

21. J. C. Rainwater and M. R. Moldover, Chemical Engineering at Supercritical Fluid Conditions, Ann Arbor, Mich. (1983), Chap. 10, pp. 199-218.
22. M. A. Anisimov, S. B. Kiselev, I. G. Kostukova, and V. A. Rabinovich, Proc. 10th Int. Conf. on the Properties of Steam, Moscow USSR (1985), Part 1, pp. 65-74.

## MACROKINETIC EQUATIONS FOR A PHASE

### TRANSITION OF THE FIRST SORT

M. I. Il'in and A. A. Zhitinkin

UDC 517.2:541.12.01

Differential equations are derived for phase transition kinetics. Analytic solutions are obtained for linear dependence of new phase growth rate on the degree of completion of the phase transition.

A phase transition of the first sort in solutions or alloys involves the simultaneous stages of new phase nucleus formation and growth [1-3]. Let  $I(t)$  be the frequency of nucleus formation per unit volume at time  $t$ , while  $v(t, \tau)$  is the volume of the growing center at the actual time  $\tau$ . In analogy to [2], but for systems in which only a definite fraction of the material  $\alpha^*$  can transform to the new phase (as is characteristic, for example, of polymer systems where  $\alpha^* = 0.1-0.9$ ), one can write the following integral equation:

$$\alpha(\tau) = \frac{\rho_A}{\rho_k} \int_0^\tau v(t, \tau) I(t) [\alpha^* - \alpha(t)] dt, \quad 0 \leq \alpha \leq \alpha^*, \quad (1)$$

where

$$v(t, \tau) = \beta \left[ \int_t^\tau G(\eta) d\eta \right]^n; \quad t \leq \eta \leq \tau. \quad (2)$$

Introducing the degree of completion  $X = \alpha/\alpha^*$ , we write Eqs. (1), (2) in the form

$$X(\tau) = a \int_0^\tau [I(t, \tau)]^n I(t) [1 - X(t)] dt; \quad (3)$$

$$I(t, \tau) = \int_t^\tau G(\eta) d\eta; \quad a = \rho_A \beta / \rho_k. \quad (4)$$

When the quantities  $I$  and  $G$  are variable, integral equation (3) is nonlinear, and its solution is extremely difficult. For constant  $I$  and  $G$  analytical solutions of Eq. (3) have been obtained [2-4], but they describe only the free growth stage up to values of  $X = 0.1-0.3$ , after which the solutions lose physical meaning.

For this reason, despite the fact that the formulation of Eqs. (3), (4) is the most physically correct and formal, at present other approaches are used to describe phase transition kinetics [1-9].

In the present study integral equations (3), (4) will be transformed to a differential equation convenient for practical applications. We write Eqs. (3), (4) in the form

$$X(\tau) = a \int_0^{\tau} [I(\tau) - I(t)]^n \frac{I(t)}{G(t)} [1 - X(t)] dl(t); \quad (5)$$

$$I(\tau) = \int_0^\tau G(\eta) d\eta; \quad I(t) = \int_0^t G(\eta) d\eta. \quad (6)$$

In accordance with [10] the integral in Eq. (5) can be replaced by a multiple integral

---

"Polimersintez" Scientific Production Union, Vladimir. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 54, No. 1, pp. 117-121, January, 1988. Original article submitted August 21, 1986.

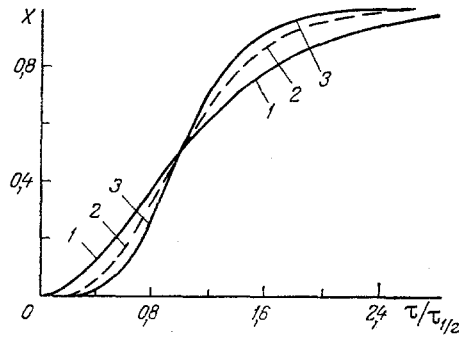


Fig. 1. Theoretical isotherms of phase transition kinetics. Digits on curves are growth dimensionality  $n$ .

