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SOME FACTORS THAT LEAD TO UNCERTAINTIES IN KINETIC STUDIES IN METALLURGY

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Kinetic studies in metallurgy involve the measurement of changes in suitable properties of systems undergoing transformation under controlled conditions. Often, such measurements are relatively easy, and it is, therefore, not difficult to generate a mass of kinetic data. Thereafter, the data are routinely processed for the fitting of kinetic models and the evaluation of kinetic parameters for identification of a 'reaction mechanism'. Unfortunately, the apparent simplicity of measurements and mathematical procedure, and even reproducibility, can be rather misleading, because there can be uncertainties at every stage and the conclusions can be erroneous. The present article discusses the sources of some of the uncertainties and their implications.

Every rate process has certain characteristic features. Some of the more important are as follows.

a) For any transformation to occur, there must be a thermodynamic driving force, i.e. the change towards the more stable state must imply a lowering of the free energy. However, the reaction rate is not necessarily dependent on this free energy change.

b) Transformation occurs only if sufficient energy is supplied to overcome a definite energy barrier (activation energy).

c) There is an underlying reaction mechanism, i.e. a logic which governs the transformation. The logic, which can change with the transformation and time, relates to the reaction mechanism.

d) A catalyst can change the mechanism and accelerate the reaction by lowering the energy barrier, but it cannot change the overall free energy change.

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e) The reaction mechanism is seldom indicated by the chemical equation which represents a chemical reaction.

f) The kinetics depends on both physical and chemical parameters.

In any system, the rate of reaction at a given time depends basically on three factors: the nature of the system (s), the time of reaction (t) and the temperature (T):

$$\text{rate} = f(s,t,T) \tag{1}$$

The rate is measured via a suitable parameter which changes with the reaction. At times, it may be difficult to have an unambiguous index of rate. Uncertainties in kinetic studies can also arise from a poor and incomplete characterization of the 'which' of the system. The word 'nature' implies not only the system under test, but also the accompanying environment. It encompasses chemical compositions, the presence of impurities which are inert and those which interfere with the reaction rate, the morphological characteristics, physical factors such as the size and shape of the particles, size distribution, etc. In view of the possible complications, it is always very difficult to understand, reliably, the mechanisms of kinetic processes in real systems; kinetic theories are therefore generally based on several simplifying assumptions. These include isothermal conditions, the supply of excess reagents so that there is no reagent starvation, the unchanging pore structure of solids, etc. The aim of the present article is to discuss briefly the nature of some of the sources of uncertainties and their implications.

Theoretical

Kinetic parameter

Uncertainties may exist about the very definition of the kinetic parameter. They may arise from several factors.

a) Not every property that changes can serve as a true kinetic parameter for direct measurement of the reaction rate. For the latter, the change in the parameter must be directly proportional to the amount of reactant consumed. Thus, changes in the dimension or the mechanical properties of a solid reflect the progress of reaction only indirectly. When they involve indirect kinetic parameters, therefore, many kinetic measurements become empirical in nature. Consider some examples.

Example 1: Densification of powder compacts: The kinetics of densification can be studied in terms of the extent of the original porosity destroyed (α). It can be shown that the degree of densification is

$$\alpha = \frac{v_p - v_s}{v_p} = \frac{\Delta V / V_o}{p} \tag{2}$$

Where v_p = the volume of pores in the original green compact,

v_s = the volume of pores in the sintered compact,

V_o = the volume of the green compact,

ΔV = (V_o-V_s), where V_s is the volume of the sintered compact,

p = the porosity, which equals $[(V_o\text{-}V_{th})/V_o]$, and $[(\rho_{th} - \rho_o)/\rho_{th}]$, where V_{th} is the volume of the sintered compact when it reaches the theoretical density ρth; ρo is the density of the green compact.

It can be shown [1] that for long cylindrical compacts

$$\frac{\Delta L}{L_o} \approx \frac{\Delta V}{V_o} \tag{3}$$

whereas for cylindrical compacts with square cross-sections

$$\frac{\Delta L}{L_o} \approx \frac{1}{3}\,\frac{\Delta V}{V_o} \tag{4}$$

Again,

$$\alpha = \frac{V_o - V_s}{V_o - V_{th}} = \left[\frac{1}{\rho_o} - \frac{1}{\rho_s}\right] / \left[\frac{1}{\rho_o} - \frac{1}{\rho_{th}}\right] = \frac{\Delta\rho}{\rho_s \,.\, p} \tag{5}$$

where ρs is the density when the volume is V_s.

An examination of Eqs. 1-5 shows that while $\Delta V/V_o$ does represent α, especially at constant porosity, the commonly used parameters $\Delta L/L_o$ and $\Delta\rho/\rho o$ do not directly represent the degree of densification in general.

