

Utility of Simple Rate Equations for Solid State Reactions

Joachim Maier*

Stuttgart, Max-Planck-Institut für Festkörperforschung

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Dedicated to Professor Arndt Simon on the Occasion of his 65th Birthday

Abstract. By considering a variety of examples with differing complexity and different deviations from equilibrium, the usefulness of simple chemical kinetics for describing solid state reactions is highlighted. In all cases point defects (or atomic constituents of higher dimensional defects) enter the kinetic equations. The formulation of the partial processes in terms of chemical kinetics is naturally beneficial for interfacial reactions far from equilibrium but

also pure transport processes can be advantageously described by a kinetic ansatz. In view of existing or induced inhomogeneities, the formulation of the rate equations has to be strictly local.

Keywords: Solid state reactions; Defect chemistry; Kinetics; Transport reactions; Catalysis

Zur Nützlichkeit einfacher chemischer Ratengleichungen für Festkörperreaktionen

Inhaltsübersicht. Verschiedene Festkörperreaktionen, die sich in puncto Komplexität und Abstand vom Gleichgewicht unterscheiden, werden diskutiert und mit einfachen chemischen Ratengleichungen beschrieben. Sofern Punktfehler (oder andere Konstituenten von höherdimensionalen Fehlern) in die Ratengleichungen mit

einbezogen sind, sind diese in der Lage, in vielen Fällen die Oberflächenreaktion wie auch den Transportschritt hinreichend zu beschreiben. Dies gilt vor allem für Situationen weit weg vom Gleichgewicht. Wegen inhärent vorhandener oder auftretender Inhomogenitäten müssen die Ansätze strikt lokal formuliert werden.

Introduction

Solid state reactions play a paramount role in nature as well in laboratory [1, 2]. They may differ substantially in terms of complexity and deviation from equilibrium. They may be as gentle and sluggish as intercalation reactions or as harsh and fast as detonation processes. Nonetheless simple chemical rate equations do good service in most cases. Their applicability extends much further than linear irreversible thermodynamics but can be rather limited in terms of concentrations. This antagonism is shown in Figure 1. In spite of this and other more basic restrictions for the bulk of the following contribution, however, their validity is taken for granted; they are not only used for properly treating chemical reactions but also advantageously for describing pure transport processes. We will start out from the simplest case of a small compositional perturbation of preexisting equilibrium and end with markedly nonlinear kinetic phenomena. The examples (much of it is based on earlier treatments) make clear that as far as the solid state is concerned, structural elements are referred to, and in particular point defects are the relevant reactive centers to be considered.

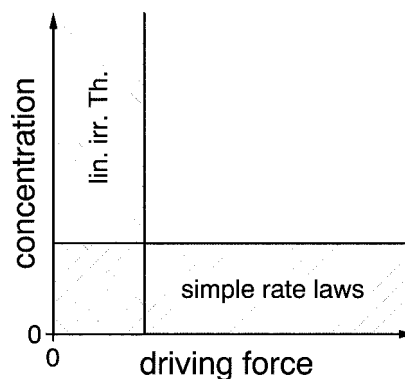


Fig. 1 The validity ranges of linear irreversible thermodynamics and simple rate equations. From Ref. [5].

So the contribution is aimed at fulfilling three goals, one to outline the role of point defects as reaction partners in interfacial chemical reactions and second, to elaborate on advantages and disadvantages of the kinetic formalism with respect to the treatment by irreversible thermodynamics. Third, the paper is meant to give a few representative examples that embed the solid state into the traditional treatment the chemist is used to as far as kinetics are concerned.

1 A few Basic Details with Respect to Chemical Kinetics

Considering a monomolecular chemical elementary reaction

* Prof. Dr. J. Maier
Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1
D-70569 Stuttgart
Fax.: +49 (0)711 689 1722
email: s.weiglein@fkf.mpg.de



the rate \mathcal{R} of which is described by $\mathcal{R} = \bar{k}[X] - \bar{k}[Z]$, the symbols denoting concentrations and \bar{k} , \bar{k} forward and backward rate constants which contain the activation free energies $\overline{\Delta G}^\ddagger$, $\overline{\Delta G}^\ddagger$. As regards Eq. (1), the terms $\bar{k}[X]$ and $\bar{k}[Z]$ are the partial reaction rates $\bar{\mathcal{R}}$ and $\bar{\mathcal{R}}$ the ratio $[Z]/[X]$ denotes the reaction quotient Q , approaching the mass action constant $K = \bar{k}/\bar{k} = [\hat{Z}]/[\hat{X}]$ in the equilibrium case (the arc denotes equilibrium value). It is obvious that

$$\bar{\mathcal{R}}/\bar{\mathcal{R}} = Q/K = \exp(\Delta G/RT) = \exp(-\mathcal{A}/RT) \quad (2)$$

holds, whereby $\Delta G = \overline{\Delta G}^\ddagger - \overline{\Delta G}^\ddagger$ and its negative value \mathcal{A} are the Gibbs reaction energy and the reaction affinity, respectively. Far from equilibrium, i.e. for $|\mathcal{A}| \gg RT$ either $\bar{\mathcal{R}} \gg \bar{\mathcal{R}}$ or $\bar{\mathcal{R}} \ll \bar{\mathcal{R}}$ i.e. only one partial rate prevails, whilst close to equilibrium they both approach the exchange rate

$$\mathcal{R} = \bar{k}[\hat{X}] = \bar{k}[\hat{Z}] = \sqrt{\bar{k}[\hat{X}][\hat{Z}]}$$

