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ANALYSIS OF KINETIC DATA BY JOHNSON-MEHL EQUATION

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Johnson-Mehl equation is written as $\frac{d\alpha}{dt} = k^n t^{n-1}(1-\alpha)$ where α is the degree of reaction, t time and n a constant. Use of this equation in kinetic analysis present problems because of the presence of a 't' term on the right hand side. The equation is not a true kinetic equation and k is not a true rate constant.

This paper presents a brief discussion on the use of this equation as such or in a modified form and also indicates the proper procedure for evaluating kinetic parameters correctly. Some experimental data on the reduction of Fe_2O_3 to Fe_3O_4 have been used to test the mathematical procedure proposed. This reaction is known to follow the typical trend described by Johnson-Mehl equation.

Kinetic model for nucleation and grain growth

Kinetics of nucleation and grain-growth is generally described by an empirical equation of the following from

$$\frac{d\alpha}{dt} = k^n t^{n-1}(1-\alpha) \tag{1}$$

where α denotes the degree of transformation, t, the time and k, a constant independent of α. The value of the exponent varies with reaction mechanism. The exponent n and the rate constant k are useful empirical parameters which provide description of isothermal reaction kinetics. Equation [1] is easily integrated to the following form

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$$\alpha = 1 - e^{-(kt)^n} \tag{2}$$

k may take any positive value. If $k > 1$ sec^{-1} the reaction is too fast to be followed experimentally [1]. Again n can take any positive value. Usually the value of n is 0.5-2.5, however it may go upto 6 occasionally. Table 1 summarises values of n for some reaction mechanisms [1].

Table 1 Some values of n in the rate equation $\alpha = 1\text{-exp}(\text{-}kt)^n$

n	Model
2/3	Growth on dislocation
1	Diffusion controlled growth of cylinders in axial direction only
3/2	Diffusion controlled growth of a fixed number of particles
2	Diffusion controlled growth of discs of constant thickness
5/2	Nucleation at constant rate and diffusion controlled growth
3	Growth of a fixed number of particles limited by the interface process
4	Nucleation at a constant rate and growth of an eutectoid cell

In Eq. [1] the term t^{n-1} accounts for increasing rate in the initial stages whereas the (1-α) term accounts for gradual decrease in rate as the reaction proceeds beyond a stage when rate is maximum. The increasing rate may be ascribed to nucleation i.e. formation of new domains of the product. During later stages the rate of growth of the new domains decreases because of mutual interference of neighbouring domains either through direct impingement or by long range competition for solute atoms.

It should be noted that though k has the dimension t^{-1} it is not a true rate constant because the right hand side of Eq. [1] contains a 't' term. Integrating Eq. [1] one obtains

$$\ln[1/(1-\alpha)] = \frac{k^n}{n}t^n = (k' t)^n \tag{3}$$

where k' equals $k/n^{1/n}$. k' is also, obviously, not a true rate constant.
From Eq. [3] one also obtains

$$[-\ln(1-\alpha)]^{1/n} = k't \tag{4}$$

This equation, and similar equations, have been proposed by Johnson and

Mehl [2] and others [3-5]. Henceforth in this paper it will be referred to as the J-M Eq. Equation [4] can be rewritten as

$$\log[1/(1-\alpha)] = \frac{1}{2.303}(k't)^n \tag{5}$$

$$\log\log[\frac{1}{1-\alpha}] = n \log t + n \log k' - \log 2.303 \tag{6}$$

Thus a graph of log log [1/(1-α)] vs. log t is linear Fig. 3 with slope $n.k'$ is obtained from the intercept. This plot has been used by Sohn and Won [6] and recommended by Burke [1]. k' can also be obtained directly from the α-t plots by noting that, according to Eq. [4], k' equals the reciprocal time when α equals 0.6321. Thus substituting $\alpha = 0.6321$ in Eq. [4] one obtains

$$k' = \frac{1}{t_{0.6321}} \tag{7}$$

Evaluation of activation energy

One can determine the activation energy value in several ways. Firstly, the slopes of the lines in Fig. 6 define the pseudo-rate constant k'. An Arrhenius type plot of values of ln k' vs. reciprocal temperature yields a value for activation energy. This plot is shown in Fig. 5 which also plots k' value obtained directly from the α-t plots using condition defined by Eq. [7]. Although the two sets of k' values match extremely well the significance of the E values shown is somewhat dubious because of the fact that k' is not the true rate constant.