Example 2: Reaction of iron oxide-carbon mixtures: During the reaction in mixtures of iron oxide and carbon, the weight decreases because of both removal of oxygen from the oxide by reduction and gasification of the carbon by oxidation. These two components cannot be delineated; therefore, some workers have used a parameter f (degree of reaction), defined as the weight loss of the mixture at a given time divided by the maximum possible weight loss [2]. This parameter has been usefully employed in kinetic studies of the reaction. However, it cannot be equated with the degree of reduction (α), especially at high values of α. It is theoretically possible for the weight to decrease entirely, due to gasification by other oxygen sources, with no corresponding removal of oxygen from the oxide.

b) Another source of uncertainty concerning the kinetic parameter arises from an ill-defined starting material. Consider, for example, the oxidation of direct reduced iron (DRI).

Most DRI samples contain some unreduced oxide. If this fact is ignored, then in a kinetic study of the reoxidation of DRI one would record an apparently very high initial rate of oxygen intake. This is misleading. The ambiguity arises from the assumption of a zero oxygen level at zero time and the consideration that the oxygen present at a given time is the total oxygen intake. The degree of oxidation must be defined in terms of oxygen actually added, without considering the oxygen already present at zero time.

c) Thirdly, a parameter may vary as a reaction progresses, but it may not be relevant from the point of view of the reaction 'logic' and the rate-controlling step. For example, in the previous example of the reaction of iron oxide and carbon, the reduction and oxidation reactions are necessarily coupled [3]. However, if gasification is the rate-controlling process, then one should study the reaction in terms of carbon removal and not oxygen removal. If the decomposition of a carbonate is controlled by heat transfer in the system, then the reaction cannot be studied in terms of changes in weight only.

Rate constant

The integral and differential forms of a rate equation are generally expressed, respectively, as follows:

$$g(\alpha) = kt \tag{6}$$

$$\frac{d\alpha}{dt} = k \, . f(\alpha) \tag{7}$$

where $g(\alpha)$ and $f(\alpha)$ are appropriate functions of α, and k is the rate constant. By differentiating Eq. (6), it is easily shown that $f(\alpha)$ equals $1/g'(\alpha)$. In many cases, $f(\alpha)$ has the form $(1-\alpha)^n$, where n refers to the reaction order with respect to the reactant to which α refers. However, this is not always so.

In some kinetic processes, while Eq. (6) is valid, the differential form is more complicated. In such cases, k cannot be termed the true rate constant. Consider, for example, the nucleation and grain growth phenomenon, the differential form for which is written as [4].

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k'^{n}\, t^{n-1}\,(1-\alpha) \tag{8}$$

where n is said to be a constant dependent on the reaction mechanism [4].

On integration, one obtains

$$g(\alpha) = [-ln(1-\alpha)]^{1/n} = kt \tag{9}$$

where k equals $k'/n^{1/n}$.

Although the form of Eq. (9) is correct, neither k nor k' is the true rate constant, because Eq. (8) contains a t term in the right-hand side (R.H.S.). It should be noted that k has the same dimension (t^{-1}) as rate, and yet it is not the true rate constant.

In a paper discussing the reduction of hematite pellets to wustite, Sarkar and Ray [4] have shown that while Eq. (9) fits the kinetic data correctly (with $n = 3$), k cannot be accepted as the true rate constant. Accordingly, values of the activation energy calculated on the basis of the variation of k with temperature are erroneous.

To obviate the problem, Eq. (8) should be modified so that there is no t term in the R.H.S. It has been shown [4] that it can be modified into the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_m(1-\alpha)\,\alpha^{(m-1)/m} \tag{10}$$

where k_m is a true rate constant, and the exponent m, which is different from n, is evaluated by a simple mathematical procedure [4]. In this equation, m is an empirical constant.

The rate constant is more reliably evaluated by using the differential form of the rate equation, Eq. (7). When $f(\alpha)$ equals $(1-\alpha)^n$, the rate constant equals the rate at zero time (zero α). Thus, in many cases, k is simply the initial slope of the α-t plots, i.e. the primary kinetic plots.

The second uncertainty about the rate constant arises from the fitting of incorrect kinetic equations. That is, if the α-t plots are linearized by using an incorrect kinetic model to fit the data to an integral equation, Eq. (6), the slope thereby obtained defines an erroneous value of the rate constant. The problem arises from the fact that in many cases different kinetic equations appear to fit a set of kinetic data and researchers may not be able to select the most appropriate one. The procedure for the correct identification of the kinetic model is discussed subsequently.

Activation energy

The common approach for the evaluation of the activation energy is as follows. An equation of the type of Eq. (6) is fitted for different isothermal data. If the plots are linear, then the slopes yield rate constant k values for different temperatures. Then, values of ln k are plotted against reciprocal temperature [$1/T(k)$] to obtain an Arrhenius type plot. The slope yields the value of E/R, where R is the gas constant. This procedure assumes an unchanging reaction mechanism, i.e. constant E and an unchanging, but known kinetic model.