For our purpose we write \mathcal{R} (see Eq. (1)) as

$$\mathcal{R} = \bar{\mathcal{R}}(1 - \exp(-\mathcal{A}/RT)) = \bar{\mathcal{R}}(1 - \exp(+\mathcal{A}/RT)) \quad (3)$$

Eq. (3) does not state an universal explicit flux force relation as $\bar{\mathcal{R}}$ and $\bar{\mathcal{R}}$ depend on \mathcal{A} in a specific, individual manner. Only close to equilibrium ($|\mathcal{A}| \ll RT$) it results that

$$\mathcal{R} = \mathcal{R}^\circ(\mathcal{A}/RT) \quad (4)$$

representing a linear relation between \mathcal{R} and \mathcal{A} which is only valid if the affinity is very small (this presupposes that the standard term may be very small or that we start out from equilibrium and perturb it only slightly). In a forthcoming paper [3] it will be proposed that \mathcal{R}/\mathcal{A} be favorably defined as integral reactivity and $d\mathcal{R}/d\mathcal{A}$ as differential reactivity. Generally, but particularly for perturbation kinetics the formalism developed in Refs. [4, 5] will be used that rewrites the rate equation in terms of perturbations, e. g. for invariant rate constants as

$$\begin{aligned} \mathcal{R} &= \bar{k}[\hat{X}] \left(\frac{[X]}{[\hat{X}]} - \bar{k}[\hat{Z}] \left(\frac{[Z]}{[\hat{Z}]} \right) \right) = \mathcal{R}^\circ \left(\frac{[X]}{[\hat{X}]} - \frac{[Z]}{[\hat{Z}]} \right) \\ &= \mathcal{R}^\circ \left(\frac{\delta[X]}{[\hat{X}]} - \frac{\delta[Z]}{[\hat{Z}]} \right) \end{aligned} \quad (5)$$

with $\delta[\dots]$ denoting the deviation from the equilibrium value (i.e. $[\dots] - [\dots]$).

The worth of the rate equations for solid state kinetics is that they can be also applied to pure transport steps if we consider a generalized heterogeneous reaction during which a species X is chemically and positionally converted [5] according to:



For $x = x'$ and $X \neq X'$ we meet the proper homogeneous chemical reaction just concerned ($X' \equiv Z$), while the other

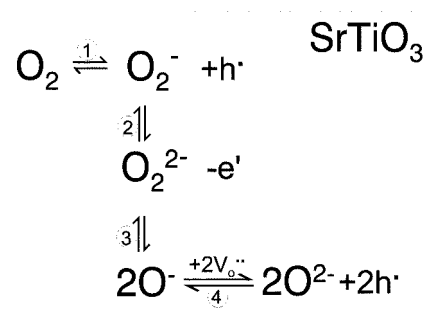


Fig. 2 Elementary steps of oxygen incorporation in SrTiO₃.

limit is $x \neq x'$ and $X \equiv X'$, describing a transport of X from x to x' . In the first case the condition $x = x'$ is actually never met and can be replaced by the weaker condition that the spatial variation is insignificant in its impact. The difference between x and x' is particularly critical if electrical fields are involved which enter \bar{k} , \bar{k} via

$$\bar{k}(\delta\phi) = \bar{k}(\delta\phi=0) \exp\left(-\frac{zF\delta\Delta\phi}{RT}\right); \quad (7)$$

$\delta\phi$ is the deviation of the electrical potential difference from its equilibrium value (for zero bias $\delta\phi=0$); $\delta\Delta\phi^\ddagger$, the respective difference between activated state and initial state, is often assumed to be half of the potential drop between x and x' [6]. Equation (7) reads analogous with \bar{k} if the directions of the arrows are exchanged.

2 The Kinetics of Stoichiometry Changes

2a Small signal behavior and chemical relaxation

Chemically most simple solid state reactions are dissolution reactions in the course of which structural variations involving bulk and interfaces are negligible, such as Li intercalation or oxygen incorporation in oxides. Only if the homogeneity range is broad or is exceeded, the occurrence of severe interactions or the formation of new phases obscure the picture. Let us consider oxygen incorporation in SrTiO₃ as a prototype example and decompose the whole process into elementary steps. We start out from equilibrium with the gas phase and suddenly change the partial pressure to a new value. All the elementary steps of the induced relaxation process involve the point defects as reactive and mobile centers. Figure 2 displays the probable mechanism according to experiments in lit. [7, 8].