$$X(\tau) = an! \underbrace{\int_0^{\tau} \int_0^{\tau} \dots \int_0^{\tau}}_{n+1} \frac{I(t)}{G(t)} [1 - X(t)] dt \dots dt,$$

and differentiation of the latter yields

$$\frac{d^{(n+1)} X(\tau)}{[G(\tau) d\tau]^{n+1}} = an! \frac{I(\tau)}{G(\tau)} [1 - X(\tau)]. \quad (7)$$

We rewrite Eq. (7) in a more expanded form:

$n = 1$  (one-dimensional growth)

$$\frac{d}{d\tau} \left[ \frac{1}{G(\tau)} \frac{dX}{d\tau} \right] = aI(\tau) (1 - X); \quad (8)$$

$n = 2$  (two-dimensional growth)

$$\frac{d}{d\tau} \left\{ \frac{1}{G(\tau)} \frac{d}{d\tau} \left[ \frac{1}{G(\tau)} \frac{dX}{d\tau} \right] \right\} = 2aI(\tau) (1 - X); \quad (9)$$

$n = 3$  (three-dimensional growth)

$$\frac{d}{d\tau} \left( \frac{1}{G(\tau)} \frac{d}{d\tau} \left\{ \frac{1}{G(\tau)} \frac{d}{d\tau} \left[ \frac{1}{G(\tau)} \frac{dX}{d\tau} \right] \right\} \right) = 6aI(\tau) (1 - X). \quad (10)$$

The initial conditions for Eqs. (7)-(10) follow from Eq. (3)

$$X(0) = 0; \quad \frac{d^{(n)} X(0)}{d\tau^n} = 0. \quad (11)$$

In practical numerical calculations it is desirable to transform from the  $(n + 1)$ -th order Eqs. (8)-(10) to a system of  $(n + 1)$  ordinary differential equations.

In integrating Eq. (7) it is necessary to specify the concrete form of the function  $G(\tau)$ , which characterizes mutual suppression (collision) of the growing surfaces. We define the mean growth rate  $G$  by means of the following material balance:  $GS = G_0S_0$ , where  $S_0$  is the freely growing surface and  $S$  is the total surface (free and covered at a given moment of time). If we assume that the fraction of free surface  $S_0/S$  is proportional to the fraction  $\alpha^* - \alpha$  of material which has yet to undergo the  $p$  phase transition, we obtain

$$G(\tau) = G_0(\tau) h\alpha^* [1 - X(\tau)], \quad (12)$$

where  $h$  is a proportionality coefficient.

We will note that for  $G_0(\tau) = \text{const}$  (for example, isothermal conditions) it follows from Eq. (12) that  $G(\tau)$  depends on time only through the degree of completion  $X(\tau)$ . Substituting Eq. (12) in Eq. (7), we obtain

$$\frac{d^{(n+1)} X}{d\tau^{n+1}} = \frac{a \cdot n!}{h\alpha^* G_0(\tau)} \frac{I(\tau)}{G_0(\tau)}. \quad (13)$$

We will consider the case  $I(\tau)/G_0(\tau) = \text{const}$ , which corresponds to isothermal or isokinetic [9] conditions. In the latter case  $I \sim G_0$  (the rates of primary and secondary nucleus formation are characterized by identical activation energies). In this case Eq. (13) can be integrated with initial conditions (11), yielding

$$X(\tau) = \frac{a}{h\alpha^*} \frac{I(\tau)}{G_0(\tau)} \left[ \int_0^{\tau} G(t) dt \right]^{n+1},$$