It is possible to evaluate E by two differential approaches which do not need an *a priori* knowledge of the kinetic equation [5].

Equation (7) can be rewritten as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{11}$$

$$\ln\left[\frac{\mathrm{d}\alpha}{\mathrm{d}t} / f(\alpha)\right] = \ln A - \frac{E}{RT} \tag{12}$$

At a given value of α, $f(\alpha)$ is constant, and plots of ln $\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\alpha$ at a fixed value of α *vs.* $1/T$ would therefore be linear, the slopes showing values of $-E/R$. Again, Eq. (7) can be rewritten as

$$\frac{\mathrm{d}\alpha}{f(\alpha)} = A \,.\, \exp\left(-\frac{E}{RT}\right) .\, \mathrm{d}t \tag{13}$$

Integrating for a fixed value of α, one obtains

$$\text{Const.} = A \, . \left[\exp\left(-\frac{E}{RT} \right) \right] . t_\alpha \tag{14}$$

Where t_α is the time required to attain the given degree of transformation. Thus, one can plot values of ln t_α against reciprocal temperature to obtain linear plots with slope E/R.

The advantages of these approaches based on the differential form of the kinetic law are as follows.

a) One can obtain the E value without an *a priori* knowledge of $g(\alpha)$ or $f(\alpha)$.

b) One can obtain E values at different levels of α.

However, there are also some problems. These approaches also assume an unchanged, although unknown, unvarying kinetic law (i.e. a fixed form of $f(\alpha)$). Also, they can evaluate E, but generally not k, because A remains unknown. Moreover, Eq. (12) involves some uncertainty, because one has to obtain slopes of α-t plots to obtain instantaneous rates $d\alpha/dt$. The last approach based on Eq. (14) gives a more accurate E, because the t_α values can be known accurately.

To obtain E unambiguously, it should be evaluated by both integral and differential approaches. For the former, one should first identify the correct kinetic equation. this is conveniently done by the use of reduced time plots. The procedure is briefly as follows [3, 20].

Equation (6) can be rewritten as

$$g(\alpha)_{\alpha = 0.5} = k \, t_{0.5} \tag{15}$$

where $t_{0.5}$ is the time required for 50% reaction. Dividing Eq. (6) by Eq. (15), one obtains the kinetic relationship in an altered form, given as

$$g(\alpha) = A \ (t / t_{0.5}) \tag{16}$$

where A is a constant dependent on the form of the function $g(\alpha)$.

Equation (16) is independent of the rate constant and is dimensionless. Thus, for a particular reaction mechanism, a single equation of this type represents all kinetic data, irrespective of the nature of the system, temperature or other factors which affect the reaction rate. Each mechanism therefore has a unique reduced time plot for isothermal data.

To ascertain the appropriate kinetic law, one first tabulates the functional values of $g(\alpha)$ for various values for different kinetic mechanisms. These are then used to calculate $t/t_{0.5}$ values. Master plots are obtained, for various kinetic laws, by plotting the α-values against the calculated values of $t/t_{0.5}$. Reduced time plots of the experimental data are then superimposed on these to determine the theoretical plot that fits the experimental data.

Uncertainty about the activation energy may also arise from the fact that it may not be independent of temperature, as is ordinarily assumed. This is particularly true for gas-solid reactions where the reaction rate is influenced, amongst other factors, by a thermodynamic driving force. Consider, for example, the carbon reduction of Fe_2O_3. The rate constant has been expressed by the following equations in the literature [7]:

$$k = \frac{k'}{\rho_o r_o}\left(C^{e}_{CO_2} - C_{CO_2}\right) . \exp[-E/RT] \tag{17}$$

$$k = \frac{k'}{\rho_o r_o}\left[\frac{C^{e}_{CO_2} - C_{CO_2}}{C^{e}_{CO_2}}\right] . \exp[-E/RT] \tag{18}$$

where C_{CO_2} is the concentration of CO_2 in the gas phase and $C^{e}_{CO_2}$ that in equilibrium with two condensed phases (i.e. Fe_2O_3 + Fe_3O_4, or Fe_3O_4 + Fe_xO, or Fe_xO + Fe, as the case may be). ρ_o is the density, and r_o the original particle size. Similar expressions for the rate constant have been given for the decomposition of carbonates. Now the constant k' is temperature-dependent. If it is written as A . exp $(-E/RT)$, then Eq. (18) may be expressed as

$$k' = \left[\frac{A}{\rho_o r_o} . \frac{C^{e}_{CO_2} - C_{CO_2}}{C^{e}_{CO_2}}\right] . \exp(-E/RT) \tag{19}$$

Since $C^{e}_{CO_2}$ is temperature-dependent, the preexponential factor within square brackets is no longer a constant. It has been found, however, that one can still find an Arrhenius type relationship to hold good [8], i.e.

$$k = A' \exp(-E'/RT) \tag{20}$$

where A' and E' are temperature-independent constants. However, it is not obvious that if A' is forcibly kept constant, $E \neq E'$. In some experiments, therefore, one obtains only an apparent, but inaccurate value of E. There can also be other reasons for this.