Grosso modo we may distinguish between the surface reaction, the transport through space charge regions, the transport through the electroneutral bulk as well as the transport across and/or along internal boundaries. In order to avoid geometrical complexities we will only consider internal grain boundaries as barriers that are positioned perpendicular to the surfaces (but see Ref. [9]). The proper surface reaction can be decomposed into adsorption, ionization, dissociation and transfer.

Let us first tackle the diffusion step and consider a hopping process of neutral X via a vacancy mechanism (v : vacancy)



which can be described by a bimolecular rate equation

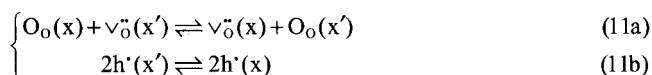
$$\mathcal{R} = \bar{k}[X(x)][v(x')] - \bar{k}[v(x)][X(x')]. \quad (9)$$

As the hopping (h) threshold is symmetrical ($\overline{\Delta G}^{\neq} = \overline{\Delta G}^{\neq}$), i.e. $\bar{k} = \bar{k} \equiv k_h$ and as $[X(x)] \approx [X(x')]$, Fick's law results as

$$\mathcal{R} \approx k_h \Delta x \partial[v]/\partial x, \quad (10)$$

obviously without any restriction with regard to the deviation from equilibrium. This is no longer the case if the rate coefficients are different, as realized if a proper chemical reaction is met or if electrical fields are involved (Eq. (7)); the latter is the case if X is charged and hence v bears a non-zero effective relative charge.

There are three possibilities to realize a steady state transport process involving charged particles: (i) A tracer exchange in which the process described by Eq. (8) is accompanied by an opposite process of the counter isotope, (ii) the steady state electrical (conductivity) experiment in which this process is balanced by an outer electronic current, or (iii) the chemical diffusion experiment in which the ion transport is balanced by an internal flow of electrons. Let us concentrate on the latter case in which we are concerned with changes in stoichiometry. In the case of p-conducting oxides we describe this chemical diffusion by (O_O and v_O^{\bullet} denote regular O^{2-} and O^{2-} vacancy, h^{\bullet} the electron hole, all in the Kröger–Vink notation with relative charges)



The treatment of chemical diffusion in terms of irreversible thermodynamics is well elaborated [1, 10, 11]. But here we want to apply chemical kinetics (table 1). The simplest cases are “electron-rich compounds” in which electrons are ubiquitous and hence of no influence for the process: then the hopping reaction (11a) is decisive in all three experiments. In the chemical experiment, where $[O_O]$ is constant, again Eq. (10) is the result, i. e. the chemical diffusion coefficient D^{δ} turns out to be proportional to k_h , while D^Q and D^* referring to the other two experiments (electric and tracer experiment) follow as proportional to $k_h[v_O^{\bullet}]$, a result which is well known from the linear laws [10] (for more details see Refs. [4, 5]). Note that for the treatment of the tracer experiment $[v_O^{\bullet}]$ is constant and the X concentration appears in an ideal way in Eq. (9) as the tracer atoms are ideally distributed. In the electrical experiment both $[O_O]$ and $[v_O^{\bullet}]$ are constant, variations only occur in the rate coefficients according to Eq. (7) leading to a non-linear current–voltage relation. As however mostly $|\delta\phi zF| \ll RT$, i.e. bias drop over Δx is small, the current–voltage relation

Table 1 The functionality of the diffusion coefficients D^{δ} , D^* , D^Q . From Ref. [14].

$D^{\epsilon} = (RT/4F^2)\sigma^{\epsilon}/c^{\epsilon}$				
D^{ϵ}	general		electron-rich	
	σ^{ϵ}	c^{ϵ}	σ^{ϵ}	c^{ϵ}
D^{δ}	$\sigma_n \sigma_v / \sigma$	$\left(\frac{1}{c_v} + 4 \frac{\chi_n}{c_n}\right)^{-1}$	σ_v	c_v
D^*	σ_v	$c_{O^{2-}}$	σ_v	$c_{O^{2-}}$
D^Q	σ_v	$c_{O^{2-}}$	σ_v	$c_{O^{2-}}$

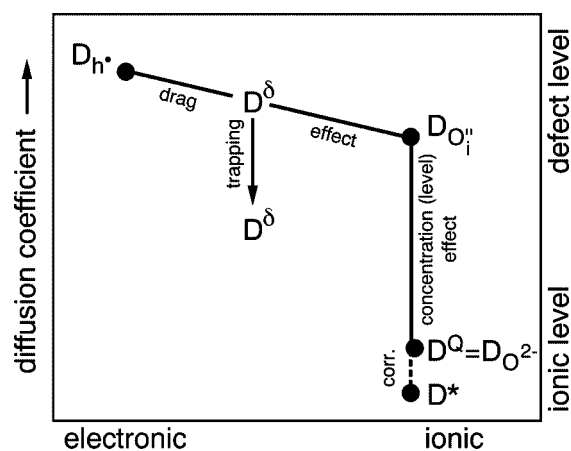


Fig. 3 The phenomenological diffusion coefficients in relation to each other and in relation with respect to the defect diffusivities (hole D_h^{\bullet} , oxygen interstitial $D_{O_i^{\bullet}}$) and ion diffusivities ($D_{O^{2-}}$). From Ref. [5].

can be linearized and Ohm's law is obtained with the ionic conductivity $\sigma \propto k_h[X]$. See table 1.