The E value can also be calculated using differential approaches without reference to any particular kinetic model [7]. We note that the rate of reaction is related to temperature and degree of reaction by the differenatial equation

$$\frac{d\alpha}{dt} = kf(\alpha) = A\exp(-E/RT)f(\alpha) \tag{8}$$

Considering a fixed value of α one gets

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln A + \ln f(\alpha) - E/RT \tag{9}$$

Since ln $(f(\alpha)$ has a fixed value for a given α it follows that a plot of the left-hand side against reciprocal temperature would be a straight line, the slope of which should yield the value of E/R.

Again Eq. [8] can be rewritten as

$$\frac{1}{A\exp(-E/RT)}\int\frac{\mathrm{d}\alpha}{f(\alpha)}=\int \mathrm{d}t \tag{10}$$

At a given value of α, therefore, one gets [8]

$$t_\alpha=\frac{\mathrm{const}}{A}\exp(E/RT) \tag{11}$$

where t_α is the time required to attain a fixed value of α. Therefore, a plot of ln t_α against reciprocal temperature should be a straight line and the slope should yield the value of E.

Both these methods have advantages over the integral approach. Neither require the knowledge of any integrated rate expression. In addition they yield E values at different levels of α. Use of Eq. [11] has the additional advantage that calculations are done more easily since there is no necessity of calculating slopes of α-t plots.

Experimental

Materials

Discs of 1.27 cm diameter and 0.5 cm thickness were made by grinding and ultrasonic cleaning of carol lake pellets. The composition is given in Table 2.

Table 2. Composition of Carol lake pellets, wt.%

Fe total	Fe^{2+}	SiO_2	CaO	MgO	Al_2O_3	S
67.76	2.88	2.30	0.32	0.20	0.62	0.06

Reducing gas

A reducing gas mixture of H_2 and H_2O having $pH_2 = 0.1$ was used in this investigation to reduce hematite to magnetite. The gas mixture was prepared by the combustion of H_2 and O_2 gases in combustion chamber fitted with a platinum ignition coil.

Reduction experiment

Figure 1 shows schematically the experimental set-up of the reduction experiment. Weight loss of the hematite discs were continuously recorded by a thermogravimetric set up. The reduction at a desired temperature was carried out by passing H_2 and H_2O gas mixture into the reaction chamber which was placed inside a furnace. The reaction chamber was flushed with nitrogen before and after the experiment. The flowrate of the gas was maintained at 2 l/min.