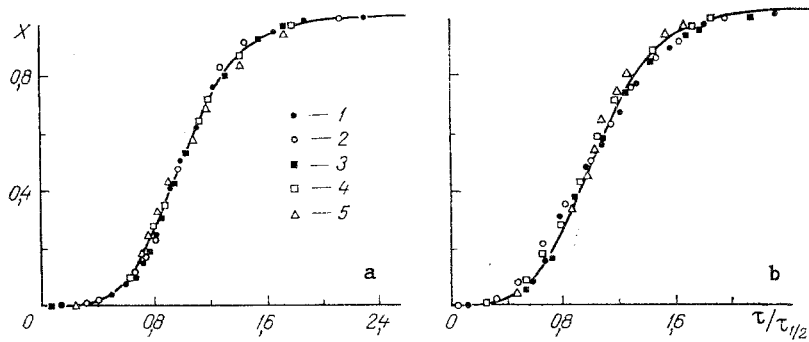


Fig. 2. Comparison of experiment (points) and calculations with Eq. (16) (solid lines) for  $n = 3$  of kinetic relationships for crystallization of polyether urethane: a) molecular mass  $M = 12,000$ , crystallization temperature  $285.5^\circ\text{K}$  (1),  $\tau_{1/2} = 50$  sec;  $287^\circ\text{K}$  (2), 61 sec;  $290.5^\circ\text{K}$  (3), 70 sec;  $293^\circ\text{K}$  (4), 125 sec;  $297.8^\circ\text{K}$  (5), 230 sec; b)  $M = 24,000$ ,  $280.5^\circ\text{K}$  (1), 82 sec;  $285.5^\circ\text{K}$  (2), 122 sec;  $287.1^\circ\text{K}$  (3), 140 sec;  $291^\circ\text{K}$  (4), 190 sec;  $298^\circ\text{K}$  (5), 685 sec.

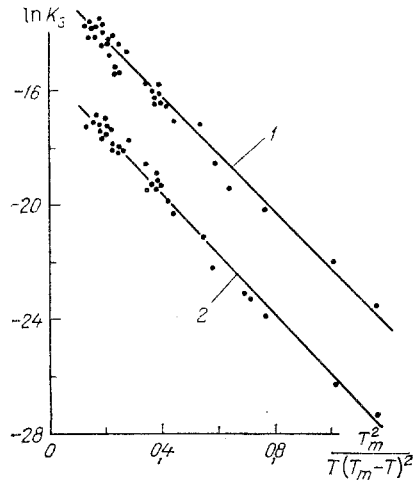


Fig. 3. Temperature dependence of phase transition coefficient. Fusion temperature  $T_m = 316^\circ\text{K}$ , 1)  $M = 12,000$ ; 2)  $24,000$ .  $K_3$ ,  $\text{sec}^{-4}$ ;  $T_m^2/[T(T_m - T)^2]$ ,  $\text{K}^{-1}$ .

which can easily be reduced to the differential form

$$\frac{dX}{d\tau} = (n+1) [K_n(\tau)]^{\frac{1}{n+1}} X^{\frac{n}{n+1}} (1-X), \quad (14)$$

where

$$K_n = aI(\tau) [\alpha^* h G_0(\tau)]^n. \quad (15)$$

After integrating Eq. (14) we obtain the following results:

$$E(\tau) = \left\{ \begin{array}{l} (n+1) K_n^{\frac{1}{n+1}} \tau - \text{for isothermal conditions, } K_n = \text{const}; \\ (n+1) \int_0^\tau [K_n(t)]^{\frac{1}{n+1}} dt - \text{for isokinetic conditions} \end{array} \right\} =$$

$$= \left\{ \begin{array}{l} \ln \frac{1+X^{1/2}}{1-X^{1/2}} \text{ for } n=1; \\ \ln \left( \frac{\sqrt{1+X^{1/3}} + X^{2/3}}{1-X^{1/3}} \right) + \sqrt{3} \left[ \text{arctg} \left( \frac{2X^{1/3} + 1}{\sqrt{3}} \right) - \frac{\pi}{6} \right] \text{ for } n=2; \\ \ln \frac{1+X^{1/4}}{1-X^{1/4}} + 2 \text{arctg} X^{1/4} \text{ for } n=3. \end{array} \right. \quad (16)$$

