Effect of Diffusion on the Kinetics of Crystallization

E. A. ARENSTEIN
Tomsk Engineering and Construction Institute

(Submitted to JETP editor August 15, 1955)
J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 414-416
(February, 1956)

IN the diffusion theory of crystal growth the only factor which is considered to influence the speed of growth is the speed of diffusion of the precipitating substance to the growing face of the crystal. The influence of the physical and chemical properties of the surface is not taken into consideration, and the concentration of the solution near the growing face is taken to be equal to the saturation concentration. This theory explains a number of interesting phenomena[1-4], but its starting point is in sharp contradiction with the Curie-Woolf principle and with a number of experimental facts - for instance with the finite speed of growth during the intensive mixing of the solution[5-6].

The relative influence of diffusion and the physical and chemical properties of the surface can be clarified by the example of the growth of the plane face. We exclude convection and mixing from our consideration. The problem reduces to solving the diffusion equation.

$$\frac{\partial c}{\partial t} + D\frac{\partial^2 c}{\partial x^2} = 0 \qquad (1)$$

(where $c(x, t)$ is the concentration, and D is the coefficient of diffusion) in the region $x > 0;\ t > 0$ for the initial and limiting conditions

$$c(x, 0) = c_\infty, \quad c(\infty, t) = c_\infty \qquad (2)$$

and for the conditions on the face of the crystal determined by the physical and chemical processes of growth. Diffusion theory assumes the condition

$$c(0, t) = c_0, \qquad (3)$$

where c_0 is the concentration of the saturated solution.

The speed of growth is determined by the necessity for the coexistance of condition (3) and the condition which expresses the law of conservation of matter on the face

$$D(\partial c/\partial x)_{x=0} = \delta V(t), \qquad (4)$$

where δ is the density of the crystal, and $V(t)$ is the speed of growth.

When the properties of the surface are taken into consideration condition (3) must be replaced by a condition of the type[7,8]:

$$V(t) = k\,[c^n(t, 0) - c_0^n] \qquad (5)$$

(where n is the order of the process and k the kinetic coefficient). This equation follows from the law of mass action, or from molecular and kinetic considerations. The speed of growth is determined by the necessity for the coexistence of (4) and (5). When the movement of the face is taken into consideration the problem is reduced to the former type by a substitution of variables, but in the second term of equation (1) there appears a factor $(\rho - c_\infty)/\rho^*$ of the order of unity. ρ is the density of the solution, ρ^* – the density of the clean solvent. We neglect this factor since it is unimportant.

Equation (1) with conditions (2) and (3) has the solution

$$c = c_\infty - (c_\infty - c_0)\,\mathrm{erfc}\,(x/2\sqrt{Dt}), \qquad (6)$$

where $\mathrm{erfc}\,(z) = \frac{2}{\sqrt{\pi}}\int\limits_z^\infty e^{-u^2}du.$ From (4) we determine the speed of growth

$$V(t) = \sqrt{D\pi t}\,(c_\infty - c_0)\,\delta, \qquad (7)$$

which, as usual, in diffusion theory does not depend on the properties of the face.

Let us discard condition (3). Equation (1) with conditions (2) and (4) has the solution

$$c = c_\infty - \frac{\delta}{\sqrt{\pi D}}\int\limits_0^t V(t')\,e^{-x^2/4D(t-t')}\frac{dt'}{\sqrt{t-t'}} \qquad (8)$$

$$= c_\infty - \frac{\delta x}{D\sqrt{\pi}}\int\limits_{x/2\sqrt{Dt}}^\infty V\left(t - \frac{x^2}{4Dz^2}\right)e^{-z^2}dz.$$

The requirement that conditions (4) and (5) hold gives the equation for the speed of growth

$$V(t) = k\left[\left(c_\infty - \frac{\delta}{\sqrt{\pi D}}\int\limits_0^t \frac{V(t')\,dt'}{\sqrt{t-t'}}\right)^n - c_0^n\right]. \qquad (9)$$

Equation (9) can be easily solved by expanding it in powers of $\sqrt{t}$: :

$$V(t) = k\,(c_\infty^n - c_0^n) \qquad (10)$$

$$- \frac{2n\delta k^2}{\sqrt{\pi D}}\,c_\infty^{n-1}(c_\infty^n - c_0^n)\sqrt{t} + \dots$$

It is obvious from the above that in the initial phase of the process diffusion plays a secondary role, but asymptotically, for large values of t, the speed of growth is determined exclusively by diffusion. Actually it is seen from Eq. (9) that when $t \to \infty$ $V \approx at^{-1/2}$; a is determined by substitution into (9), and we obtain the asymptotic speed of growth, which coincides with (7).