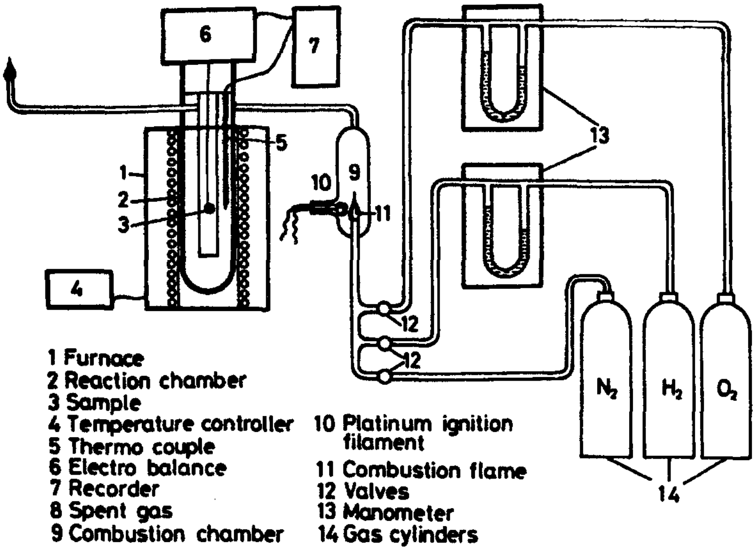

Fig. 1 Schematic diagram of the experimental set-up

Results and discussion

Figure 2 shows the α-t plots obtained at four temperatures using partial pressure of hydrogen in the gas mixture as 0.1. Figure 3 shows plots of log $\log \frac{1}{1-\alpha}$ vs. log t. The plots, which are linear, yield for n a value 3, excepting for the data for 850° which does not fit into this trend. It is known that beyond about 800° the reduced pellets begin to sinter and the reaction mechanism is likely to alter. These data have not been taken into account for the present analysis. Figure 4 shows the linear plots according to the following kinetic equation.

$$[-\ln(1-\alpha)]^{1/3} = k't \tag{12}$$

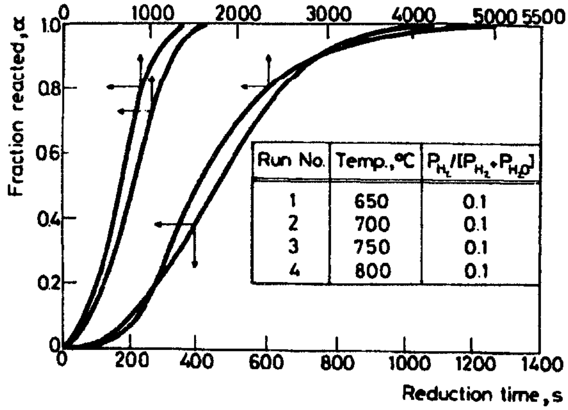

Fig. 2 Kinetic data for reduction of hematite to magnetite

Figure 5 shows the Arrhenius plots of ln k' vs. $1/T$. It also shows (the points indicated by squares) k' values obtained using Eq. [6]. The plot indicates for E a value of 119 kJ/mole. It should be noted that a smaller value may be considered more accurate because the approach followed in this case does not assume any particular model.

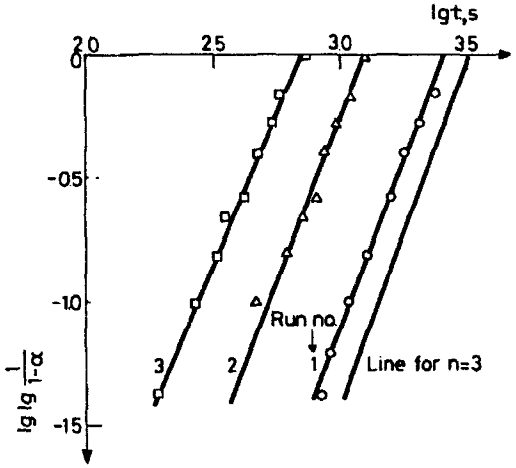

Fig. 3 Plot of kinetic data according to Eq. [6]

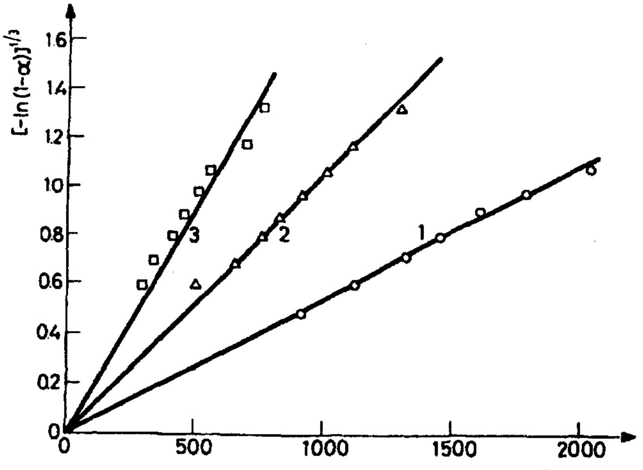

Fig. 4 Plots of kinetic data according to Eq. [4]

