last equalities and substituting (3.4) into (3.2), we get for the unknown function $\psi(x, t)$ the equation

$$\frac{\partial \psi(x, t)}{\partial t} = \frac{1}{Z_c(x)} \frac{\partial}{\partial x} \left[D(x) Z_c(x) \frac{\partial \psi(x, t)}{\partial x} \right], \quad (3.8)$$

with an initial condition

$$\psi(x, 0) = -F_{st}(x) \quad (x > 1), \quad (3.9)$$

and homogeneous boundary conditions

$$\psi(1, t) = 0, \quad \psi(N, t) = 0. \quad (3.10)$$

Further, following Chakraverty¹¹⁾, we try a solution of (3.8) in the form

$$\psi(x, t) = f(x) v(t).$$

Substitution of this expression into (3.8) gives

$$\frac{dv(t)}{v(t) dt} = \frac{1}{Z_c(x) f(x)} \frac{d}{dx} \left[D(x) Z_c(x) \frac{df(x)}{dx} \right] = -\lambda,$$

where λ is the separation constant. From this we find immediately that

$$v(t) = A e^{-\lambda t}, \quad A = \text{const.}$$

and $f(x)$ is given by the Sturm-Liouville equation

$$\frac{d}{dx} \left[D(x) Z_c(x) \frac{df(x)}{dx} \right] + \lambda Z_c(x) f(x) = 0, \quad (3.11)$$

under the boundary conditions

$$f(1) = 0, \quad f(N) = 0. \quad (3.12)$$

When eq. (3.11) is written in the form $(pv') - qv + \lambda pv = 0$ (ref. 14, p. 292), $q=0$ and therefore (ref. 14, p. 294), $\lambda > 0$. Furthermore, if $f_n(x)$ and λ_n are respectively the eigenfunctions and eigenvalues of (3.11), we can write the general solution of (3.8) as¹⁴

$$\psi(x, t) = \sum_{n=1}^{\infty} A_n f_n(x) e^{-\lambda_n t}, \quad (3.13)$$

where the constants A_n must be determined from the initial condition (3.9).

Thus the problem is to find all the $f_n(x)$, λ_n and A_n . Let us consider the equation

$$\frac{d}{dx} \left[D(x) Z_c(x) \frac{du(x)}{dx} \right] = 0,$$

in which $u(x)$ is unknown. As it may be directly verified, the function

$$u_1(x) = \int_1^x \frac{d\xi}{D(\xi) Z_c(\xi)} \quad (3.14)$$

satisfies the above equation with the boundary condition $u_1(1)=0$ and the function

$$u_2(x) = 1 - \left[\int_1^N \frac{dx}{D(x) Z_c(x)} \right]^{-1} \int_1^x \frac{d\xi}{D(\xi) Z_c(\xi)} \quad (3.15)$$

satisfies the same equation with the boundary condition $u_2(N)=0$.

It is known (ref. 14, p. 358) that eq. (3.11) with eq. (3.12) is equivalent to the Fredholm homogeneous integral equation of the second kind

$$f(x) = \lambda \int_1^N G(x, \xi) Z_c(\xi) f(\xi) d\xi. \quad (3.16)$$

Since $\lambda=0$ is not an eigenvalue of (3.11), the Green function $G(x, \xi)$ is determined as¹⁴

$$G(x, \xi) = \begin{cases} \frac{1}{c} u_1(x) u_2(\xi) & x \leq \xi \\ \frac{1}{c} u_2(x) u_1(\xi) & x \geq \xi \end{cases} \quad (3.17)$$

where

$$c = -D(x) Z_c(x) \left[u_1 \frac{du_2}{dx} - u_2 \frac{du_1}{dx} \right] = \text{const.} \quad (3.18)$$

Then (3.16) becomes

$$f(x) = \frac{\lambda}{c} u_2(x) \int_1^x u_1(\xi) Z_c(\xi) f(\xi) d\xi + \frac{\lambda}{c} u_1(x) \int_x^N u_2(\xi) Z_c(\xi) f(\xi) d\xi. \quad (3.19)$$

