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Heterogeneous kinetics: from solid–gas reaction to solid–liquid dissolution

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Abstract

The extension of the formal kinetics of solid–gas reactions to solid–liquid dissolution is investigated theoretically. The work is based on modelling the dissolution of a solid in a closed system by a stoichiometrically simple chemical reaction $A_{solid} \rightleftarrows A_{liquid}$ proceeding up to either an equilibrium state if the solid phase is initially in excess or exhaustion in the reverse situation. The initial amount of solid compared to the capacity of the liquid phase appears as a major factor of complexity. First, the rate equation is formulated in terms of the intensive variables without any assumption about the mechanism and the rate-limiting step. The resulting equations are compared to those derived from Nersnt boundary-layer theory of dissolution. Only when the solid phase is initially in deficit does the kinetic approach turn to be in the wrong if the rate of dissolution is assumed to depend on the maximum of the concentration gap. At this stage, the dissolution mechanism has to be taken into consideration and the rate equation adjusted accordingly. Finally, algebraic expressions for the fractional dissolution curves can be obtained. Except for particular solid liquid ratios they are *not* superimposable by an affinity relation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous kinetics; Solid–liquid dissolution

1. Introduction

A theoretical investigation of the dissolution of a solid constituent, A, in a liquid phase is conducted in the following conditions. The problem is simplified by considering that the molecular integrity of the solid is preserved in the dissolution process and that the latter obeys a single and stoichiometrically simple equation written as follows:

$$A_1 \rightleftarrows A_2 \qquad (1)$$

Indices 1 and 2 refer to the solid and the liquid phase, respectively. Eq. (1) is also assumed reversible, which means that the equilibrium saturation state of the liquid phase can be physically realised provided the initial amount of solid A_1 is sufficient. Indeed, the objective being to build a reasoning, not to exhaustively investigate all conceivable experimental situations, we have restricted the problem to the *isothermal* dissolution in a *closed* system of *finite* volume noted V_2. The latter is also assumed to remain *constant* despite the transfer of matter. The reason for this is that taking its increase into account would greatly complicate the equations. However, care should be paid to the fact that this may become a poor approximation in certain particular situations. It is also finally assumed that the liquid phase is "ideally" agitated and

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that the simple problem where the solute would fill gradually a stagnant liquid by diffusion is not pertinent.

In contrast, it is mathematical trivial to include in the problem the assumption that the liquid is not necessarily a pure solvent but may contain an initial concentration of the solute, noted C_2^0, intermediate in value between 0 and the saturation concentration C_2^{eq}. But the innovative contribution of the present work is in the exhaustive investigation of the influence of the initial amount of the solid phase on the kinetics. Indeed, that amount expressed here as number of moles n_1^0, may be lower than, equal to or larger than the amount effectively consumed by the reaction (dissolution) and this proves to have important consequences.

In contrast to other theoretical approaches, ranging from that of Nernst [1] and other contemporaries [2,3] at the beginning of the century to more recent ones based on a more elaborate modelling of interfacial mass transfer [4,5], the present works starts from a *purely kinetic* point of view. We have tried to apply the formal heterogeneous kinetic theory developed among others by one of us for modelling solid–gas reactions to the present topic. More precisely, the rate equation is investigated starting from purely logical grounds and the simplest possible assumptions about the possible dependence of the rate of reaction on the concentration of the liquid phase. The reasoning is pushed as far as possible without making any assumption as to the particular physical mechanism that may be kinetically limiting, but finally encounters a limitation in the particular case of an initial deficit of solid A_1. This appears in the comparison with the other mentioned theory based explicitly on the assumption of diffusion control, and the kinetic theory then has to be adjusted accordingly.

Nevertheless, it must be emphasised that the formulation of the dissolution kinetics in terms of a dimensionless conversion degree proves quite fruitful. It allows one for instance to include the variation of the surface area of the dissolving solid in a straightforward manner without any particular assumption on the shape of the average solid particle, except that it remains unchanged in the process. In particular, no such unjustifiable assumption as that the rate of reduction of the radius of the solid particle should remain constant is introduced. And the final result is that the rate equation can be integrated in all cases to provide an equality between a reduced time variable and a more or less intricate function of the conversion degree and of a parameter related to the initial excess or deficit of solid A_1.

2. Application of the formal theory of heterogeneous kinetics to solid–liquid dissolution

The rate of a chemical reaction such as reaction (1) is not just the rate of change of the concentration of component A_2 in the solution or of the number of moles of the reactant A_1. It must be defined as the derivative with respect to time of a suitable variable measuring the progress of the reaction. The latter, which is referred to by various names (fractional reaction, conversion degree, etc.) derives from the basic law of definite proportions.

2.1. Extensive and intensive variables expressing the progress of reactions

Let us consider a general chemical equation involving several components (reactants and products) and representing a reaction taking place in a closed system. The number of moles of component i is noted n_i and its stoichiometric coefficient in the reaction v_i. The infinitesimal progress of such a reaction is related to the infinitesimal change of the number of moles of each component by:

$$\frac{\mathrm{d}n_1}{v_1} = \frac{\mathrm{d}n_2}{v_2} = \cdots = \frac{\mathrm{d}n_i}{v_i} = \mathrm{d}\xi \qquad (2)$$

and the rate of reaction can be defined with respect to the variable ξ as:

$$r_\xi = \frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad (3)$$

However, ξ is an *extensive* variable and is dependent on how the coefficients v_i are counted (they may be multiplied by any arbitrary constant). This is the reason why one wants to define an *intensive* variable, α, to represent the conversion degree of the reactants and measure the progress of the reaction. The definition of α stems logically from that of limiting reactant, the exhaustion of which is the cause of the end of the reaction where the variable ξ achieves its largest value $\xi^{\max}$:

$$\alpha = \frac{\xi}{\xi^{\max}} \tag{4}$$

The corresponding reaction rate is then:

$$r_\alpha = \frac{d\alpha}{dt} = \frac{1}{\xi^{\max}}\frac{d\xi}{dt} \tag{5}$$

However, in the particular case of the dissolution reaction expressed by Eq. (1), the reactant A_1 may or may not be fully consumed at the end of the reaction. If the concentration of A_2 in solution reaches the saturation value C_2^{sat}, the reaction stops because equilibrium is reached not because the limiting reactant is exhausted. To take this distinction into account in the following it is convenient to define the number of moles of reactant A_1 remaining at equilibrium, n_1^{xs}, as the difference between the initial number, n_1^0 and the number just needed to saturate the solution, $(n_1^0)^{\mathrm{sat}}$. If the volume of the liquid phase is noted V_{liq} (and assumed invariable as a first approximation) this comes to:

$$n_1^{\mathrm{xs}} = n_1^0 - (n_1^0)^{\mathrm{sat}} = n_1^0 - (C_2^{\mathrm{eq}} - C_2^0)V_{\mathrm{liq}} \tag{6}$$