If electronic effects are also important for the rate, the description of chemical diffusion is more complicated. The most simple kinetic approach would be to consider a hop of an electroneutral ion/electron complex. In this case we would apply Eq. (9) to the sum of Eqs. (11a,b). This would however describe the jump of a strongly correlated associate. Rather, one has to consider ion and electron jump as parallel reactions, the rate constants of which being coupled through the common electric field. As will be shown elsewhere [3] the kinetic equations reduce to the expression well-known from the ambipolar treatment given in table 2 after linearization. The more subtle differences between D^{δ} , D^* , D^Q are visualized in Figure 3 (which may be compared it with table 1).

The transport through space charge regions is more complicated, as here the coupling field cannot be calculated from electroneutrality, rather one has to invoke Poisson's equation. Hence in space charge zones, electron and ion transport are less strictly coupled. One carrier, typically the electronic carrier, is usually faster. If the redox signal is propagating into the boundary zones of the solid, first a hole

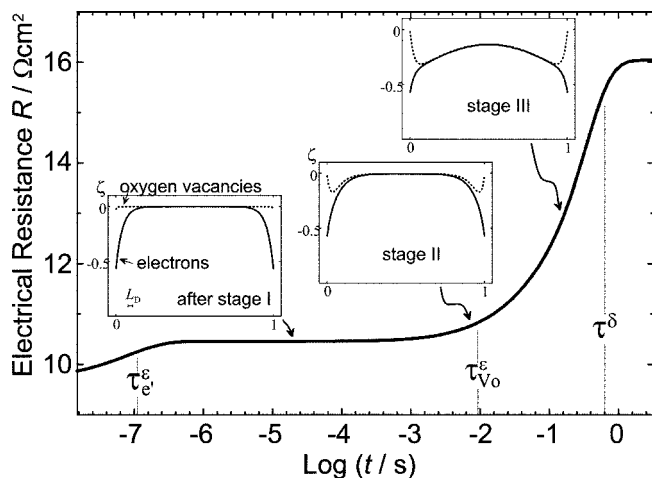


Fig. 4 If the oxygen potential pressure over (n-type conducting) SnO_2 is changed, three processes with different time constants characterize the induced resistance change: electron trapping to adsorbed oxygen, oxygen incorporation in the space charge zones, oxygen diffusion into the bulk. From Ref. [44].

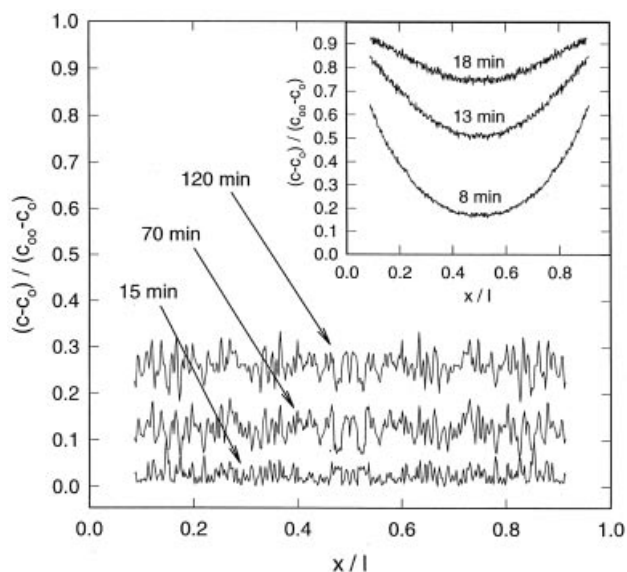


Fig. 5 Reaction-controlled and diffusion-controlled (insert) stoichiometry profiles derived from space resolved optical in-situ experiments on SrTiO_3 . From Ref. [45].

injection (or electron trapping, i.e. redox signal) occurs conferring an excess charge (in addition to the equilibrium charge) to the space charge region, which will be nullified by the subsequent penetration of the O^{2-} incorporation (acid/base signal). For details of this complicated process involving equilibrium and kinetic space charges see *Jamnik* and *Maier* [12]. Figure 4 refers to oxygen incorporation in SnO_2 where pronounced kinetic space charge effects occur during the process.

The proper surface steps can usually also be treated by bimolecular reaction equations, whereby reaction constants can involve field effects (e.g. the transfer reaction) (see Eq.