In many studies on solid-state reactions and gas-solid reactions, the apparent E value has been found to vary over a wide range. This phenomenon has been particularly studied with reference to the decomposition of $CaCO_3$. It has been found, however, that variation in the E' value is accompanied by a systematic variation in the value of A', as is expected. Generally, a relationship such as rollows is also obeyed:

$$\ln A' - \frac{E'}{RT} = \text{Const} \tag{21}$$

That is, plots of ln A' *vs.* E'/T are linear. This is popularly known as the kinetic compensation effect (k.c.e.).

Kinetic models

Kinetic models are often fitted indiscriminately with no concern for rationality. The various equations available in the literature are for the specific situations under which the kinetic process is assumed to take place. For example, the equation developed for the reaction of a spherical particle would not be applicable for that of a cylindrical or a plate-like solid. One should not consider equations which are not relevant. For example, in a recent paper, data for the reoxidation of irregular particles of a DRI were analysed by using the parabolic law [10]. This is not correct, because the parabolic law for a diffusion-controlled reaction is valid only for solids in the shape of plates.

In another common approach, the reliability of selection of a model depends on the goodness of fit. That is 20-30 known models are used to analyse the experimental data and the mathematically most consistent model, which gives the best fit, is chosen. This approach, unfortunately, ignores possible errors in the kinetic data themselves.

The best approach comprises use of the reduced time plots for preliminary identification of the correct kinetic equation, and then plotting the data according to it. The choice is confirmed as correct if the E values determined by using integral and differential approaches match well. For further confirmation, one should examine the dependence of k on r_o. For spherical pellets, k is proportional to $1/r_o$ for a phase boundary-controlled reaction, and to $1/r_o^2$ for product layer diffusion control. k is independent r_o of for a total internal reaction. Diffusion control can be further substantiated by marker experiments. There are several tests which help identify the reaction mechanism. For example, if the reaction involves gas phase diffusion control, then the reaction rate is sensitive to the flow rate of gas. For liquids, the influence of stirring indicates liquid phase mass transfer.

A kinetic equation or a so-called kinetic model does not necessarily define a reaction mechanism. For example, if one fits to kinetic data the phase boundary control rate equation for spherical particles

$$1-(1-\alpha)^{1/3}=kt \qquad (22)$$

it does not necessarily mean that the process is controlled by a chemical reaction at the interface. All it requires to derive the equation is the condition that the reaction rate is proportional to the interfacial area - a condition which can arise from different phenomena. For example, the dissolution of a quartz sphere in glass by liquid phase mass transfer would also follow Eq. (22) if the composition of the glass melt is approximately constant.

Particle size and shape

The kinetics of solid-fluid reactions are often discussed with reference to single solid particles of given geometry. Both the shape and size of the particle must be defined, since both influence the form of the kinetic equation. For example, considering a reaction mechanism where the reaction rate is proportional to the interfacial area of the unreacted core (i.e. a phase boundary-controlled reaction), one obtains the following equations:

a) For a spherical particle of radius $r_o: 1-(1-\alpha)^{1/3}=\frac{k}{\rho_o r_o}.t$ (23)

b) For a cube of solid, with side l: $1-(1-\alpha)^{1/3}=\frac{2k}{\rho_o . 1}.t$ (24)

c) For a cylindrical particle of length $1>>d$ (d, the diameter, equals $2r_o$): $1-(1-\alpha)^{1/2}=\frac{k}{\rho_o r_o}.t$ (25)

d) For a flat plate of small thickness with total surface area A: $\alpha = \frac{k}{\rho_o y_o} . t$ where yo is the original thickness of the plate.

If the actual shape of the solid particle is irregular, then no definite kinetic equation can be valid and matching of the data with any specific equation may be taken as merely a happy coincidence. Single polygonal irregular particles, however, often conform to the equation for the sphere. Even if the geometry is well defined, a kinetic equation can be invalidated if a solid particle splits during reaction and different particles sinter. Both these phenomena effectively change the 'original' particle size r_o.