Thus, in case $n_1^{\mathrm{xs}} > 0$, the maximum value reached by the variable ξ is no longer depending merely on the initial amount of the limiting reactant but also on a thermodynamic equilibrium parameter. This makes an important difference, and the conversion degree is then represented by a different symbol:

$$\eta = \frac{\xi}{\xi^{\mathrm{eq}}} \tag{7}$$

The corresponding reaction rate writes:

$$r_\eta = \frac{d\eta}{dt} = \frac{1}{\xi^{\mathrm{eq}}}\frac{d\xi}{dt} \tag{8}$$

The next step is to define and investigate the properties of the so-called rate equation. The rate of a single reaction, as defined by either Eq. (5) or Eq. (8), is expected from the theory to be a function of physical variables, among which temperature and concentrations of the various components play a major role, and of the conversion degree. It takes the general form:

$$\frac{d\xi}{dt} = r_\xi(T, C_i; \xi) \tag{9}$$

In view of the aforementioned definitions of the conversion degrees α and η (Eqs. (5) and (8)) there is no difficulty to redefine the rate equation with respect to these variables when appropriate, i.e. in case of an initial deficit or excess of solid A_1, respectively:

$$\frac{d\alpha}{dt} = r_\alpha(T, C_i; \alpha) \quad \text{or} \quad \frac{d\eta}{dt} = r_\eta(T, C_i; \eta) \tag{10}$$

Each physical constant may in principle be imposed a certain time dependence. Of course, the simplest situation is that where they are kept constant during the reaction.

The final objective of heterogeneous kinetics is to interpret experimental data in order to formulate the rate equation and show how to use it in order to understand, as far as possible, the underlying reaction mechanism. It is well known [6–8] that this task is greatly simplified whenever the conversion variables ξ, α or η can be separated from the physical variables in the rate equation which then takes the form:

$$\frac{d\xi}{dt} = k(T, C_i) \times f_\xi(\xi) \quad \text{or} \quad \frac{d\alpha}{dt} = k(T, C_i) \times f_\alpha(\alpha)$$
$$\text{or} \quad \frac{d\eta}{dt} = k(T, C_i) \times f_\eta(\eta) \tag{11}$$

Then, that particular property of the rate equation can be inferred and demonstrated directly from experiment if different fractional reaction curves, $\alpha(t)$ or $\eta(t)$, obtained for different fixed values of one physical variable prove to be affine with respect to the variable t. If so, one such curve can be superimposed on another one by multiplying its time scale by an appropriate constant number, noted b. For instance, if temperature proves the only physical variable that is changed from one curve to the other, taking the values T_1 and T_2, respectively, the condition of affinity would be expressed by the equality:

$$\alpha(T_1, t) = \alpha(T_2, bt) \tag{12}$$

This is made obvious by integration of Eq. (11), which shows that the conversion degree can be put in the form:

$$\alpha \text{ or } \eta = \Phi[k(T, C_i) \times (t - t^0)] \tag{13}$$

For a set of finite values of $k(T, C_i)$, Eq. (13) represents indeed the general equation of a set of curves that can be superimposed on any one of them by application of the affinity transformation $[\alpha, (t - t^0)] \rightarrow [\alpha, b(t - t^0)]$.

In contrast to that somewhat ideal situation, if experimental dissolution curves turn to be non-affine, it can be stated that the conversion degree and the physical variables cannot be separated in the rate equation. It is going to be shown in the following that, somewhat unexpectedly, this constitutes the general rule with dissolution and that this rule is only broken in very particular experimental situation the simplest one being when $n_1^0 = (n_1^0)^{\mathrm{sat}}$.

2.2. Expression of experimental dissolution kinetics in terms of conversion degree

In a closed system, it is in principle a simple task to follow the progress of the dissolution of a solid A_1 by monitoring the concentration C_2 of the liquid phase. If the volume of the latter is assumed constant, it is particularly easy to express the conversion variable ξ and hence α or η as functions of the initial and final compositions of the system. In the initial state, the concentration of the solute may not necessarily be zero and its value, noted C_2^0, can be readily incorporated in the equation. It can be regarded as another parameter of action on the rate of dissolution.

In order to write down the relations between the composition of the system and the conversion degree at any given time t, one starts with the integration of Eq. (2) according to:

$$\xi = \frac{n_i}{v_i} + Z \tag{14}$$

where Z is the integration constant. Since, by definition, at initial time, t^0, the value of ξ is just 0 and $n_1 = n_1^0$, it appears that $Z = -n_1^0/v_1$. The expression for ξ, α and η are derived in Table 1 for the case of Eq. (1) where $v_1 = -1$ and $v_2 = 1$. In the particular situation where one would start with the exact amount of solid required to reach saturation, $n_1^0 = (n_1^0)^{\mathrm{sat}} = (C_2^{\mathrm{eq}} - C_2^0)V_{\mathrm{liq}}$, the conversion degree would have the following expression:

$$\alpha \text{ or } \eta = \frac{C_2 - C_2^0}{C_2^{\mathrm{eq}} - C_2^0} \tag{15}$$