Table 2 The application of rate equations to transport processes for the special case of electron-rich materials. From Ref. [14].

	$\mathcal{R} = \bar{k}_h A V' - \hat{k}_h A' V$	
experiment (ϵ)	\mathcal{R}	const D
electrical (Q)	$\hat{A} V \Delta k = \mathcal{R}_h^o \left(\frac{\bar{k} - \hat{k}}{\bar{k}} \right)$	$\hat{k} A V \propto \mathcal{R}_h^o \propto \sigma_{\text{ion}}$
tracer (*)	$\hat{k} V \Delta A = \mathcal{R}_h^o \left(\frac{A - A'}{\hat{A}} \right)$	$\hat{k} A V \propto \mathcal{R}_h^o \propto \sigma_{\text{ion}}$
chemical (δ)	$\hat{k} \hat{A} \Delta V = \mathcal{R}_h^o \left(\frac{V - V'}{\hat{V}} \right)$	$\hat{k} \hat{A} \propto \mathcal{R}_h^o / \hat{V} \propto \hat{u}_{\text{ion}}$

(7)). Here, the analogues to the diffusion coefficients are effective rate coefficients \bar{k}^δ that are directly obtained from the concentration profiles $c(x,t)$ (Fig. 5). They are defined [13] via

$$\mathcal{R} = \bar{k}^\delta \delta c_s \quad (12)$$

where c_s refers to the value at the surface ($c(x,t)=c(0,t)$). (In the usual definition \mathcal{R} is replaced by the flux density so that an additional factor Δx is of relevance).

If the surface reaction is fast, the surface is immediately in equilibrium, i. e. $c_s = \hat{c}_s$ i.e. $\delta c_s = 0$, and the concentration profiles are determined by diffusion. If, however, the surface reaction is rate determining, $\partial c / \partial x = 0$, hence internal profiles $c(x,t)$ are horizontal but develop with intercepts $c(0,t)$ increasing from the initial value $c(0,0)$ up to \hat{c}_s , that yield \bar{k}^δ as effective rate coefficient [13]. Figure 5 shows experimental evidence for these two extreme cases for SrTiO_3 . The challenge is to correlate the effective value \bar{k}^δ with the underlying mechanism [3].

Before we explicitly treat this problem let us consider two examples of homogeneous kinetics.

First we address a first order reaction. If we combine the mass balance $[X] + [Z] = \text{const.}$ with the rate equation for this process, we directly obtain Eq. (12) in the form $\mathcal{R} = d[Z]/dt = d([Z] - [\hat{Z}])/dt = -(\bar{k} + \hat{k})(Z - [\hat{Z}])$, i.e. $\bar{k}^\delta = \bar{k} + \hat{k}$. Hence an exponential $c(t)$ law arises with $(\bar{k}^\delta)^{-1}$ being proportional to the time constant. Obviously Eq. (12) is here fulfilled for any deviation from equilibrium.

For higher order reactions, however, Eq. (12) is only fulfilled close to equilibrium. In order to show this, let us consider a second order reaction e.g.



The same analysis as above leads to $dZ / (dt = \bar{k} - \hat{k}) P^{(2)}$ where $P^{(2)}$ is a second order polynomial. $P^{(2)}$ is given by the (two) zeros in the form $([Z] - [\hat{Z}])([Z] - z)$ one of which (vz. $[\hat{Z}]$) being the equilibrium value. Only close to equilibrium (where $[Z] - z \rightarrow \text{const} = [\hat{Z}] - z$) a proportionality to $\delta[Z]$ is arrived at and only then \bar{k}^δ is constant. (If z and $[\hat{Z}]$ should be identical, then $dZ/dt \propto \delta[Z]^2 \rightarrow 2[\hat{Z}]\delta[Z]$.) This is directly generalizable for higher order reactions. Obviously Eq. (12)

requires small perturbations in order to be generally correct.

As a material example let us consider the example treated in Ref. [1], viz. the relaxation time of the Frenkel defect reaction in a silver halide (Ag_{Ag} : regular silver ion, v_i : vacant interstitial site, Ag_i^* : interstitial silver ion, v'_{Ag} : silver ion vacancy)



as an internal homogeneous reaction and apply the formalism expressed by Eq. (5). Then $\mathcal{R} = \bar{k} - \bar{k}[\text{Ag}_i^*][v'_{\text{Ag}}] = \bar{\mathcal{R}} \left(1 - \frac{[\text{Ag}_i^*][v'_{\text{Ag}}]}{[\text{Ag}_i^*][v'_{\text{Ag}}]} \right)$. Since $[\text{Ag}_i^*][v'_{\text{Ag}}] \equiv c$, in pure materials

and since as $\bar{k}/\bar{k} = [\text{Ag}_i^*][v'_{\text{Ag}}] = K_{\text{F}}$ we arrive, instead of Eq. (12) at