This equation gives us the possibility of drawing some conclusions about $f(x)$, but before doing so we must find explicitly $u_1(x)$ and $u_2(x)$. In order to calculate the integral (3.14) we shall neglect the size dependence (2.3) of $D(x)$ and we shall assume according to ref. 6 that

$$D(x) \approx \alpha x_k^2 \equiv D_k. \quad (3.20)$$

Since $\Delta G(x)$ from (2.5) has a sharp maximum at $x=x_k$, the Taylor development

$$\Delta G(x) \approx \Delta G(x_k) + \frac{1}{2} \left[\frac{d^2 \Delta G(x)}{dx^2} \right]_{x=x_k} (x-x_k)^2$$

may be used and the equilibrium distribution (2.4) becomes⁶

$$Z_c(x) = Z_k \exp \kappa (x-x_k)^2, \quad (3.21)$$

where

$$Z_k \equiv Z_c(x_k),$$

$$\kappa = -\frac{1}{2kT} \left[\frac{d^2 \Delta G(x)}{dx^2} \right]_{x=x_k} > 0. \quad (3.22)$$

Then from (3.14) we find

$$u_1(x) = \frac{\sqrt{\pi}}{2\sqrt{\kappa D_k Z_k}} \{ \phi[\sqrt{\kappa}(x-x_k)] - \phi[\sqrt{\kappa}(1-x_k)] \},$$

where $\phi(z)$ is the error integral

$$\phi(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\zeta^2) d\zeta. \quad (3.23)$$

Denoting $\phi_x \equiv \phi[\sqrt{\kappa}(x-x_k)]$, we get

$$u_1(x) = \frac{\sqrt{\pi}}{2\sqrt{\kappa}D_kZ_k} (\phi_x - \phi_1) \quad (3.24)$$

and proceeding in the same manner we obtain from (3.15)

$$u_2(x) = \frac{\phi_N - \phi_x}{\phi_N - \phi_1}. \quad (3.25)$$

It must be noted that the approximation made [eq. (3.20)] is not a severe one, since the dependence of $D(x)$ on size, which is not very strong in itself, is of minor importance in view of the sharp maximum of $Z_c(x)$ for $x=x_k$.

The properties of the error integral (3.23) are such that $\phi(2) \approx 0.995$ (ref. 15), and therefore we may consider that its z -dependence is essential only for $|z| < 2$. When $|z| \geq 2$, with a good approximation $|\phi(z)| = 1$. Hence for the function ϕ_x we shall have

$$\phi_x = \begin{cases} -1 & 1 \leq x \leq x_k - \varepsilon \\ \phi_x & |x - x_k| < \varepsilon \\ 1 & x_k + \varepsilon \leq x \leq N \end{cases}$$

where the constant ε is given by the relation

$$\varepsilon\sqrt{\kappa} = 2. \quad (3.26)$$

Two cases are possible:

a) $\sqrt{\kappa}(x_k - 1) \geq 2$.

b) $\sqrt{\kappa}(x_k - 1) < 2$.

In case a), taking into account the behaviour of ϕ_x , we have $\phi_1 = -1$ and $\phi_N = 1$. From (3.24) and (3.25) we find for the functions $u_1(x)$ and $u_2(x)$

$$u_1(x) = \begin{cases} 0 & 1 \leq x \leq x_k - \varepsilon \\ \frac{\sqrt{\pi}}{2\sqrt{\kappa}D_kZ_k} (\phi_x + 1) & |x - x_k| < \varepsilon \\ \frac{\sqrt{\pi}}{\sqrt{\kappa}D_kZ_k} & x_k + \varepsilon \leq x \leq N \end{cases} \quad (3.27)$$

$$u_2(x) = \begin{cases} 1 & 1 \leq x \leq x_k - \varepsilon \\ \frac{1}{2}(1 - \phi_x) & |x - x_k| < \varepsilon \\ 0 & x_k + \varepsilon \leq x \leq N. \end{cases}$$

In case b), $\phi_1 \neq -1$, $\phi_N = 1$ and the functions $u_1(x)$ and $u_2(x)$ become

$$u_1(x) = \begin{cases} \frac{\sqrt{\pi}}{2\sqrt{\kappa}D_kZ_k} (\phi_k - \phi_1) & 1 \leq x < x_k + \varepsilon \\ \frac{\sqrt{\pi}}{2\sqrt{\kappa}D_kZ_k} (1 - \phi_1) & x_k + \varepsilon \leq x \leq N \end{cases}$$

$$u_2(x) = \begin{cases} \frac{1 - \phi_x}{1 - \phi_1} & 1 \leq x < x_k + \varepsilon \\ 0 & x_k + \varepsilon \leq x \leq N. \end{cases}$$

Case a) will be the subject of further considerations.

