REFERENCES

1. *Goldstein M. I, Grin A. V., Bljum E. E., Panfilov L. M.* Hardening of structural steels by nitrides. Moscow, “Metallurgy”, 1970. p. 224
2. *Stomakhin A. J.* // Izvestiya VUZov. Ferrous metallurgy — 1979 — №1 — p. 47
3. *Kotelnikov G. I., Stomakhin A. Y., Sereznov V. N., Grigoryan V. A.* // Izvestiya VUZov. Ferrous metallurgy — 1979 — №1 — p. 42
4. Theoretical Principles of Electric Steelmaking / *Grigoryan V. A, Belyanchikov L. N., Stomakhin A. Y.* — Moscow: Metallurgy, 1987.
5. *Kan M. Y.* Study of Nitrogen Interaction with a scandium — bearing melts and improvement of database on thermodynamic of nitrogen solutions in iron-and nickel based alloys. — Ph. D. thesis. — Moscow: MISA, 1991.
6. *Elliot D. F., Gleiser M, Ramakrishna V.* Thermochemistry of steel-smelting processes. Moscow, “Metallurgy”, 1969.

The method of calculation of the kinetics of metallurgical processes at produce of ferrous metals

I. I. Beloglazov, I. N. Beloglazov, Y. V. Sharikov

Saint Petersburg State Mining Institute (Technical University)

In the present article we try to formulate a unified approach to the question of the transposition of the kinetic equations of various degrees of complexity which describe the kinetics homogeneous and heterogeneous chemical processes, which take place in the metallurgical equipment of the ferrous industry. As the simplest universal method one can use the simplex method, whereby a kinetic curve equation is transposable to a dimensionless form by the use of analog simplexes corresponding to several values of c_i and τ_i which are chosen from the experimental kinetic curve (where ci is the concentration of the reacting component at instant τ_i) [1–8]. Thus, for example, for any two values c_i and c_{i+1} corresponding to instants τ_i and τ_{i+1} and located on the experimental kinetic curve and, provided that the kinetic equation is transposed to the form $\tau_i = f(c_i)$, we can write: 1) for instant τ_i, $\tau_i = f(c_i)$; 2) for instant τ_{i+1}, $\tau_{i+1} = f(c_{i+1})$.

In the case of the relevant time interval $\Delta\tau_i$, the form of the functional dependence of $\Delta\tau$ and S_i on c_i and c_{i+1} is determined by:

$$\Delta = \tau_{i+1} - \tau_i = \varphi_1(c_i; c_{i+1}), \qquad (1)$$

$$S_x = \tau_{i+1}/\tau_i = \varphi_2(c_i; c_{i+1}). \qquad (2)$$

The simultaneous solution of the equations $\Delta\tau_i = f(c)$ and $S_i = f(c)$ makes it possible to derive the criterion relationship describing the kinetics of the chemical process being studied. The possibility of using the simplex method to transpose kinetic equations describing the kinetics of homogeneous and heterogeneous processes to the dimensionless form is illustrated by the examples set out below.

1. The kinetic equation describing the kinetics mechanism of simple nth (where n =0) order reactions has the form:

$$\frac{c}{c_0} = 1 - k_0 \frac{\tau}{c_0}, \qquad (3)$$

where m is the order of the reaction, k_0 is the reaction rate constant, c_0 and c_i are, respectively, the initial and instantaneous concentrations of the reacting component, $\tau_i = 0$ and τ_i is the time.

The values of the reaction rate constant can be calculated from the equation

$$-\frac{\Delta c}{\Delta\tau} = k_0. \qquad (4)$$

2. The kinetic equation describing the kinetics mechanism of simple nth (where $n = 1$) order reactions has the form:

$$\frac{c}{c_0} = \exp(-k_1\tau), \qquad (5)$$

where k_1 is the reaction rate constant (where $n = 1$).

$$\Delta\tau = (1/k_1)\ln S_c^{-1}, \qquad (6)$$

$$\Delta c = c_0 = (S_c^{S_\tau/S_\tau - 1} - S_c^{1/S_\tau - 1}) \qquad (7)$$

and

$$-\frac{\Delta c}{\Delta\tau} = k_1 c_0 (S_c^{S_\tau/S_\tau - 1} - S_c^{1/S_\tau - 1})/\ln S_c. \qquad (8)$$

3. The kinetic equation describing the kinetics mechanism of simple nth (where $n > 1$) order reactions has the form:

$$\frac{c}{c_0} = \left(\frac{1}{1 + (n-1)\, k_n c_0^{n-1}\tau}\right)^{1/(n-1)}, \qquad (9)$$

where k_n is the reaction rate constant (where $n > 1$)

$$\Delta\tau = [1/(n-1)\, k_n c_0^{n-1}]\, \frac{(1 - S_c^{n-1})(S_\tau - 1)}{S_\tau S_c^{n-1} - 1}, \qquad (10)$$

$$\Delta c = c_0 \frac{(S_\tau S_c^{n-1} - 1)^{1/(n-1)}(S_c - 1)}{(S_\tau - 1)^{1/(n-1)} S_c} \quad (11)$$

and

$$-\frac{\Delta c}{\Delta\tau} = (n-1)\, k_n\, c_0^n \frac{(S_\tau S_c^{n-1} - 1)^{n/(n-1)}(1 - S_c)}{(S_\tau - 1)^{n/(n-1)}(1 - S_c^{n-1}) S_c}, \quad (12)$$

$$(n-1)\, k_n\, \Delta\tau\, \Delta c^{n-1} = (1 - S_c^{n-1})\left(\frac{S_c - 1}{S_c}\right)^{n-1}. \quad (13)$$