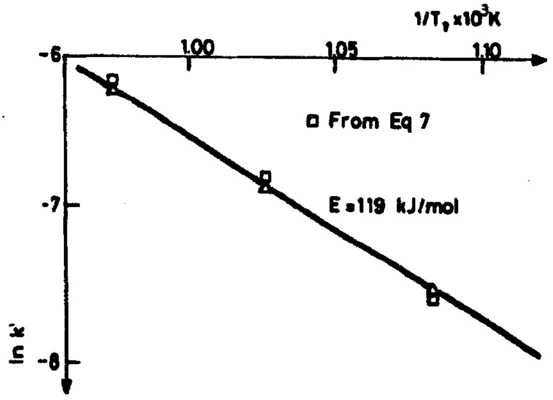

Fig. 5 Arrhenius type plots

Modification of kinetic equation

For small values of α, $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ is proportional to t^{n-1} i.e. α is proportional to t^n or t is proportional to $\alpha^{1/n}$. Hence, $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ is proportional to $\alpha\frac{n-1}{n}$. Equation 1 can, therefore, be modified to the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_m(1-\alpha)\,\alpha^{(m-1)/m} \tag{13}$$

where k_m is a true rate constant and exponent m is not necessarily equal to n. Equation [13] is analogous to the general expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{14}$$

where $f(\alpha)$ denotes the functional form $(1-\alpha)\alpha^{(m-1)/m}$.

Exponent m may be determined without the necessity of integration. Differentiating with respect to $\ln\alpha$, Eq. [13] becomes

$$\frac{\mathrm{d}\ \ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}\ \ln\alpha}=\frac{\mathrm{d}\ \ln k_m}{\mathrm{d}\ \ln\alpha}-\frac{\alpha}{1-\alpha}+\frac{m-1}{m} \tag{15}$$

The procedure is to determine the gradient of the α-t plots at each of a series of α values. Values of ln $(\mathrm{d}\alpha/\mathrm{d}t)$ are then plotted against ln α. Since k_m is not a function of α the first term in the right hand side in Eq. [15] becomes zero. The gradient of the plot thus gives $\alpha/(1\text{-}\alpha)$ and the intercept, $(m\text{-}1)/m$. The latter yields the value of m for Eq. [13].

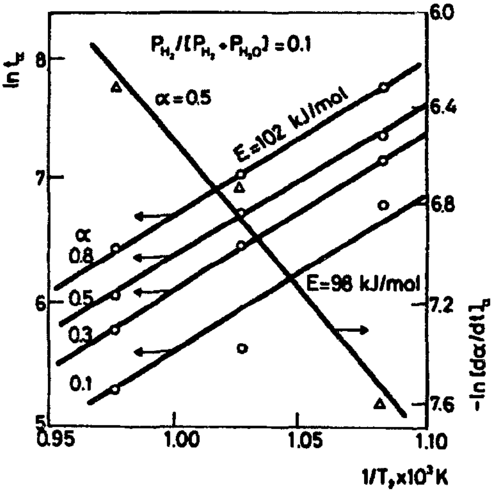

Fig. 6 Evaluation of activation energy using Eq. [9] and Eq. [11] for $pH_2/(pH_2+pH_2O)=0.1$

Figure 7 shows plots of $\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ vs. ln α and Fig. 8. shows a plot of

$$\frac{\mathrm{d}\ \ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{\mathrm{d}\ \ln\alpha}\ \mathrm{vs.}\ \frac{\alpha}{1-\alpha}$$

This plot yields for m a value approximately equal to 3.

The modified Johnson-Mehl equation, therefore, may be written as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_m(1-\alpha)\alpha^{2/3} \tag{16}$$

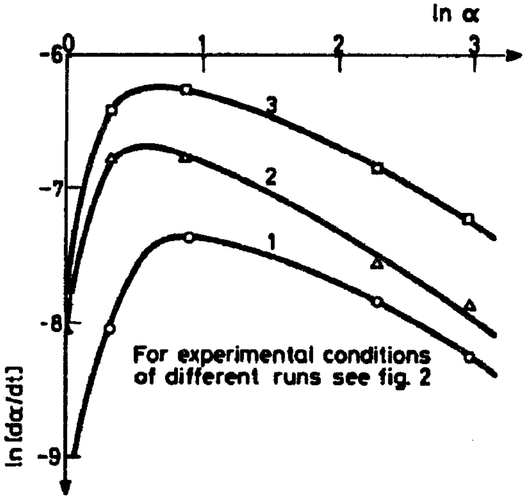

Fig. 7 Plots according to Eq. [15]