In case of an initial excess of solid A_1, the conversion degree η would be given by the same Eq. (15) with η as the conversion degree, whereas in case of an initial deficit of A_1 (such that the reaction reaches an end because the limiting reactant is exhausted), one would get:

$$\alpha = \frac{C_2 - C_2^0}{C_2^{\mathrm{max}} - C_2^0} \tag{16}$$

Table 1
The expression for ξ, α and η

Component	A_1			A_2		
Time	0	t	t^{max}	0	t	t^{max}
$n_1^0 = (n_1^0)^{\mathrm{sat}} = V_{\mathrm{liq}}(C_2^{\mathrm{eq}} - C_2^0)$						
$n_{1 \text{ or } 2}$	n_1^0	n_1	0	n_2^0	n_2	$n_2^{\mathrm{max}} = n_2^{eq}$
ξ	0	$n_1^0 - n_1$	n_1^0	0	$n_2 - n_2^0$	$n_2^{\mathrm{eq}} - n_2^0$
Z in Eq. (14)	n_1^0			$-n_2^0$		
$\alpha = \xi/\xi^{\mathrm{max}}$	$(n_1^0 - n_1)/n_1^0$			$(n_2 - n_2^0)/(n_2^{\mathrm{max}} - n_2^0) = (C_2 - C_2^0)/(C_2^{\mathrm{max}} - C_2^0)$		
$n_1^0 > (n_1^0)^{\mathrm{sat}}$ $(n_1^0 = (n_1^0)^{\mathrm{sat}} + n_1^{\mathrm{xs}})$						
$n_{1 \text{ or } 2}$	n_1^0	n_1	n_1^{xs}	n_2^0	n_2	n_2^{eq}
ξ	0	$n_1^0 - n_1$	$n_1^0 - n_1^{\mathrm{xs}}$	0	$n_2 - n_2^0$	n_2^{eq}
Z in Eq. (14)	n_1^0			$-n_2^0$		
$\eta = \xi/\xi^{\mathrm{eq}}$	$(n_1^0 - n_1)/(n_1^0 - n_1^{\mathrm{xs}})$			$(n_2 - n_2^0)/(n_2^{\mathrm{eq}} - n_2^0) = (C_2 - C_2^0)/(C_2^{\mathrm{eq}} - C_2^0)$		
$n_1^0 < (n_1^0)^{\mathrm{sat}}$ $(n_2^{\mathrm{max}} < n_2^{\mathrm{eq}})$						
$n_{1\mathrm{or}2}$	n_1^0	n_1	0	n_2^0	n_2	n_2^{max}
ξ	0	$n_1^0 - n_1$	n_1^0	0	$n_2 - n_2^0$	$n_2^{\mathrm{max}} - n_2^0$
Z in Eq. (14)	n_1^0			$-n_2^0$		
$\alpha = \xi/\xi^{\mathrm{max}}$	$(n_1^0 - n_1)/n_1^0$			$(n_2 - n_2^0)/(n_2^{\mathrm{max}} - n_2^0) = (C_2 - C_2^0)/(C_2^{\mathrm{max}} - C_2^0)$		

These equations can be written in terms of "concentration gaps" defined as the differences between either the instantaneous or final values of the solute concentration on the one hand and its initial value on the other hand. Symbolising these concentration gaps by the capital letter E, one can write:

$$E_0^{\max} = C_2^{\max} - C_2^0 \quad \text{and} \quad E_0^{\text{eq}} = C_2^{\text{eq}} - C_2^0 \tag{17}$$

$$E^{\max} = C_2^{\max} - C_2 \quad \text{and} \quad E^{\text{eq}} = C_2^{\text{eq}} - C_2 \tag{18}$$

Thus Eqs. (15) and (16) can be transformed into:

$$E^{\max} = E_0^{\max}(1-\alpha) \quad \text{and} \quad E^{\text{eq}} = E_0^{\text{eq}}(1-\eta) \tag{19}$$

The instantaneous value of a concentration gap is merely the product of a linear function of the conversion degree by its initial value $E_0^{\max}$ or E_0^{eq}. It seems legitimate to consider that, apart from temperature, the latter constitutes the physical factor controlling the rate of reaction, and it is the role of the rate equation to clarify its influence in mathematical terms.

Noting that $\mathrm{d}\alpha = \mathrm{d}\eta = \mathrm{d}C_2$, the dissolution rate can finally be obtained as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = -\frac{1}{E_0^{\max}} \times \frac{\mathrm{d}E^{\max}}{\mathrm{d}t} = \frac{1}{E_0^{\max}} \times \frac{\mathrm{d}C_2}{\mathrm{d}t} \quad \text{or}$$
$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\frac{1}{E_0^{\text{eq}}} \times \frac{\mathrm{d}E^{\text{eq}}}{\mathrm{d}t} = \frac{1}{E_0^{\text{eq}}} \times \frac{\mathrm{d}C_2}{\mathrm{d}t} \tag{20}$$

2.3. Utilisation of the rate equation to interpret experimental dissolution kinetics

As can be seen from Eqs. (11), (19) and (20) the rate equation (and its integral form as a consequence) derived from the formal kinetic analysis appear essentially as functions of the limit values of the variable used to express the composition of the system, $E_0^{\max}$ or E_0^{eq}, and of time. The experimental investigation is most usually carried out in such a way as to generate fractional dissolution curves $\alpha(t)$ or $\eta(t)$ at constant temperature for different values of $E_0^{\max}$ or E_0^{eq}.

As already mentioned, a favourable situation arises if the curves so obtained turn to be related by an affinity relation of the form $[\alpha, t] = [\alpha, bt]$. Accordingly, the first logical step of any data analysis should be to test that possibility. Let us consider two curves related by such an affinity relation and indexed R and S, respectively in Fig. 1. They are supposedly obtained at the same temperature for distinct values of concentration gap, $E_{0,R}^{\max}$ and $E_{0,S}^{\max}$.

Since, by definition, the variables t and α (or η) are separated in the rate equation, it is obvious from the integration of the latter, that, for any particular value α^* of the conversion factor, the equality $k_R t_R = k_S t_S$ should be verified, where $k_S/k_R = b$ is the affinity ratio (see Fig. 1). One may assume that the dependence of

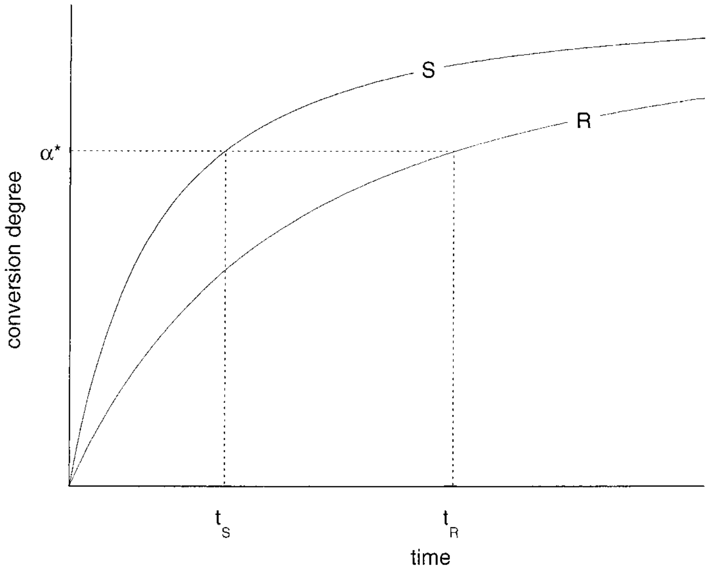

Fig. 1. Schematic representation of two fractional reaction curves related by an affinity relation. The ratio of the time values t_R and t_S defines the affinity constant b.