The values of the c o and n can be calculated from the equations

$$c_0 = \Delta c S_c (S_\tau - 1)^{1/(n-1)} / (S_c - 1)(S_\tau S_c^{n-1} - 1)^{1/(n-1)}, \quad (14)$$

$$n = 1 + \frac{1}{\ln S_c} \ln\left[\frac{S_{\Delta\tau}(S_{\tau,i} - 1) - (S_{\tau,j} - 1)}{S_{\Delta\tau} S_{\tau,j}(S_{\tau,j} - 1) - S_{\tau,j}(S_{\tau,j} - 1)}\right]. \quad (15)$$

4. The kinetic equation describing the kinetics mechanism of the heterogeneous process of the dissolution of solid particles has the form:

$$c_i / c_0 = (1 - T_i)^n = (1 - \tau_i/\tau_0)^n, \quad (16)$$

where n is the exponent; $T = \tau_i/\tau_0$ is the relative time and equal to the absolute time τ_i divided by the time τ_0 to the final (or assumed final) completion of the process.

The values of the parameters n and τ_0 can be determined with the equation

$$\frac{\tau_0}{\Delta\tau} = \frac{S_\tau - S_c^{1/n}}{(1 - S_c^{1/n})(S_\tau - 1)}, \quad (17)$$

$$\frac{\Delta c}{c_0} = \frac{(S_c - 1)(1 - S_\tau)^n}{(S_c^{1/n} - S)^n} \quad (18)$$

and

$$\frac{\Delta c}{\Delta\tau} = \frac{c_0}{\tau_0} \frac{(S_\tau - 1)(1 - S_c)^{n-1}}{(1 - S_c^{1/n})(S_c^{1/n} - S_\tau)^{n-1}}. \quad (19)$$

4. The kinetic equation describing the kinetics mechanism of the heterogeneous oxidation process of solid particles has the form:

$$c/c_0 = 1 - \exp(-k\tau^n), \quad (20)$$

where n is the exponent and k_n is the reaction rate constant.

The values of the parameters n and k_n can be determined with the equation

$$k\Delta\tau^n = \frac{(S_\tau - 1)^n}{(S_\tau^n - 1)} \ln S_c^{-1}, \quad (21)$$

$$c_0 = \Delta c \left(S_c^{\frac{S_\tau}{S_\tau^n - 1}} - S_c^{\frac{1}{S_\tau^n - 1}} \right)^{-1}. \quad (22)$$

and

$$\frac{\Delta c}{\Delta\tau} = k^{1/n} c_0 \left(S_c^{\frac{S_\tau^n}{S_\tau^n - 1}} - S_c^{\frac{1}{S_\tau^n - 1}} \right)(S_\tau^n - 1)^{1/n}(S_\tau + 1)\ln^{1/n} S_c^{-1} \quad (23)$$

5. The kinetic equation describing the kinetics mechanism of the heterogeneous oxidation process of solid particles has the form:

$$\frac{k_i}{k_0} = T_i^m \exp\left(-\frac{E}{RT}\right), \quad (24)$$

where m is the exponent, E is the energy of activation, and R is the gas constant, k_i and k_0 are respectively, the constants of the temperature T_i and T_0.

$$\frac{R\Delta T}{E} = \frac{(S_T - 1)^2}{S_T \ln S_k S_T^{-m}}. \quad (25)$$

When $m = 0$

$$\frac{R\Delta T}{E} = \frac{(S_T - 1)^2}{S_T \ln S_k}. \quad (26)$$

Analyzing of the equations (4), (5) — (8), (10) — (15), 18, 19, (21) (22), (25), (26) one can conclude that the value of parameters of the metallurgical processes is clearly independent from each other, but that it is unequivocally dependent on the character of the kinetic curve. This situation has a considerable practical importance because the use of equations excludes subjectivity in the determination of the values of parameters of the metallurgical processes.

REFERENCES

1. *N. M. Emanuel and D. G. Knorre*, Chemical Kinetics Course [in Russian], Vyssh. Shkola, Moscow (1969), p. 432.
2. *A. A. Bezdenezhnykh*, Engineering Methods for Obtaining the Equation Describing Reaction Rates and Calculating Kinetic Constants [in Russian], Khimiya, Leningrad (1973), p. 206.
3. *G. N. Dobyokhotov*, Processes and Equipment for Hydrometallurgy Manufactures [in Russian], Leningradskii Gornyi Institut, Leningrad (1978), p. 97.
4. *P. G. Romankov and M. I. Kurochkina*, Extraction from Solid Materials [in Russian], Khimiya, Leningrad (1983), p. 256.
5. *H. W. Kropholler, D. J. Spikins, and T. Wildman*, Brit. Chem. Eng., 10, No. 2, p. 109 (1965).
6. *F. Rodriquez*, Chem. Eng., 70, No. 7, p. 159 (1963).
7. *I. N. Beloglazov*, Solid-Phase Extractors (Engineering Calculation Methods) [in Russian], Khimiya (1985), p. 240.
8. *I. N. Beloglazov, M.I. Kurochkina* / Journal of Applied Chemistry, 1985, v. 58, № 10, p. 2250–2253.