The interval $[x_k - \varepsilon, x_k + \varepsilon]$ with a length

$$\Delta_k = 2\varepsilon \quad (3.28)$$

has a simple physical meaning: it corresponds to the critical region, introduced by Zeldovich⁶⁾, in which the difference $\Delta G(x_k) - \Delta G(x)$ is less than kT .

From (3.28) we get by means of (3.26)

$$\Delta_k = 4 \left(\frac{-2kT}{[d^2 \Delta G(x)/dx^2]_{x=x_k}} \right)^{\frac{1}{2}}. \quad (3.29)$$

Returning to eq. (3.19) and using (3.27), we find that

$$f(x) \equiv 0 \quad (3.30)$$

for every value of x outside the critical region. Within it ($|x - x_k| < \varepsilon$), $f(x) \neq 0$ and eq. (3.19) holds. Double differentiation of eq. (3.19) gives

$$\frac{d^2 f(x)}{dx^2} = \frac{\lambda}{c} \left[\left(u_1 \frac{du_2}{dx} - u_2 \frac{du_1}{dx} \right) Z_c(x) f(x) + \frac{d^2 u_2}{dx^2} \int_1^x u_1 Z_c f d\xi + \frac{d^2 u_1}{dx^2} \int_x^N u_2 Z_c f d\xi \right].$$

We may obtain an approximate solution of this equation by considering that $u_1(x)$ and $u_2(x)$ are linear functions of x when $|x - x_k| < \varepsilon$. Then

$$\frac{d^2 u_1}{dx^2} = \frac{d^2 u_2}{dx^2} = 0,$$

and by means of (3.18) and (3.20) the above equation becomes

$$\frac{d^2 f(x)}{dx^2} + \frac{\lambda}{D_k} f(x) = 0. \quad (3.31)$$

In accordance with (3.30) the boundary conditions of (3.31) will be

$$f(x_k - \varepsilon) = 0, \quad f(x_k + \varepsilon) = 0, \quad (3.32)$$

i.e. we have "shifted" (3.12) to the ends of the critical region.

The solution of eq. (3.31) with (3.32) is known¹⁴). By using (3.26) for the eigenfunctions $f_n(x)$ and the eigenvalues λ_n , we obtain

$$f_n(x) = \sin(n\pi/2\varepsilon)(x - x_k + \varepsilon), \\ \lambda_n = \frac{1}{16} n^2 \pi^2 \kappa D_k, \quad n = 1, 2, 3, \dots$$

From these equalities together with (3.4) and (3.13) we find that, when $|x - x_k| \leq \varepsilon$,

$$F(x, t) = F_{st}(x) + \sum_{n=1}^{\infty} A_n \sin(n\pi/2\varepsilon)(x - x_k + \varepsilon) \times \\ \times \exp(-\frac{1}{16} n^2 \pi^2 \kappa D_k t), \quad (3.33)$$

where

$$A_n = -\frac{1}{\varepsilon} \int_{x_k - \varepsilon}^{x_k + \varepsilon} F_{st}(x) \sin(n\pi/2\varepsilon)(x - x_k + \varepsilon) dx$$

in view of the initial condition (3.3).

It must be noted that the precise calculation of the constants A_n from the last equality runs into mathematical difficulties. However, the considerations adduced below allow them to be replaced by

$$A'_n = -\frac{1}{\varepsilon} \int_{x_k - \varepsilon}^{x_k + \varepsilon} [\frac{1}{2} - (\kappa/\pi)^{\frac{1}{2}}(x - x_k)] \sin(n\pi/2\varepsilon)(x - x_k + \varepsilon) dx. \quad (3.34)$$