the rate constants k_R and k_S on the concentration gaps may be expressed by a power law, where the exponent q would be some equivalent of the order of the reaction in homogeneous chemical kinetics. Accordingly, one would write:

$$k_R = k_T(E_{0,R}^{\max})^q, \qquad k_S = k_T(E_{0,S}^{\max})^q \tag{21}$$

and the exponent q would be readily be computed according to:

$$q = \frac{\ln t_S - \ln t_R}{\ln E_{0,R}^{\max} - \ln E_{0,S}^{\max}} \tag{22}$$

Its value should, by definition, remain constant along the curves and independent of the particular pair of curves selected in the isothermal set.

These preceding properties of the fractional dissolution curves stem from the assumption that the rate of reaction is proportional to a power function of the instantaneous concentration gap, i.e. the rate equation takes the well-known practical form:

$$\frac{d\alpha}{dt} = k_T[E_0^{\max}(1-\alpha)]^q \times f_\alpha(\alpha) \tag{23}$$

or

$$\frac{d\eta}{dt} = k_T[E_0^{\mathrm{eq}}(1-\eta)]^q \times f_\eta(\eta) \tag{24}$$

However, the dependence of the reaction rate and the maximum concentration gap can take other forms and only experiment or the independent knowledge of the reaction mechanism can decide of the proper rate law.

As for the influence of temperature, the major physical parameter, the usual practice is to verify if a set of curves obtained at various temperatures verify the apparent Arrhenius exponential law. In which case, referring again to Fig. 1 but with the assumption that the curves represent fractional conversion at temperatures T_S and T_R, then $b = k(T_S)/k(T_R)$ and

$$\ln t_S - \ln t_R = \frac{E}{R}\left[\frac{1}{T_S} - \frac{1}{T_R}\right] \tag{25}$$

The apparent activation energy value is usually computed from the slope of the graph obtained by plotting ln(t) or ln(r) versus $1/T$ and should remain constant if the value of α^* is varied.

In contrast, it is often observed experimentally, that the value of E so obtained varies along the curves with the value of α^*. This does *not* mean that the Arrhenius law is no valid but simply that it is obscured by the contribution of other thermally activated parameter. Indeed, the other situation (frequent in practice) is when the curves $\alpha(t)$ or $\eta(t)$ are *not* related by the aforementioned affinity relation. Then, for instance, changing the temperature affects the equilibrium state and hence the value of E_0^{eq}. Then, the foregoing considerations are no longer valid and it is important to realise that the activation energy of the reaction can no longer be obtained as mentioned, e.g. using Eq. (25). This can be made obvious by considering the explicit integral forms of the rate equation derived in the next section.

3. Confrontation to experimental kinetics

There are neither place nor sufficient motivation of the authors to embark upon reviewing the heap of published experimental data about solid–liquid dissolution kinetics in such fields as pharmaceutical or geological applied sciences. Instead, and based on the current knowledge that the Nernst Eq. (5) correctly models a number of such experimental results, it is simply assumed that a test of the present formal kinetic analysis can be reduced to a comparison of its predictions with those inferred from Nernst equation. The latter has been derived by Nernst [1] and also by other authors [2,3] based on the assumption that the mass transfer through the boundary (diffusion) layer is the rate-limiting step of the reaction. In other words, and in contrast with the present approach, it requires the reaction mechanism to be known beforehand.

In our notation, Nernst equation would write:

$$V_{\mathrm{liq}}\frac{dC_2}{dt} = \frac{D}{\delta}S_1(t)[C_2^{\mathrm{eq}} - C_2] = hS_1(t)[C_2^{\mathrm{eq}} - C_2] \tag{26}$$

In Eq. (26), D is the diffusion coefficient of the solute in the liquid phase, δ the boundary-layer thickness, and the ratio of both can be identified with the mass transfer coefficient h.

If and only if $C_2^{\max} = C_2^{\mathrm{eq}}$ and $q = 1$, can one strictly identify our Eq. (23) with Eq. (26). As for Eq. (24), it remains valid whatever the initial excess of solid S_1, but then the solid phase surface area reaches a finite final value. In both cases, one can transform Eq. (26) into:

$$V_{\text{liq}}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = hS_1(t)[1-\alpha] \quad \text{or} \quad V_{\text{liq}}\frac{\mathrm{d}\eta}{\mathrm{d}t} = hS_1(t)[1-\eta] \tag{27}$$

and the following relations hold between parameters in both notations:

$$k_T E_0^{\text{eq}} \equiv \frac{h}{V_{\text{liq}}} \quad (\text{dimension}: \mathrm{T}^{-1}\mathrm{L}^{-2}) \tag{28}$$

$$f_\alpha(\alpha) \equiv S_1(t) \quad \text{and} \quad f_\eta(\eta) \equiv S_1(t)$$
$$\text{in accordance with theory (3)} \tag{29}$$

Then, the only remaining problem before integrating the rate equation is to express the surface area of the solid phase, $S_1(t)$, as a function of either α or η.

In contrast, when $C_2^{\max} < C_2^{\text{eq}}$, Nernst equation is *no longer* equivalent to our Eq. (23), because the term $E_0^{\max}$ is now replaced by E_0^{eq}. This minor change in script bears of fundamental significance: the assumption that the reaction rate is function of (here proportional to) the availability of the limiting reactant is not valid here. Accepting this, Nernst equation can now be written as: $V_{\text{liq}}\,\mathrm{d}C_2/\mathrm{d}t = hS(t)[C_2^{\text{eq}} - C_2^0 - (C_2 - C_2^0)]$ and, by use of Eqs. (17)–(20) one obtains:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{h}{E_0^{\max}V_{\text{liq}}}S_1(t)[E_0^{\text{eq}} - E_0^{\max}\alpha] = \frac{h}{V_{\text{liq}}}S_1(t)\left[\frac{E_0^{\text{eq}}}{E_0^{\max}} - \alpha\right] \tag{30}$$

One proceeds now to the calculations in these different cases, up to the integration of the rate equation. This is made possible because the surface area can be expressed as a function of α or η as considered first.