Multiparticle ensemble: Gas-fluid reactions in real systems, e.g. those during ore reduction, roasting, leaching, etc., involve a mass of solid particles at a time. Such multiparticle ensembles pose several uncertainties from the point of view of kinetic theory. If the mass is large, then the reagents (gas/liquid) may not have free excess to all particles and the interiors may be starved of the reagent. In such a case, the reaction rate will be nonuniform. Secondly, since the rate is dependent on the particle size, then, in an ensemble, different particles tend to react at different rates. Thus, even if all particles are strictly spheres, no well-defined equation for a single spherical solid can be accurately fitted to the kinetic data which represents a mass average value. It is possible, however, to establish a modified equation on the basis of the 'population balance', which takes into account the particle size distribution and an overall average for the whole mass [12]. Equation derived for single particles may be approximately valid for multiparticle systems only when the variation in particle size fall within a narrow range. The situation becomes far more complicated, however, if the shape of the particles also becomes nonuniform. If a kinetic equation fits the kinetic data for a mass of particles of indefinite shape and size, then it can only be accepted as an empirical relationship. Conversely, if an equation that applies for a single solid sphere fails to fit the data for a real system of a multiparticle polydisperse ensemble with particles of indefinite shape, the validity of the equation itself should not be questioned. Even if the reaction mechanism is the same, the nonconformity can arise from geometric factors alone. It is therefore desirable for studies on solid-fluid reaction to take as close a range of particle size as possible. In addition, one should also examine the shape of the individual particles microscopically.

Surface area of particles: Interesting insight into a process may also be obtained through measurement of the surface area of the particles. For example, consider the leaching of a mass of solid particles. If the single particles simply dissolve away, then the surface area of the solid should gradually diminish. On the other hand, if there is a reaction product which adheres on the solid surface, then the surface area may diminish, remain unchanged or even increase, depending on the density of the solid product. Recently, studies involving the leaching of multimetal sulphides with ammonia have shown [13] that the surface area increases steadily, although there may not be any adhering reaction product. This increase could be due to several factors. Cracks could be generated in the solid, or the particles could undergo splitting. More likely, the increase in surface area may merely be due to the fresh surface created by the release of gangue materials. However, these factors must be taken into account prior to the interpretation of the kinetic studies.

Equation for diffusion through the product layer

There are four common equation to describe the reaction of a spherical solid with a fluid when the rate-controlling process is diffusion through a product layer that envelops the solid particle. These equations are:

a) the Jander equation:
$$1-(1-\alpha)^{1/3}=\frac{k}{r_o^2}.t \tag{27}$$

b) the Crank-Ginstling-Brounshtein equation:
$$1-\frac{2}{3}-(1-\alpha)^{2/3}=\frac{k}{r_o^2}.t \tag{28}$$

c) the Carter-Valensi equation:
$$\frac{[1+(z-1)\alpha]^{2/3}+(z-1)(1-\alpha)^{2/3}-z}{2(1-z)}=\frac{k}{r_o^2}t \tag{29}$$

where z is the ratio of the volume of the product to that of the reactant.
For a plate, the equation is
$$\alpha^2 = kt \tag{30}$$

Often, uncertainties arise because these equations are used indiscriminately. There are some essential conditions. All product formed must remain on the unreacted core. The equations cannot be used if product flakes off or disintegrates. The parabolic law cannot be used for three-dimensional solids. The Jander equation applies only in the very initial stages of a reaction. Moreover, both Eq. (27) and Eq. (28) assume that the densities of the product and the reactant are comparable. When the densities differ, then Eq. (28) is the exact equation. There can be no simple equation for a multiparticle ensemble with varying particle size and shape.

Nevertheless, Eq. (28) has been found to be applicable for many real systems where the conditions of particle geometry, shape and size distribution are far from ideal. One should therefore be careful in drawing conclusions based on kinetic theory for an idealized system.

Other sources of uncertainties

Uncertainties in kinetic studies on real systems arise from many factors, some of which are listed here:

a) Presence of impurities.
b) Prediction of packed bed reaction rates from single particle experiments.
c) Multiparticle nature of systems.
d) Nonisothermal conditions.
e) Variations of pore structure in solid.
f) Change in reaction mechanism and E with time.
g) Reagent starvation.
h) Role of heat transfer in rate control.
i) Reaction controlled by two or more reaction steps simultaneously.
j) Overlapping and interfering reactions, etc., etc.

The implications of some of these have been discussed already. Some additional comments follow.

Change in kinetic laws with temperature:

In many instances, a kinetic law applicable for a given process at one temperature is not applicable at another. Different reaction mechanisms may sometimes overlap and the rate equation may be a combination of two or more laws. Consider the oxidation of metals, for which some of the commonly followed rate equations for samples in the form of strips are as follows:

$$\Delta m = k_1 t \tag{31}$$

$$\Delta m^2 = k_2 t \tag{32}$$

$$\Delta m^2 = k_3 t + C \tag{33}$$

$$\Delta m^3 = k_4 t \tag{34}$$

$$\Delta m = \mathrm{k}_5 \log (at + t_0) \tag{35}$$

where Δm is the weight gain per unit surface area. a, t_0 and C are constants.

Oxidation reactions often follow different equations at different temperatures [14]. Combinations of two or more of these relationships in a single oxidation-time curve are also common. For example, for copper, the equations valid as the temperature is progressively increased are: logarithmic, cubic and then parabolic [12]. In such cases, experiments must be carried out in sets in close temperature ranges, or else kinetic data analysis would be erroneous. The oxidation of lead, on the other hand, follows a simple parabolic law up to the melting point [15].