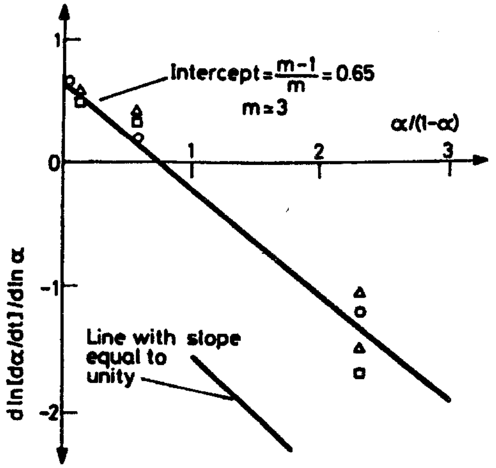

Fig. 8 Plots for evaluation of m

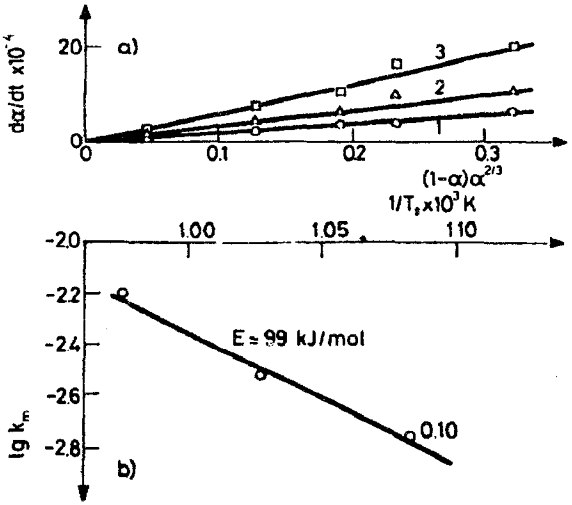

Fig. 9 a) Plots according to modified form of J-M equation; b) Arrhenius type plot

where k_m is the rate constant. Figure 9a shows the kinetic plots according to Eq. [16] and Fig. 9b shows the Arrhenius plots in terms of slopes obtained from Fig. 9a. The E values obtained matches excellently with the E values obtained earlier using the differential approaches.

Conclusions

It is shown that use of conventional Johnson-Mehl equation may lead to erroneous values of kinetic parameters. Correct values are obtained by modifying the equation such that it becomes a true kinetic equation. Correct values can also be obtained by employing differential approaches which do not assume any kinetic model. These observations are very well corroborated by a detailed analysis of experimental data on reduction of hematite to magnetite by H_2 and H_2O mixture.

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Zusammenfassung - Die Johnson-Mehl-Beziehung lautet: $\frac{d\alpha}{dt} = k^n t^{n-1}(1-\alpha)$ mit der Reaktionskoordinate α, der Zeit t und der Konstante n. Eine Anwendung dieser Gleichung in der kinetischen Analyse verursacht Probleme, da auf der rechten Seite der Gleichung ein 't'-haltiger Ausdruck steht. Die Gleichung ist keine wirkliche kinetische Gleichung und k ist keine wahre Geschwindigkeitskonstante.

Diese Arbeit beschreibt eine kurze Diskussion der Anwendung dieser Gleichung in dieser oder einer modifizierten Form und beschreibt, wie korrekte kinetische Parameter erhalten werden können. Zum Testen des vorgeschlagenen mathematischen Verfahrens wurden einige experimentelle Daten der Reduktion von Fe_2O_3 zu Fe_3O_4 benutz. Diese Reaktion ist bekannt, dem typischen, durch die Johnson-Mehl-Gleichung beschriebenem Trend zu folgen.