$$\mathcal{R} = -(\mathcal{R}^\circ / K_{\text{F}}) \delta c^2 \quad (15)$$

with $\delta c = c - \hat{c}$. Only for $\mathcal{R} \rightarrow 0$, $\bar{\mathcal{R}}$ tends to \mathcal{R}° , and a relaxation law ($\partial \delta c / \partial t \propto \delta c$) results with $\mathcal{R} = -\frac{2\mathcal{R}^\circ}{c} \delta c \equiv -\bar{k}_{\text{F}} \delta c$

with the relaxation time being given by $1/\bar{k}_{\text{F}}$. As $\mathcal{R}^\circ = \sqrt{\bar{\mathcal{R}}\bar{\mathcal{R}}} = \sqrt{\bar{k}\hat{k}\hat{c}^2}$ and $K_{\text{F}} = \bar{k}/\hat{k} = \hat{c}^2$, the effective rate constant \bar{k}_{F} is given by $2\sqrt{\bar{k}\hat{k}}$.

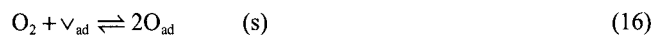
The situation met for heterogeneous reactions such as the oxygen incorporation is more difficult. Yet a detailed analysis [4, 5, 14] shows that \bar{k}^δ is unambiguously connected with the individual rate constants of the mechanism and that it generally depends on the concentrations and concentration changes far from equilibrium. Approaching equilibrium, \bar{k}^δ is determined by rate constants and equilibrium concentrations only. This is extensively shown in detail in our earlier work [4, 5, 14]. Here a simplified mechanism is considered and the situation briefly discussed for different mechanistic situation. We assume that one step is rate determining (rds), i.e. kinetically much more difficult than the others; in addition we assume that the surface absorbs much less oxygen than the bulk so that very soon after the partial pressure change in the gas phase a (pseudo-) steady state is established in which the reaction rates of all the surface steps are more or less identical.

The treatment makes extensive use of Eq. (5). If again electronic influences can be neglected, proportionalities are obtained that are analogous to the above diffusion case (where for the electronic rich electron conductor we obtained a proportionality of the diffusion constants to ion mobility ($\propto \sigma_{\text{ion}}/[v]$) for chemical diffusion or to ion conductivity (σ_{ion}) for tracer, electrical experiment). We only have to replace σ_{ion} by the exchange rate of the rate determining step $\mathcal{R}_{\text{ds}}^\circ$. (In fact σ_{ion} plays the role of an exchange rate for the hopping process.) The results for this extreme case are given in table 3.

If electronic effects are important, more subtle difference in the rate constants appear (Fig. 5). In order to investigate the role of the electrons let us deal with a simplified mechanism in which first oxygen is adsorbed dissociatively (low coverage assumed)

Table 3 Kinetic treatment of the effective rate constants. From Ref. [14].

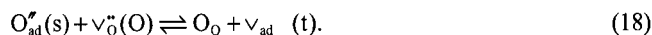
experiment (ϵ)	$\mathcal{R} = \bar{k}_t V - \bar{k}_r A$	const \bar{k}^ϵ
electrical (Q)	$\mathcal{R}_t^\circ \left(\frac{\bar{k}}{\hat{k}} - \frac{\bar{k}}{\hat{k}} \right) = \mathcal{R}^\circ f(\eta)$	$\mathcal{R}_t^\circ / \hat{A}$
tracer (*)	$\mathcal{R}_t^\circ \left(1 - \frac{A}{\hat{A}} \right) = \frac{\mathcal{R}^\circ}{\hat{A}} \delta A$	$\mathcal{R}_t^\circ / \hat{A}$
chemical (δ)	$\mathcal{R}_t^\circ \left(\frac{V}{\hat{V}} - 1 \right) = \frac{\mathcal{R}^\circ}{\hat{V}} \delta V$	$\mathcal{R}_t^\circ / \hat{V}$



then fully ionized



and hereafter transferred into the bulk



If (s) is rate determining, $\mathcal{R} = \mathcal{R}_{\text{s}}$ and (i) and (t) can be treated as being in pseudo equilibrium, hence (see Eq. (5))

$$\mathcal{R} = \bar{k} P_{\text{O}_2} - \bar{k}[\text{O}_{\text{ad}}]^2 = -\mathcal{R}_{\text{s}}^\circ \frac{\delta[\text{O}_{\text{ad}}]^2}{[\text{O}_{\text{ad}}]^2} \approx 2\mathcal{R}_{\text{s}}^\circ \frac{\delta[\text{O}_{\text{ad}}]}{[\text{O}_{\text{ad}}]} \quad (19)$$

Because the subsequent steps are in equilibrium, $[\text{O}_{\text{ad}}]$ is given by the succeeding mass action constants (reactions i, t) via $K_i K_t = \frac{1}{[\text{O}_{\text{ad}}][e'(s)]^2 [v'_0(O)]}$ (note that electric fields cancel in the mass action constant) from which it follows that

$$\mathcal{R} = 4\mathcal{R}_{\text{s}}^\circ \left\{ \frac{1}{[v'_0]} + 2 \frac{1}{[e']^2} \frac{\delta[e']}{\delta[v'_0]} \right\} \delta[v'_0] = -4\mathcal{R}_{\text{s}}^\circ (w_{\text{O}} / c_{\text{O}}) \delta c_{\text{O}} \quad (20)$$

The bracketed term $\{...\}$ is proportional to the so-called thermodynamic factor (w_{O}) known from irreversible thermodynamics ($[Z']$) and even includes trapping effects ($\delta[e']/\delta[v'_0]$) [11].