3.1. Expression of S_1 as a function of α or η

Let us consider the "isomorphous" contraction of a sphere or any other 3D non-fractal geometrical object as modelling the dissolution of an average particle of solid A_1. The relations between the value of the volume or surface area at time t and the initial values at $t = 0$ are simple functions of the conversion factor α or η. Furthermore, at any time, the surface area remains proportional to the volume raised to the power 2/3. Thus, if the initial solid A_1 is fully dissolved at the end of the reaction, its volume and surface area can be expressed as:

$$V_1 = V_1^0(1-\alpha) \quad \text{and} \quad S_1 = S_1^0 \times (1-\alpha)^{2/3} \tag{31}$$

In contrast, in case there is an initial excess of A_1 which will remain in suspension at the end of the dissolution process, the final values of its volume and surface area, noted V_1^{xs} and S_1^{xs}, respectively, are finite. Whence:

$$V_1 = V_1^0 \times (1-\eta) + V_1^{\text{xs}} \quad \text{and}$$
$$S_1 = S_1^0 \times (1-\eta)^{2/3} + S_1^{\text{xs}} \tag{32}$$

Eqs. (31) and (32) are *independent* of the shape factors that would appear in expressions of either volume or surface area in terms of a linear dimension of the particles. As stated in different terms, this remains true only and only if the shape of the particles remains unchanged during the dissolution process.

3.2. Expression of the conversion-functions $\alpha(t)$ and $\eta(t)$ in case $q = 1$

Based on the foregoing, it is now possible to obtain the conversion-functions $\alpha(t)$ or $\eta(t)$ by integrating the rate equation. Only the simple assumption $q = 1$ in the rate equation is investigated here because it corresponds to common experimental observation as expressed by the general validity of Nernst equation. The three following situations are considered successively: the initial amount of solid A_1 is either equal to, larger or lower than the amount needed to reach saturation of the liquid phase at the end of the process.

$C_2^{\max} = C_2^{\text{eq}}$, i.e. $n_1^0 = (n_1^0)^{\text{sat}} = V_{\text{liq}} \times (C_2^{\text{eq}} - C_2^0)$

Since in this situation $E_0^{\max} \equiv E_0^{\text{eq}}$, the combination of Eqs. (23) and (29) with expression (31) for $S_1(t)$ yields the simple ordinary differential Eq. (33):

$$\frac{\mathrm{d}\alpha}{(1-\alpha)^{5/3}} = S_1^0 E_0^{\text{eq}} k_T\,\mathrm{d}t \equiv S_1^0\frac{h}{V_{\text{liq}}}\,\mathrm{d}t \tag{33}$$

Integrating Eq. (33) from zero initial time to t gives:

$$(a) \quad F(\alpha) = (1-\alpha)^{-2/3} - 1 = \tfrac{2}{3}S_1^0 E_0^{\text{eq}} k_T t \tag{34}$$

Here, it is possible to reverse the integral form Eq. (34) and obtain the algebraic expression of the conversion degree in function of time:

$$\alpha = 1 - \frac{1}{[1+(2/3)S_1^0E_0^{\mathrm{eq}}k_Tt]^{3/2}} = 1 - \frac{1}{1+[(2/3)(t/t^*)]^{3/2}} \tag{35}$$

Defining the time constant $t^* = 1/S_1^0E_0^{\mathrm{eq}}k_T$ allows one to reduce all curves obtained for different values of the physical variables to a single master curve plotted in Fig. 2. $F(\alpha)$ in Eq. (34) is the so-called linear transform of the dissolution curve $\alpha(t)$ from which the numerical value of the time constant can be readily computed.

(*b*) $n_1^0 > (n_1^0)^{\mathrm{sat}}$

Solution to Eq. (27) requires that the final surface area of the remaining solid phase when equilibrium is reached be taken into account. A simple way to do it is as follows. The fractional reaction variable η can be written as:

$$\eta = \frac{n_1 - n_1^0}{n_1^{\mathrm{xs}} - n_1^0} = \frac{V_1 - V_1^0}{V_1^{\mathrm{xs}} - V_1^0} = \frac{(S_1)^{3/2} - (S_1^0)^{3/2}}{(S_1^{\mathrm{xs}})^{3/2} - (S_1^0)^{3/2}} \tag{36}$$

Eq. (36) stems from the trivial proportionality relations between volume and number of moles, n on the one hand and between volume and the fractional power 3/2 of the surface area on the other. Accordingly, $(S_1)^{3/2} = \eta \times [(S_1^{\mathrm{xs}})^{3/2} - (S_1^0)^{3/2}] + (S_1^0)^{3/2}$ and:

$$\frac{S_1}{S_1^0} = [1 - a\eta]^{2/3} \tag{37}$$

where $a = (n_1^0)^{\mathrm{sat}}/n_1^0 = 1 - (S_1^{\mathrm{eq}}/S_1^0)^{3/2} > 0$ represents the *soluble fraction* of the initial amount of solid A_1. Combination of Eqs. (27) and (28) (with η as the conversion degree) and Eq. (37) yields:

$$\int_0^\eta \frac{\mathrm{d}\eta}{(1-\eta)[1-a\eta]^{2/3}} = S_1^0E_0^{\mathrm{eq}}k_Tt = \frac{t}{t^*} \tag{38}$$

The definite integral on the LHS of Eq. (38) admits the following solution (obtained using Maple V symbolic computation code):

$$\begin{aligned} F(a,\eta) = {} & \frac{1}{(1-a)^{2/3}}\Bigg\{ -\ln[(1-a\eta)^{1/3} - (1-a)^{1/3}] + \frac{1}{2}\ln[(1-a)^{2/3} + (1-a)^{1/3}(1-a\eta)^{1/3} + \cdots \\ & + [1-a\eta]^{2/3}] + \sqrt{3}\arctan\left[\frac{\sqrt{3}}{3}\left(\frac{2(1-a\eta)^{1/3}}{(1-a)^{1/3}} - 1\right)\right]\Bigg\} \\ & - \frac{1}{(1-a)^{2/3}}\Bigg\{ -\ln[1-(1-a)^{1/3}] + \cdots + \frac{1}{2}\ln[(1-a)^{2/3} + (1-a)^{1/3} + 1] \\ & + \sqrt{3}\arctan\left[\frac{\sqrt{3}}{3}\left(\frac{2}{(1-a)^{1/3}} - 1\right)\right]\Bigg\} = \frac{t}{t^*} \end{aligned} \tag{39}$$

The graphs of Eq. (39) for different values of parameter a are shown in Fig. 3 (the numerical values of $F(\alpha, \eta)$ constitute the values of the abscissa t/t^* and those of η from which they were computed constitute the ordinate).