Mutual interference of reactions:

Kinetic studies on any rate process can involve serious uncertainty if one ignores the interference of other parallel processes. For example, liquid cadmium (400-550°) oxidizes in accordance with the parabolic law. Whereas 1% Pb, Bi or Cu has no effect on the oxidation as little as 0.05% Zn prevents the oxidation completely, zinc oxidizing to ZnO according to the parabolic law [16]. It is well known that the roasting of copper sulphides is suppressed when iron sulphides are present. However, it is not so widely appreciated that similar interference can be present during the leaching of sulphide minerals. The kinetics of leaching of a given sulphide is likely to be sensitive to the presence of other sulphides in a mineral. Such interferences can be understood on the basis of thermodynamics and galvanic interaction. In the case of the leaching of multimetal sulphides, such interactions are almost always present, although their overall effect on the form of the kinetic equation and the rate constant may or may not be significant.

Mixed control:

Most kinetic equations are derived on the assumption of a single rate-controlling step. This assumption is often not valid and it requires a combination of two or more kinetic equations to explain the data properly. There have been different approaches to develop equations for mixed control. One is by the use of Sohn's additivity law. The law essentially states that the total time is the sum of times required by the individual steps in the absence of all other steps. Thus, for fluid-solid reactions, the time required to attain a given α value will be the sum of the time required to attain the same α in the absence of product layer diffusion resistance plus that required under such diffusion control. For a combination of phase boundary reaction and product layer diffusion during the reaction of a spherical solid reaction with a fluid, one therefore obtains

$$t = t_1 + t_2 = \frac{1-(1-\alpha)^{1/3}}{k_1/\rho r_o} + \frac{1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}}{k_2/r_o^2} \tag{36}$$

or

$$\rho k_2 [1 - (1 - \alpha)^{1/3}] + r_o k_1 [1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}] = \frac{k k_2 t}{r_o} \qquad (36)$$

An an example, consider the acid leaching of chrysocolla. The reaction is written as

$$CuO \,.\, SiO_2 \,.\, 2H_2O + 2H^+ = Cu^{2+} + SiO_2 \,.\, n\, H_2O + (3\text{-n})H_2O \qquad (37)$$

The kinetic data in this case has been found to fit an equation of the following form [18]:

$$[1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}] + \frac{\beta}{r_o}[1 - (1 - \alpha)^{1/3}] = \frac{\gamma [H^+]}{r_o^2} t \qquad (38)$$

where β and γ are constants. This equation is similar to Eq. (36).

A consequence of mixed control is an alteration of the activation energy. If two rate-controlling steps are involved, then the overall activation energy is often an arithmatic average of the activation energies of the individual steps. Obviously then, analysis of kinetic data for the fitting of kinetic equations and the evaluation of activation energy will be erroneous if one ignores a mixed control mechanism where it exists.

Reactions controlled by reagent supply:

It is not essential for the reaction rate always to be controlled by one or more rate-controlling steps. Sometimes, under a given set of conditions, all the steps may be sufficiently rapid for the overall reaction rate to be limited only by the rate of supply of reagents. To eliminate this possibility, one must ensure an excess supply of reagent at all times, and the independence of the reaction rate in relation to this supply.

Reagent starvation may manifest itself indirectly in the case of packed beds of particles. While there may be an excess of reagent in the exterior at all times, the diffusion of the reagent into the interior of the solid mass may be hindered, so that reaction is inhibited. It has often been found that in multiparticle ensembles where the reaction rate is proportional to the surface area of the particles, the rate initially increases, as expected, on grinding of the particles. However, if the particles are too fine, then the trend is reversed. This can be explained on the basis on hindrance for the reagent to diffuse into the mass when the particles are too fine, and accordingly the pores are more resistant to reagent permeation.

Heat transfer control:

Many reactions in metallurgy are accompanied by appreciable heat effects. During the reaction, heat flows either out of the system (exothermic reaction) or into the system (endothermic reaction). As a result, the temperature in the interior of a reaction mixture may deviate appreciably from those of the outer regions and the environment. When the reaction temperature becomes uncertain, then all kinetic analysis becomes questionable. For endothermic reactions, there is an additional problem. Since heat is absorbed in the interior regions of the solid, heat must be supplied continually from outside to keep the reaction occurring. Under certain conditions, this heat transfer process can become slower than any other reaction step. In such a situation, the reaction is said to be heat transfer-controlled and kinetic theories become irrelevant.

As an example, one can consider the decomposition of calcium carbonate, which is an endothermic reaction. It has been conclusively shown that, when the carbonate is in the form of a lump, the reaction depends not on kinetic steps, but on a heat transfer step [19]. For a 1 cm sphere, the interior temperature can be about 100 deg lower than the exterior, and the thermal properties become important. Heat transfer problems are lessened or eliminated when the solid sample size is small and the solid is powdery. To take care of uncertainties due to heat transfer, one should measure temperature changes within a sample during a reaction.