If (i) is rate limiting (see appendix A in [14]),

$$\mathcal{R} = \mathcal{R}_i^\circ \left(\frac{\delta[\text{O}_{\text{ad}}^*]}{[\text{O}_{\text{ad}}^*]} - 2 \frac{\delta[e'(s)]}{[e'(s)]} \right) \quad (21)$$

which after linearisation leads to an equation similar to Eq. (20), but with \mathcal{R}_i° instead of $\mathcal{R}_{\text{s}}^\circ$:

$$\mathcal{R} = -\mathcal{R}_i^\circ \{...\} \delta[v'_0] \quad (22)$$

Finally if (t) is rate determining, the derivation is quite lengthy (see App. B in [14]) but eventually leads to the not unexpected result

$$\mathcal{R} = -\mathcal{R}_t^\circ \{...\} \delta[v'_0] \quad (23)$$

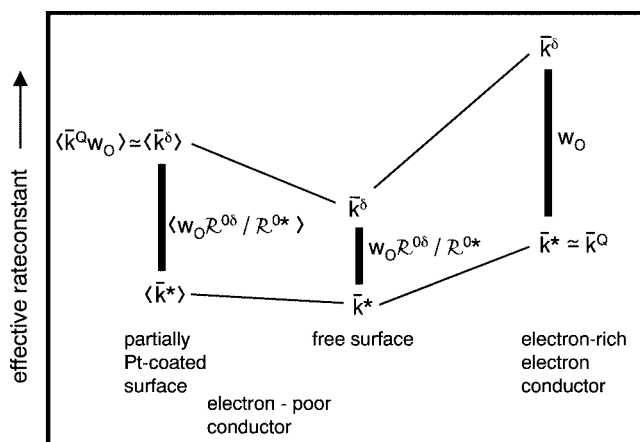


Fig. 6 Relations of the effective rate constants for different cases. From Ref. [14].

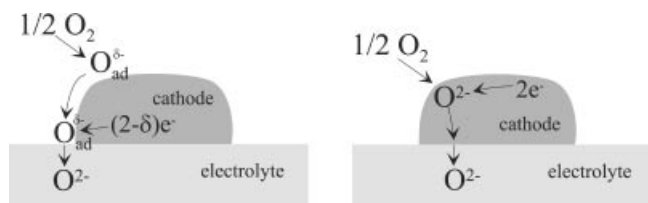


Fig. 7 Oxygen incorporation mechanism at mixed conducting cathodes of high temperature fuel cells. From Ref. [46].

If we agree in incorporating factors stemming from different molecularities (such as 4 in Eq. (20)) formally in \mathcal{R}^c , we find in all cases $\mathcal{R}^\delta = -\mathcal{R}_{rds}^\circ (w_O/c_O)\delta c$. (It may be noted that for the electrical and the tracer experiment the same results but with $w = 1$ are obtained (see Fig. 6).)

Of course the small signal result can be obtained from linear irreversible thermodynamics independent of the mechanism [4, 5]. However the worth of the above derivation lies in the knowledge of the validity range and of the corrections if one deviates from proximity to equilibrium.

Most importantly, given the mechanism, \bar{k}^δ (as well as \bar{k}^Q, \bar{k}^*) can now be rigorously obtained as a function of temperature, partial pressure and doping content [4]. In turn, the measurement of these dependencies allows one to trace back the mechanistic situation. Note that owing to the manifold of mechanisms a very large information content is necessary indeed to reliably deduce a mechanistic scheme such as in Fig. 2.

Fig. 7 refers to an example of electrode kinetics in high temperature fuel cells in which not only complicated serial steps but also different parallel steps occur. In the steady state of such an experiment \bar{k}^Q is relevant while \bar{k}^δ is also important for transients.