(*c*) $n_1^0 < (n_1^0)^{\mathrm{sat}}$

The liquid phase is not saturated at the end of the process. In this case and as already mentioned, the rate equation Eq. (30) has to be used instead of Eq. (23). It can be written as:

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{(a-\alpha)(1-\alpha)^{2/3}} = S_1^0E_0^{\mathrm{max}}k_Tt$$

$$\text{where } a = \frac{E_0^{\mathrm{eq}}}{E_0^{\mathrm{max}}} = \frac{(n_1^0)^{\mathrm{sat}}}{n_1^0} \tag{40}$$

Solution to Eq. (40) writes:

$$\begin{aligned} F(a,\alpha) = {} & \frac{1}{(a-1)^{2/3}}\Bigg\{ -\ln\frac{(1-\alpha)^{1/3} + (a-1)^{1/3}}{1+(a-1)^{1/3}} + \frac{1}{2}\ln\frac{(1-\alpha)^{2/3} - (1-\alpha)^{1/3}(a-1)^{1/3} + (a-1)^{2/3}}{1-(a-1)^{1/3} + (a-1)^{2/3}} \\ & - \sqrt{3}\arctan\left[\frac{\sqrt{3}}{3}\left(1 - 2\frac{(1-\alpha)^{1/3}}{(a-1)^{1/3}}\right)\right] + \sqrt{3}\arctan\left[\frac{\sqrt{3}}{3}\left(1 - 2\frac{1}{(a-1)^{1/3}}\right)\right]\Bigg\} = \frac{t}{t^*} \end{aligned} \tag{41}$$

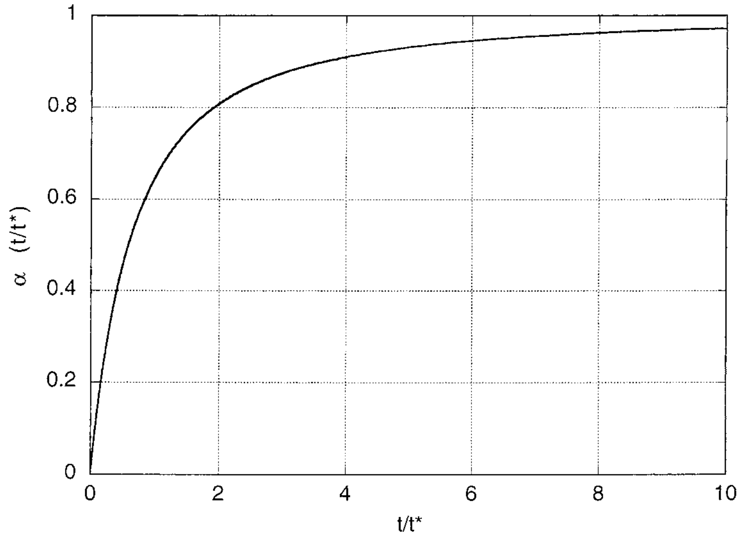

Fig. 2. Graph of the fractional dissolution curves $\alpha(t/t^*)$ expressed by Eq. (35) if $n_1^0 = (n_1^0)^{\text{sat}}$.

The graphs of Eq. (41) for different values of the deficit parameter a are shown in Fig. 4. The major difference with graphs of Eqs. (35) and (39) in Figs. 2 and 3 is that the reaction now stops at a finite time $t^{\max}$. An expression for the dependence of $t^{\max}$ on the solid excess parameter a can be obtained by setting $\alpha = 1$ in Eq. (41):

$$t^{\max} = \frac{t^*}{(a-1)^{2/3}}\left[-\ln\frac{(a-1)^{1/3}}{1+(a-1)^{1/3}} + \frac{1}{2}\ln\frac{(a-1)^{2/3}}{1-(a-1)^{1/3}+(a-1)^{2/3}} - \cdots - \sqrt{3}\frac{\pi}{6} + \sqrt{3}\arctan\left[\frac{\sqrt{3}}{3}\left(1-2\frac{1}{(a-1)^{1/3}}\right)\right]\right] \quad (42)$$

The limit value of $t^{\max}$ as $a \to \infty$ is 0 whereas if $a \to 1^+$, $t^{\max} \to \infty$.

It has been amply emphasised in Section 2 that the fractional conversion curves $\alpha(t)$ have the interesting property of being superimposable by an affinity transformation if the conversion degree is separated from all physical variables and time in the rate equation. Let us reconsider this point in the light of the foregoing results.

In the particular case where $n_1^0 = (n_1^0)^{\text{sat}} = V_{\text{liq}}(C_2^{\text{eq}} - C_2^0)$, the condition of affinity is obviously fulfilled in Eq. (34) and it is easy to demonstrate that the graph in Fig. 2 may be regarded as the superimposition of all possible $\alpha(t)$ by appropriate time scale multiplication. As an example, let us consider two temperature values, T_1 to T_2, and the corresponding pair of curves $\alpha(t, T_1)$ and $\alpha(t, T_2)$. That the former can be superimposed on the latter if its time scale is multiplied by the constant factor (affinity ratio) $b = t_2^*/t_1^* = k(T_1)/k(T_2)$ is readily proved by considering Eq. (34) and noting that for any particular value of α, one can write:

$$F(\alpha) = \frac{3}{2}\left[(1-\alpha)^{-2/3} - 1\right] = \frac{t_1}{t_1^*} = \frac{t_2}{t_2^*} \Rightarrow t_2 = \frac{t_2^*}{t_1^*} \times t_1 = bt_1 \quad (43)$$

In case of either initial excess or deficit of solid phase, the LHS of the integral rate Eqs. (38) and (40) is no longer function of the sole conversion degree but contains the extra factor, a. The consequence of this