Nonisothermal kinetics

An isothermal reactor is an abstraction, and most reaction in real systems take place under nonisothermal conditions. However, although nonisothermal kinetics has received increasing attention from applied chemists, polymer chemists, researchers in the explosives industry, glass and ceramic scientists, etc, it has, as yet, not received due recognition from metallurgists.

Nonisothermal studies involve some special uncertainties. Usually, they are carried out under rising temperature conditions. It is necessary for the temperature-time function to be accurately known. Otherwise, the kinetic data cannot be analysed. Since rising temperature conditions can only be imposed by heating the sample in a furnace, one has the problem of creating thermal gradients within the sample itself. This is effectively minimized in thermal analysis by using very small samples. However, the small samples (~50 mg) recommended for thermal analysers may not be representive of many metallurgical systems. The author has developed a special technique for nonisothermal studies to obviate this problem. The technique, called the moving bed technique, has been discussed in several publications [20].

Nonisothermal kinetic data are analysed on the basis of three basic equations:

a) The differential form of the kinetic equation;
b) the Arrhenius type relationship; and
c) the equation relating temperature with time.

Combination of the first two equations yields

$$\ln\frac{(\mathrm{d}\alpha/\mathrm{d}t)}{f(\alpha)} = \ln A - \frac{E}{RT} \tag{12}$$

This equation remains valid irrespective of how the temperature changes with time, so long as $(\mathrm{d}\alpha/\mathrm{d}t)$ is measured as an instantaneous rate. It has been used to analyse kinetic data obtained under conditions of temperature rising at a fixed rate, as well as under fluctuating temperature condition [20, 21]. It is to be noted, however, that one requires an *a priori* knowledge of $f(\alpha)$. Thus, it is necessary first to conduct isothermal experiments to establish the form of $f(\alpha)$ (which equals $1/g'(\alpha)$).

An integral approach is possible when the variation of temperature with time is well defined and preferably linear. If the variation can be written as

$$T = A + Bt \tag{39}$$

where A and B are constants, then

$$\mathrm{d}T = B\,\mathrm{d}t \tag{40}$$

Combining this with Eq. (11) gives

$$\frac{\int \mathrm{d}\alpha}{f(\alpha)} = \frac{A}{B}\int \exp\left(-\frac{E}{RT}\right).\mathrm{d}T \tag{41}$$

Unfortunately, this equation has no exact solution. Different workers have proposed different approximate solutions, all of which involve some uncertainty. Thus, the same kinetic data processed according to the different solutions proposed in the literature yield [22] different values of E. Again, in all these approaches, one needs to know the form of $f(\alpha)$.

Some workers have attempted to obviate the problem by using a trial and error approach such as the following. One well-known approximate solution is that proposed by Coats and Redfern [23].

$$\frac{g(\alpha)}{T^2} = \left[\frac{AR}{3BE}\left\{1 - \frac{2RT}{E}\right\}\right] \exp(-E/RT) \tag{42}$$

The term within square brackets in the R.H.S. is normally taken as constant, and therefore a plot of $g(\alpha)/T^2$ versus reciprocal temperature should yield a straight line. In the trial and error approach, one tries out various $g(\alpha)$ functions to check which one yields the best fit. This model is then taken as the correct model. Such an approach, however, is likely to involve substantial uncertainty, because Eq. (42) itself is based on assumptions. It is always best to establish $f(\alpha)$ and $g(\alpha)$ via separate isothermal experiments.

Nonisothermal kinetic measurements are sensitive to several experimental variables, e.g. sample size, particle size, extent of packing, gas flow rate (for g/s reactions), rate of heating, etc., and these parameters need to be controlled. Even when much care is taken to standardize the experimental conditions, there is often inconsistency vis-à-vis isothermal data. For example, the E values obtained under isothermal and nonisothermal conditions often differ. Where this is a result of thermal gradients in samples during nonisothermal experiments, and consequently the temperature uncertainties, a closer match of E values may be obtained in the following way.

The nonisothermal E values are obtained under different heating rates and the correct value, which should be comparable with the isothermal E value, is obtained by extrapolation to 'zero' rate of heating. In theory, however, the E value should not depend on the heating rate. The nonisothermal E value should sometimes be different from the isothermal E value because of various factors. The subject has been discussed elsewhere [9].

Experimental conditions

So far we have examined the sources of uncertainties largely from the theoretical point of view. Errors can, of course, arise from many experimental factors. Only a few of these are considered here as examples.

Reaction time: For a reliable analysis of the kinetic data one has to define reaction time properly. There is sometimes difficulty about specifying the zero time. Suppose one wants to study the reaction of a solid with a flowing gas under isothermal conditions. Generally, one would first maintain an inert gas atmosphere and heat the solid to the desired temperature. Once the predetermined temperature is reached, then only the reaction gas is to be allowed in. The moment of switch-over, however, cannot be taken as the zero time, because some time elapses before the inert gas is purged out of the system and the new gas atmosphere is established. That is, the zero time comes somewhat later than the switch-over time.