Since, according to (2.6) and (3.1), $J_k(t)$ is given by the relationship

$$J_k(t) = -D_k Z_k \left[\frac{\partial F(x, t)}{\partial x} \right]_{x=x_k}, \quad (3.35)$$

it appears that for its derivation it is enough to know $F(x, t)$ only in one arbitrarily small neighbourhood $[x_k - \delta, x_k + \delta]$ of x_k ($0 < \delta < \varepsilon$). By virtue of (3.5) and (3.15), $F_{st}(x) \equiv u_2(x)$ and in this neighbourhood it can be considered approximately as a straight line passing through the point $(x_k, \frac{1}{2})$ with a slope

$$\left[\frac{dF_{st}(x)}{dx} \right]_{x=x_k} = - \left[D_k Z_k \int_1^N \frac{dx}{D(x) Z_k(x)} \right]^{-1}.$$

Since in accordance with (3.14) and (3.27)

$$\int_1^N \frac{dx}{D(x) Z_k(x)} = u_1(N) = \frac{\sqrt{\pi}}{\sqrt{\kappa D_k Z_k}}, \quad (3.36)$$

for $F_{st}(x)$ we shall have $(|x - x_k| \leq \delta)$

$$F_{st}(x) = \frac{1}{2} - (\kappa/\pi)^{\frac{1}{2}}(x - x_k).$$

Thus when $|x - x_k| \leq \delta$, we get from (3.33) and the last expression

$$F(x, t) = \frac{1}{2} - \left(\frac{\kappa}{\pi}\right)^{\frac{1}{2}}(x - x_k) + \sum_{n=1}^{\infty} A'_n \sin \frac{n\pi}{2\varepsilon}(x - x_k + \varepsilon) \times \\ \times \exp(-\frac{1}{16} n^2 \pi^2 \kappa D_k t), \quad (3.37)$$

in which the constants A'_n are given by (3.34). Their derivation does not present any difficulty:

$$A'_n = \frac{1}{n\pi} \left(\cos n\pi - 1 - \frac{4}{\sqrt{\pi}} - \frac{4}{\sqrt{\pi}} \cos n\pi \right).$$

Substitution of this result in (3.37) gives $F(x, t)$ when $|x - x_k| \leq \delta$

$$F(x, t) = \frac{1}{2} - \left(\frac{\kappa}{\pi}\right)^{\frac{1}{2}}(x - x_k) + \\ + \sum_{n=1}^{\infty} \frac{1}{n\pi} \left[\cos n\pi - 1 - \frac{4}{\sqrt{\pi}}(1 + \cos n\pi) \right] \sin \frac{n\pi}{2\varepsilon}(x - x_k + \varepsilon) \times \\ \times \exp(-\frac{1}{16} n^2 \pi^2 \kappa D_k t) \quad (3.38)$$

4. Transient nucleation rate

By using (3.35) and (3.26), we find from (3.38) for the transient nucleation rate

$$J_k(t) = J_{st} \left(1 + 2 \sum_{n=1}^{\infty} \cos(\frac{1}{2}n\pi) \exp(-\frac{1}{16} n^2 \pi^2 \kappa D_k t) \right) \quad (4.1)$$

since in accordance with (3.5), (3.35) and (3.36) the steady state rate of nucleation J_{st} is given by the relation

$$J_{st} = \frac{\sqrt{\kappa D_k Z_k}}{\sqrt{\pi}}. \quad (4.2)$$

Since it may be directly verified that

$$\sum_{n=1}^{\infty} \cos(\frac{1}{2}n\pi) \exp(-\frac{1}{16} n^2 \pi^2 \kappa D_k t) = \sum_{n=1}^{\infty} (-1)^n \exp(-\frac{1}{4} n^2 \pi^2 \kappa D_k t)$$

then (4.1) becomes

$$J_k(t) = J_{st} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 t/\tau) \right], \quad (4.3)$$

where τ , the time-lag, is given by

$$\tau = 4/\pi^2 \kappa D_k.$$

When $t > \tau$, only the first term contributes practically to the infinite sum. Using (3.22), we obtain from the last equality

$$\tau = - \frac{8kT}{\pi^2 D_k [d^2 \Delta G(x)/dx^2]_{x=x_k}}. \quad (4.4)$$

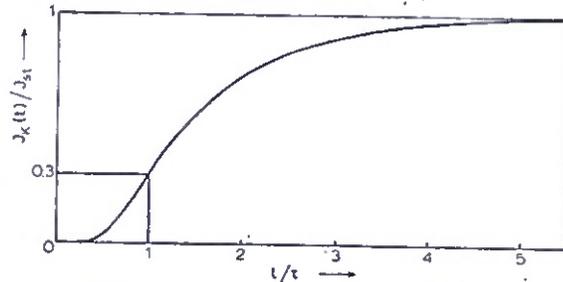


Fig. 1. Plot of $J_k(t)/J_{st}$ versus the ratio t/τ .