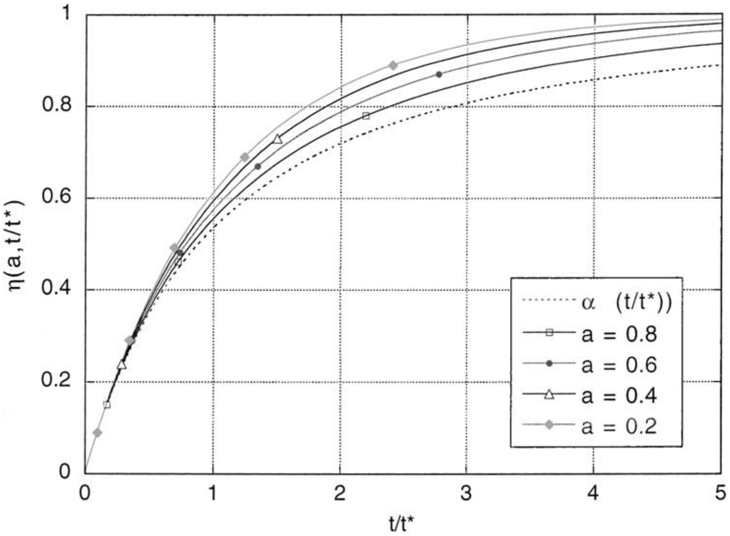

Fig. 3. Graph of the fractional dissolution curves $\eta(a, t/t^*)$ expressed by Eq. (39) in case there is an initial excess of solid phase, i.e. $n_1^0 > (n_1^0)^{\text{sat}}$.

on the mathematical property of the fractional conversion curve requires attention and is not the same as in the former case.

One considers first the case $n_1^0 > (n_1^0)^{\text{sat}}$ remembering that parameter a stands for the soluble fraction of solid A_1, and that, in the limit case $a = 1$, $\alpha \equiv \eta$ and the rate Eq. (38) reduces to Eq. (33). The set of curves $\eta(t)$ shown in Fig. 3 may be tested for affinity by adjusting their respective time scale to that of the curve $\alpha(t/t^*)$ in Fig. 2 and the process can be put in the following mathematical terms: for any particular value of the conversion degree η and α, we define the ratio of the corresponding time values:

$$R_{a,1} = \frac{F(a,\eta)}{F(1,\eta)} = \frac{F(a,\eta)}{F(\alpha)} = \frac{t/t_a^*}{t/t_{a=1}^*} \tag{44}$$

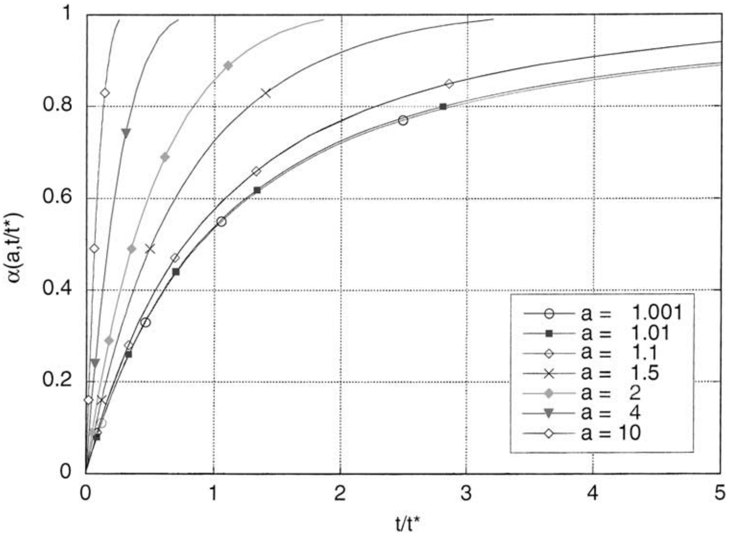

Fig. 4. Graph of the fractional dissolution curves $\alpha(a, t/t^*)$ expressed by Eq. (41) in case there is an initial deficit of solid phase, i.e. $n_1^0 < (n_1^0)^{\text{sat}}$.

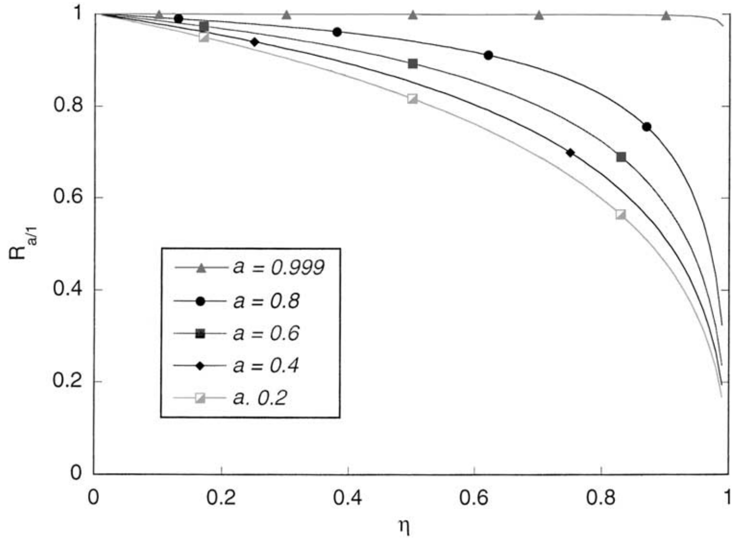

Fig. 5. The value of the ratio $R_{a,\,1}$ defined by Eq. (44) varies with α if the parameter a is not maintained constant.

The values of $R_{a,\,1}$ thus computed from the curves in Fig. 3 are show in Fig. 5, from which it is clearly seen that $a \neq 1 \Rightarrow R_{a,1} \neq 1$ and the curves are *not* superimposable. However, this is not generally valid for there exists a restricted subset of such curves that can be superimposed on one of them by affinity. Let us focus again on a pair of $\eta(t)$ curves obtained at temperatures T_1 and T_2 and remark that the value of the saturation concentration is normally expected to vary with temperature. Let us also assume that this dependence is accurately known. Accordingly one is capable in principle to conceive an experiment in which the initial amount of solid would be adjusted in such a way as to maintain the value of a constant. Indeed at temperature T_1, one may write:

$$T_1 \rightarrow C_2^{\mathrm{eq},T_1} \rightarrow a(T_1) = \frac{(n_1^0)^{\mathrm{sat},T_1}}{n_1^{0,T_1}} = \frac{V_{\mathrm{liq}}(C_2^{\mathrm{eq},T_1} - C_2^0)}{n_1^{0,T_1}} \tag{45}$$

and the equivalent at temperature T_2. Obviously, the value of a may be made constant if:

$$\frac{n_1^{0,T_1}}{n_1^{0,T_2}} = \frac{C_2^{\mathrm{eq},T_1} - C_2^0}{C_2^{\mathrm{eq},T_2} - C_2^0} \tag{46}$$

If the condition expressed by Eq. (46) is fulfilled, a particular set of superimposable $\eta(t)$ curves can be obtained since then, whatever the value of η:

$$a(T_1) \equiv a(T_2) \Rightarrow F(a(T_1), \eta) \equiv F(a(T_2), \eta)$$
$$\Rightarrow \frac{t_1}{t_1^*} = \frac{t_2}{t_2^*} \Rightarrow t_2 = \frac{t_2^*}{t_1^*} \times t_1 = bt_1 \tag{47}$$

The very same reasoning applies to the case $n_1^0 < (n_1^0)^{\mathrm{sat}}$. The experimental parameter a in Eq. (40) is defined in the same way but takes values larger than unity: $a = E_0^{\mathrm{eq}}/E_0^{\mathrm{max}} = (n_1^0)^{\mathrm{sat}}/n_1^0 > 1$.