Our conclusions, as one can easily be convinced, are preserved for a different choice of conditions on the face, for instance, for a condition of the type

$$V(t) = k\,[c(0,\, t) - c_0]^n. \tag{11}$$

Equation (9) can be easily solved for the case of a process of the first order, $n = 1$. Dividing Eq. (9) for $n = 1$ by $\sqrt{t'' - t}$, , integrating with respect to t from 0 to t'', and changing the order of integration in the last term, we get the equation

$$\frac{\sqrt{\pi D}}{\delta}(c_\infty - c_0) - \frac{\sqrt{\pi D}}{k\delta} V(t) = 2k\,(c_\infty - c_0)\sqrt{t} - \frac{k\delta\sqrt{\pi}}{\sqrt{D}} \int_0^t V(t')\,dt',$$

which has the following solution

$$V(t) = k\,(c_\infty - c_0)\, e^{k^2\delta^2 t/D} \operatorname{erfc}(k\delta\sqrt{t/D}). \tag{12}$$

Using the asymptotic expansion

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}}\, e^{-z^2} \sum_{n=0}^{\infty} \frac{(-1)^n\,(2n)!}{n!\,(2z)^{2n-1}},$$

we obtain the known expression for the asymptotic behavior of the speed of growth and the criterion for the applicability of diffusion theory in the form

$$k^2\delta^2 t/D \gg 1. \tag{13}$$

From Eq. (8) one can easily determine the thickness of the depleted zone: $\Delta = 2\sqrt{Dt}$. Then criterion (13) assumes the form $k\delta\Delta/D \gg 1$. Diffusion is the dominating factor after the solution is depleted in an adequately wide zone; however, this factor is inhibiting. Mixing and convection reduce the influence of diffusion to zero, and the properties of the surface become of primary importance. The role of heat-transfer during crystallization after smelting is considered in a similar way.

---

[1] I. V. Salli, J. Exptl. Theoret. Phys. (U.S.S.R.) 25, 208 (1953).

[2] F. S. A. Sultan, Phil. Mag. 43, 1099 (1952).

[3] J. A. Barton, R. C. Prim and W. P. Slicter, J. Chem. Phys. 21, 1987, 1991 (1953).

[4] N. I. Litunovskii and O. M. Todes, J. Tech. Phys. (U.S.S.R.) 23, 1125 (1953).

[5] M. Tovbin, Zh. Fiz. Khim. 20, 1435 (1946).

[6] A. V. Beljustin, J. Exptl. Theoret. Phys. (U.S.S.R.) 28, 725 (1955).

[7] D. A. Frank-Kamenetskii, Zh. Fiz. Khim. 13, 756 (1939).

N. A.

[8] N. A. Figurovskii and T. A. Komarova, Zh. Fiz. Khim Khim. 28, 1479 (1954).

Translated by M. Polonsky
75

Relativistic Repulsion Effects in a Scalar Field and Attraction Effects in a Vector Field

IA. P. TERLETSKII
Institute of Nuclear Problems

(Submitted to JETP editor November 10, 1955)
J. Exptl. Theoret. Phys. (U.S.S.R.) 30
419-420 (February, 1956)

IN the recent times, it has been shown by a number of authors[1-6] that in the relativistic theory of a particle moving in a scalar field, the effect of relativistic repulsion takes place. For instance, in the case of a radial field with a purely attractive potential this effect produces a repulsion in the neighborhood of the center. In quantum mechanics this effect has been discovered and investigated by Kuni and Taksar[1], in the case of a Dirac particle with spin. The effect of relativistic repulsion for a classical particle has been investigated most prominently by Werle[2] , Marks and Chamosi[3] and also by Infeld.[4] Werle[5] considered also the case of a spinless quantum particle, subject to the Klein-Gordon equation, in a scalar and a vector field, and showed that, in the non-relativistic approximation, some additional effective potentials appear which can be considered as repulsive potentials in the case of a scalar field, and as attractive potentials in the case of a static vector field. It is easy to show, however, that the latter deduction can be made without making a non-relativistic approximation. Furthermore, for a spinless particle, the existence of relativistic effects--repulsive in a scalar field and attractive in a static vector field--can be deduced in a very convincing and clear manner.

The Klein-Gordon equation for a spinless particle in a scalar field with potential Φ, and simultaneously in a vector field with potential A, A_4