The time dependence of the transient nucleation rate is plotted in fig. 1. It is immediately seen that at the moment $t_{tr} \approx 5\tau$, $J_k(t)$ reaches 99% of its steady state value J_{st} . Consequently, we can consider that after the transition time

$$t_{tr} = - \frac{4kT}{D_k [d^2 \Delta G(x)/dx^2]_{x=x_k}}, \quad (4.5)$$

we achieve the steady state nucleation rate.

5. Possibilities for comparison with experiment

The relationship (4.3) cannot be verified by direct experiment. Usually one observes the time dependence of the total number $N_k(t)$ of nuclei, formed in the system. It is clear that $N_k(t)$ will be given by the integral

$$N_k(t) = \int_0^t J_k(\theta) d\theta. \quad (5.1)$$

Substitution of $J_k(t)$ from (4.3) in this equality gives after a formal integration of the infinite series

$$N_k(t) = J_{st} \left[t - \frac{1}{6} \pi^2 \tau - 2\tau \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-n^2 \frac{t}{\tau}\right) \right], \quad (5.2)$$

in which we have used¹⁶⁾

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} = -\frac{1}{12} \pi^2.$$

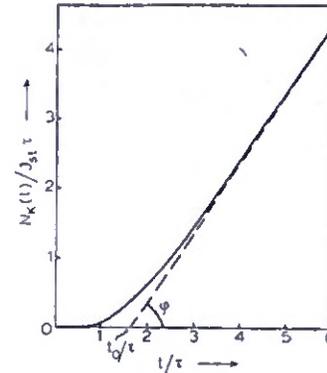


Fig. 2. Plot of $N_k(t)/J_{st}$ versus the ratio t/τ .

The dependence of $N_k(t)$ on t is shown in fig. 2. The asymptote of (5.2) is the following straight line

$$N_{as}(t) = J_{st} (t - \frac{1}{6} \pi^2 \tau). \quad (5.3)$$

For $t > t_{tr}$, $N_{as}(t)$ and $N_k(t)$ are practically identical. Denoting by φ the angle between the asymptote and the time axis, and by t_0 the t -value for which $N_{as} = 0$ (fig. 2), we find from (5.3)

$$J_{st} = t_0 \varphi, \quad \tau = \frac{6}{\pi^2} t_0. \quad (5.4)$$

These expressions give the relation between the theoretically obtained J_{st} , eq. (4.2), and τ , eq. (4.4), and the experimental quantities $t_0 \varphi$ and t_0 .

6. Discussion

The consideration of the non-steady state nucleation problem in the above manner enables some conclusions to be made. Thus the critical region with

a length Δ_k , introduced by Zeldovich⁶⁾, has the following physical meaning: only within it, in view of (3.1), (3.4), (3.13) and (3.30), does the non-steady state distribution $Z(x, t)$ differ essentially from the steady state distribution $Z_{st}(x)$. This important fact has allowed us to "shift" the boundary conditions (3.12) to the ends of the critical region. As Lyubov and Roitburd¹²⁾ show, a similar operation has been tacitly performed in certain papers⁶⁻¹⁰⁾ without rigorous justification.

We consider that the relationships (4.3), (5.2) and (5.4) also hold good when the nucleation is heterogeneous. In this case, however, it is necessary to replace J_{st} and τ in them with the steady state rate J_{st}^* and time-lag τ^* corresponding to the heterogeneous nucleation. The derivation of J_{st}^* and τ^* for different cases is discussed by Hirth and Pound¹⁷⁾ and by Toshev and Gutzow¹⁸⁾.

Acknowledgements

The author acknowledges gratefully the interest and encouragement of Professor R. Kaischew. Thanks are also due to Drs. D. Nenow, S. Toshev and S. Stoyanov for stimulating discussions.