Since Eq. (40) reduces to Eq. (34) if $a = 1$, one can again define the following ratio $R_{a,\,1}$ for testing the condition of affinity:

$$R_{a,1} = \frac{F(a,\alpha)}{F(1,\alpha)} = \frac{F(a,\alpha)}{F(\alpha)} = \frac{t/t_a^*}{t/t_{a=1}^*} \tag{48}$$

As shown in Fig. 6 its value is different from unity for all values of parameter a larger than unity, which constitutes evidence that the curves of Fig. 4 cannot be superimposed. But again, there exist particular experimental conditions that can allow one to obtain a subset of superpimposable $\alpha(t)$ curves, and they are determined by the same constrain a = constant, which can be achieved for instance if C_2^0 is set equal to zero and $n_1^0/V_{\mathrm{liq}}C_2^{\mathrm{eq},T}$ is kept constant.

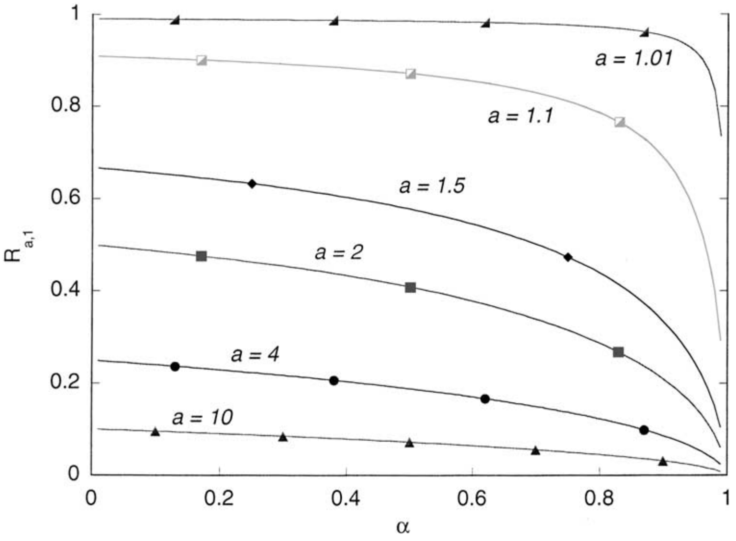

Fig. 6. The value of the ratio $R_{a,1}$ defined by Eq. (48) varies with α if the parameter a is not maintained constant.

4. Conclusion

At start, the present theoretical investigation was intended to clarify the equivalence between the different formulations of the dissolution kinetics by comparing the ''predictions'' of a purely kinetic approach with those inferred from a particular ''reaction'' mechanism. Because one considers a closed system, the solid–liquid fraction proves an essential parameter.

The first result is to show that the ''limiting reactant'' concept *and* the rate equation derived from it strictly apply to solid–liquid dissolution only in the particular case where the initial amount of the solid phase equals the amount required to saturate the liquid at constant temperature. This comes from the fact that the end of the reaction is reached when the solid phase which constitutes the limiting reactant it exactly consumed and the final value of the concentration gap $E^{\max}$ exactly equals the equilibrium value E^{eq}.

When the initial amount of solid is lower than needed to saturate the liquid phase, the reaction does not reach an end because equilibrium is reached but because the limiting reactant is exhausted. Accordingly, the maximum value of the conversion degree ξ, then equal to the initial number of mole of reactant ($v_1 = -1$), is determined solely by a choice of the experimenter not by a particular thermodynamic state. In such condition, if the rate of reaction is set proportional ($q = 1$) to the instantaneous concentration gap $E^{\max}$ (the term finally appearing in the rate constant will be $E_0^{\max}$) and translated in terms of the solute concentration value, C_2, it will be at variance with Nernst equation. This comes from the fact that the driving force for the dissolution process was intentionally ignored in the formal kinetic approach. In contrast, if a reasonable reaction mechanism is postulated (in fact here the physical process of interfacial mass transfer) then, rate and fractional dissolution (integral) equations derived from the formal kinetic theory and Nernst equation are equivalent: the effective concentration gap E^{eq}, the difference between the saturation and instantaneous average concentration in the bulk of the liquid phase, has to be substituted to $E^{\max}$. The interest of the kinetic approach lies in the formulation in terms of conversion degree and the possibility to obtain integrated expressions (39) and (41) of the fractional dissolution curves without the need for approximations such as setting $S_1(t)$ constant to integrate Nernst equation in the so-called ''sink conditions''.

In the last case where the initial amount of solid is larger than needed to saturate the liquid phase, the kinetic approach is valid, but the active surface area of the solid and consequently the dissolution rate are larger than in the former cases for the same fraction dissolved.

Thus it appears that the lowest experimentally achievable dissolution rate of a particular solid–liquid system is obtained when the amount of solid equals the amount needed to saturate the solution.

The second result of the present work is to prove that the conversion degree and the physical variable E_0 are not separated in the rate equation whenever this last condition is not fulfilled. Accordingly, in such common experimental conditions as the ''sink conditions'' widely used in practical applications, the dissolution curves are not related by an affinity relation except if the initial amount of solid is tuned accurately. Indeed, it is proved that, provided the temperature dependence of the saturation concentration is known, it is possible in principle to make the fractional dissolution curves superimposable by affinity by maintaining constant the excess-deficit parameter, $a = n_1^0 \equiv V_{\text{liq}}(C_2^{\text{eq},T} - C_2^0)$. Then, they can be interpreted in the usual way to determine the correct value of the activation energy, which otherwise would be impossible.

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