If the gas atmosphere is maintained from the very beginning then reactions (nonisothermal) are initiated early, and the zero time therefore comes earlier than the so-called zero time when the predetermined temperature is reached.

For either case, however, a reliable time correction is possible if the kinetic data for the bulk of the reaction later are fitted to an equation, $g(\alpha) = kt$, where t is the apparent time. Such a plot does not go through $\alpha = 0$ at $t = 0$. Where a time lag exists because of the gas switch-over, the line cuts the x-axis at $\alpha = 0$. In the second case, the line cuts the y-axis at $t = 0$. The correct zero time is obtained by extrapolation. All subsequent analysis should be carried out with corrected time.

In the first example discussed, the apparent incubation period is ascribed to a time error. However, the incubation period may sometimes be a genuine result of a specific reaction mechanism, e.g. nucleation and grain growth or autocatalysis. Therefore, all kinetic data showing an apparent incubation period should be critically examined.

Any error in the time factor would completely invalidate the use of reduced time plots which use a ratio such as $t/t_{0.5}$. In fact, if the zero time is wrongly defined, then one may come to a wrong conclusion altogether concerning the kinetic model.

Temperature: It has been mentioned earlier that, due to the reaction heat, the temperature of a reaction system may not be uniform. During a gas-solid reaction, therefore, the gas temperature in the furnace may be substantially different from the temperature in the interior of the solid. Kinetic data cannot be meaningfully analysed unless the reaction temperature is measured properly. Therefore, one should perform direct measurement of the temperature of the solid by having a thermocouple embedded within the solid. For a given furnace temperature, the solid temperature can vary, depending on the size and physical characteristics of the reacting solid, its thermal properties, the reaction heat, the geometry of the system, the gaseous environment and the gas flow rate.

Gas pressure: When a reactant is gaseous and the kinetics is influenced by the partial pressure of a gas, then accurate determination of this pressure becomes necessary. It is well known that there can be different factors causing segregation in gas mixtures. Thorough mixing is therefore essential. If the gas is produced *in situ*, then the partial pressure can often become ill-defined because of temperature uncertainties. The importance of this is often not understood properly.

Consider the reaction of gaseous $ZrCl_4$ with solid NaCl, a reaction studied by Majumdar et al. [24]. $ZrCl_4$ gas was produced by heating solid $ZrCl_4$ in a glass bulb kept in a hot zone with accurately controlled temperature, and the vapour was allowed to react in a closed chamber with solid NaCl spheres. It was necessary to ensure that the temperature in all other regions in the chamber was higher than that at the bulb, whose temperature was used for calculation of the partial pressure. Any region with a lower temperature would have lowered the partial pressure of $ZrCl_4$ (g) because of the equilibrium there.

There are many other experimental uncertainties which can complicate kinetic studies. The aim of the preceding examples was merely to indicate uncertainties that can bead to major errors.

Conclusions

It may be concluded that kinetic studies in real metallurgical systems involve many uncertainties. These uncertainties can arise from both theoretical and experimental factors. Some of the major theoretical considerations include the following. Inadequate definitions of the kinetic parameter and the rate constant, identification of an incorrect kinetic equation and evaluation of an erroneous E value, the use for real systems of equations derived for ideal systems, the assumption off an incorrect rate-controlling step, etc. It is therefore advisable to carry out separate tests to corroborate conclusions of any kinetic analysis. It is also advisable to eliminate sources of theoretical and experimental errors, as far as possible, by careful planning, cros-examination and finally a thorough evaluation, keeping in mind possible errors. Many kinetic equations have only limited theoretical significance, even if they fit the kinetic data extremely well. Very often they are basically empirical.

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Zusammenfassung — Kinetische Untersuchungen in der Metallurgie schließen Messungen von Veränderungen geeigneter Parameter an Systemen ein, wobei diese unter kontrollierten Bedingungen bestimmte Umwandlungen eingehen. Solche Messungen sind oft sehr einfach und es ist nicht allzu schwer, eine große Menge von Versuchsdaten zu bekommen. Anschließend werden die Daten völlig routinemäßig an einigen kinetischen Modellen erprobt und die kinetischen Parameter ermittelt, um einen 'Reaktionsmechanismus' zu entwickeln. Unglücklicherweise kann die scheinbare Einfachheit der Messungen, der mathematischen Verarbeitung der Daten, ja selbst die Reproduzierbarkeit zu Mißschlüssen führen, da jeder Schritt mit unsicherheiten behaftet sein kann und sich somit ein fehlerhafter Schluß ergeben kann. Vorliegende Arbeit beschäftigt sich mit dem Ursprung solcher Unsicherheiten und ihren Folgen.