References

- 1) M. Volmer and A. Weber, *Z. Physik. Chem.* **119** (1925) 277.
- 2) L. Farkas, *Z. Physik. Chem.* **125** (1927) 236.
- 3) R. Kaischew and I. Stranski, *Z. Physik. Chem. B* **26** (1934) 317.
- 4) R. Becker and W. Döring, *Ann. Physik* **24** (1935) 719.
- 5) J. I. Frenkel, *Kinetic Theory of Liquids* (Oxford Univ. Press, London, 1946).
- 6) J. B. Zeldovich, *Acta Physicochim. URSS* **18** (1943) 1.
- 7) R. F. Probst, *J. Chem. Phys.* **19** (1951) 619.
- 8) A. Kantrowitz, *J. Chem. Phys.* **19** (1951) 1097.
- 9) H. Wakeshima, *J. Chem. Phys.* **22** (1954) 1614.
- 10) F. C. Collins, *Z. Elektrochem.* **59** (1955) 404.
- 11) B. K. Chakraverty, *Surface Sci.* **4** (1966) 205.
- 12) B. J. Lyubov and A. L. Roitburd, in: *Problemy Metallovedeniya i Fiziki Metallov*, Vol. 5 (Metallurgizdat, Moscow, 1958) p. 91.
- 13) J. Lothe and G. M. Pound, *J. Chem. Phys.* **36** (1962) 2080.
- 14) R. Courant and D. Hilbert, *Methods of Mathematical Physics*, Vol. 1 (Interscience, New York, 1953).
- 15) E. Janke, F. Emde and F. Lösch, *Tafeln höherer Funktionen* (B. G. Teubner, Stuttgart, 1960).
- 16) I. M. Rijik and I. S. Gradstein, *Tablitsi Integralov, Summ, Ryadov i Proizvedenii* (Fizmatgiz, Moscow, 1962).
- 17) J. P. Hirth and G. M. Pound, *Condensation and Evaporation* (Pergamon Press, London, 1963).
- 18) S. Toshev and I. Gutzow, *Phys. Status Solidi* **21** (1967) 683.

THERMODYNAMICS OF SURFACE PHASE SYSTEMS*

V. CONTRIBUTION TO THE THERMODYNAMICS OF THE SOLID-GAS INTERFACE

JAN CHRISTER ERIKSSON**

Physical Sciences Division, Georgia Institute of Technology, Atlanta, Georgia, U.S.A.

Received 7 July 1968

A thermodynamic fundamental equation is derived for the surface phase of a solid exposed to an adsorbing gas. This equation is more general than the corresponding equation given by Gibbs in the sense that it is applicable with less restriction as to the state of strain of the solid surface. An equation relating the surface tension to the reversible cleavage work which is similar to the Shuttleworth equation is shown to be implied in the fundamental equation deduced. Some new thermodynamic expressions are obtained for the effect of temperature and gas pressure changes on the surface tension and on the reversible cleavage work. Measurements of adsorbent dimensional changes, heats of adsorption and surface structure transitions are discussed on the basis of the formalism developed.

1. Introduction

In this series of papers the thermodynamics of plane surface phase systems is treated on the basis of the Gibbs-Verschaffelt-Guggenheim approach with special emphasis on problems related to the use of *two* dividing surfaces for the definition of a surface phase of non-zero thickness. The systems considered in the previous papers of the series¹⁻⁴⁾ are in the first place fluid surface phase systems. Using similar theoretical methods, in the present paper a rather general thermodynamic analysis of the solid-gas interface is attempted.

Gibbs⁵⁾ pointed out that the actual surface tension γ at a solid-fluid interface can differ from the excess free energy surface density g_{ex}^* and he made a distinction between the work of *stretching* the surface that is related to γ and the work of *forming* new surface area that is related to g_{ex}^* .*** He also stated that the ordinary fundamental equation of the Gibbs-Duhem kind in the thermodynamics of fluid surface phase systems which may be

* Work supported in part by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under Contract F 44620-68C-0008.

** Permanent address: Institute of Physical Chemistry, University of Gothenburg, Gothenburg, Sweden.

*** The nomenclature used here is essentially the same as that of Benson and Yun⁶⁾ and we accordingly avoid the confusing usage of the name "surface tension" for g_{ex}^* .