Theoretical dependences, constructed in the coordinates  $X - \tau/\tau_{1/2}$  with Eq. (16) for isothermal conditions are shown in Fig. 1. The time  $\tau_{1/2}$  of the semiperiod for which  $X = 1/2$  is related to the phase transition coefficient as follows:  $K_1\tau_{1/2}^2 = 0.7768$ ;  $K_2\tau_{1/2}^3 = 0.8244$ ;  $K_3\tau_{1/2}^4 = 0.8554$ .

Figure 2 shows a comparison of experimental results on the kinetics of isothermal crystallization of polyether urethane with calculations by Eq. (16) for  $n = 3$  (curves). The kinetics of the polyether urethane phase transition from a melt to the crystalline state have been studied by x-ray and optical methods [11, 12]. The temperature dependence of the phase transition coefficient in coordinates corresponding to the theory of [2, 3, 9] is shown in Fig. 3.

In conclusion, we note that to describe the nonisothermal kinetics of a phase transition with the aid of Eqs. (7)-(10) it is necessary to use the model of [2, 3, 13] for primary nucleus formation  $I(\tau)$  and free growth rate  $G_0(\tau)$ . As a rule, time dependence of these quantities is realized through temperature change with time. In this case it is only possible to obtain numerical solutions of the nonisothermal phase transition kinetics problem, analysis of which is of both practical and theoretical interest.

#### NOTATION

$I$ , frequency of nucleus formation per unit volume;  $G$ , mean linear growth velocity;  $G_0$ , free growth velocity;  $t$ ,  $\tau$ , time for formation of new phase nucleus and current time;  $X$ , degree of completeness of phase transition;  $\rho_A$ ,  $\rho_K$ , densities of old and new phases;  $n = 1$ , (one-dimensional new phase growth);  $n = 2$ , (two-dimensional);  $n = 3$ , (three-dimensional);  $K_n$ , phase transition coefficient;  $\tau_{1/2}$ , time of phase transition semiperiod.

#### LITERATURE CITED

1. E. M. Lifshits and L. P. Pitsevskii, Physical Kinetics [in Russian], Vol. 10, Moscow (1979).
2. L. Mandel'kern, Polymer Crystallization [in Russian], Moscow (1966).
3. B. Vunderlikh, Physics of Macromolecules [in Russian], Vol. 2, Moscow (1979).
4. M. C. Tobin, J. Polymer Phys. Ed., 12, 399-405 (1974).
5. A. N. Kolmogorov, Izv. Akad. Nauk SSSR, Ser. Mat., No. 3, 335-343 (1937).
6. M. Avrami, J. Chem. Phys., 7, No. 12, 1103-1121 (1939); 8, No. 2, 212-225 (1940); 9, No. 2, 177-189 (1941).
7. K. Nakamyra and K. Katayama, J. Appl. Polym. Sci., 17, No. 4, 1031-1039 (1973).
8. V. P. Begishev, I. A. Kipin, and A. Ya. Malkin, Vysokomolek. Soed. B, 24, No. 9, 656-660 (1982).
9. A. Zyabitskii, Theoretical Principles of Filament Formation [in Russian], Moscow (1979).
10. N. M. Matveev, Differential Equations [in Russian], Minsk (1968).
11. M. I. Il'yin, N. N. Zhegalova, N. A. Funtova, et al., Chemistry and Technology of Production, Processing, and Application of Polyurethanes and Their Raw Materials [in Russian], Vladimir (1984), pp. 55-57.
12. M. I. Il'in, Yu. V. Sharikov, A. A. Zhitinkin, and P. V. Chernyavskii, Teor. Osn. Khim. Tekhnol., 17, No. 1, 44-49 (1983).
13. Yu. K. Godovskii, Thermophysical Methods of Polymer Study [in Russian], Moscow (1976).