2b Free energy relations: activation threshold vs. reaction affinity

Ref. [15] reports a surprising relation between \bar{k} and D for tracer incorporation (index *), stating that within the family

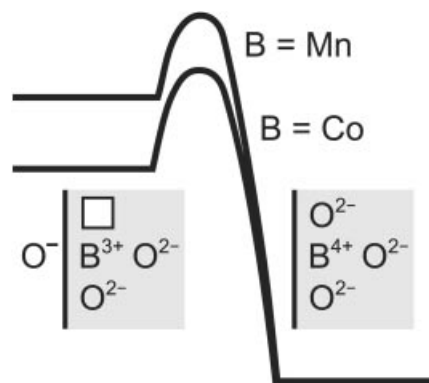


Fig. 8 For slight chemical variations within the same family of materials, thermodynamically and kinetically relevant (free) energy differences are expected to change monotonically. The first order approximation is that the ratio of these variations is constant.

of $(La,Sr)TO_{3-\delta}$ (T transition metal oxide or mixture of various transition metal oxides such as Fe, Co, Ni, Mn) \bar{k}^* vs D^* have been found to be correlated in a linear manner. This is surprising as within such a plot the materials, and hence ΔG^\ddagger and ΔG° , vary. Evidently there must be a deeper lying connection between such parameters. In fact it could be shown [16] that the linearity is equivalent to a relation of the type

$$\Delta_M \Delta G^\ddagger = \alpha \Delta_M \Delta G^\circ \quad (24)$$

where the operator Δ_M describes the variation of the material within the given family and where α is independent of that variation.

Figure 8 sketches the situation for such a proportionality of the variations of ΔG^\ddagger and ΔG° . The most straightforward explanation for this relation is structural similarity: if only slight variations in the ground structure occur, both ΔG° and ΔG^\ddagger will vary similarly and as long as these variations are small, they will be approximately proportional to each other. Such relations are well-known in chemistry of the liquid state (see Brønsted's relation [17] in homogeneous catalysis, Hammett's relations [18] in organic chemistry); Ref. [16] gives the first clear example of such a family relation for solids.

2c Surface kinetics far from equilibrium

In order to corroborate the mechanism in Fig. 2 also experiments far from equilibrium, i.e. oxygen exchange experiments with large P_{O_2} changes have been performed [7]. According to Eq. (2), it holds that for short times after the P_{O_2} change either $\mathcal{R} \approx \bar{\mathcal{R}}$ or $\bar{\mathcal{R}}$ i. e. either forward or backward rate dominates, and thus independent information is obtained. Moreover P_{O_2} changes have been performed from the same initial value to different final values but also from different initial values to the same final values. According to the respective conditions the part of the reaction chain before or after the rate determining step can then be con-

sidered to be invariant. As an additional means in-situ UV irradiation was applied [7] to study the influence of the electronic concentration in particular that of the electronic minority species.

A further degree of complexity is introduced if not O_2 but H_2O is incorporated into $SrTiO_3$. As well-known for oxides, the OH^- part then occupies oxygen vacancies while the H^+ part reacts with a regular O^{2-} resulting in the formation of 2 OH^- ions which allow for fast internal proton transport (not by O^- hopping but by phonon assisted proton transfer [18–20]). The activated state is a more or less symmetrical $O\cdots H\cdots O$ arrangement. For this to occur the oxygens have to come sufficiently close. Tunneling effects are not of rate determining influence at the high temperatures but can have an influence of the transition barrier. The details of the computer simulation [20] show that even the conduction process in the bulk of a homogeneous conductor is not a simple event.

In this context we mention an unexpected kinetic situation that has been observed recently [21]. It refers to water incorporation into the mixed conducting Fe-doped $SrTiO_3$ and is caused by the mobility of the three carriers O^{2-} (via \check{O}), H^+ (via OH^*) and e^- (via h^*): The water molecule is split at the surface. Protons and oxygen ions are not necessarily simultaneously incorporated via ambipolar motion of O^{2-} and H^+ ; rather in this case – owing to the favorable kinetics – the hydrogen part diffuses in first (counter motion of H^+ and e^-) leading to a reduction of the sample much below the expected level (not that H_2O is after all only acid–base active), while O diffusion (O^{2-} and e^-) occurs at a later stage and re-establishes the expected redox degree. In the case of two carriers such an overshooting could only be possible in the space charge zones (see Fig. 4) whilst here the partial signal can penetrate quite deep. If oxygen incorporation did overshoot also, a damped oscillation would occur. In fact oscillations have been observed in the context of protonically conducting oxides but are probably due to complex surface kinetics [22]. In the following characteristic non-linear phenomena connected with chemical kinetics far from equilibrium will be shortly considered.

Before turning to this subject let us not leave unmentioned the fact that the point defects within the surface being present due to the configuration entropy and representing locally centers of enhanced energy, are per se reactive centers and are expected to play a significant role in catalysis. A few studies are available that explicitly show this [23–25]. Refs. [26, 27] treat point defects explicitly in terms of their acid-base reactivity.

3 Non-linearity Phenomena in Chemical Kinetics

The departure from the linear range can lead to very unexpected situations, situations that are more familiar to us in the context of biology rather than inorganic chemistry [28–30]. As in semiconductor physics negative differential conductivities are a decisive ingredient for phenomena such

ENTROPY PRODUCTION CLOSE TO AND FAR FROM EQUILIBRIUM

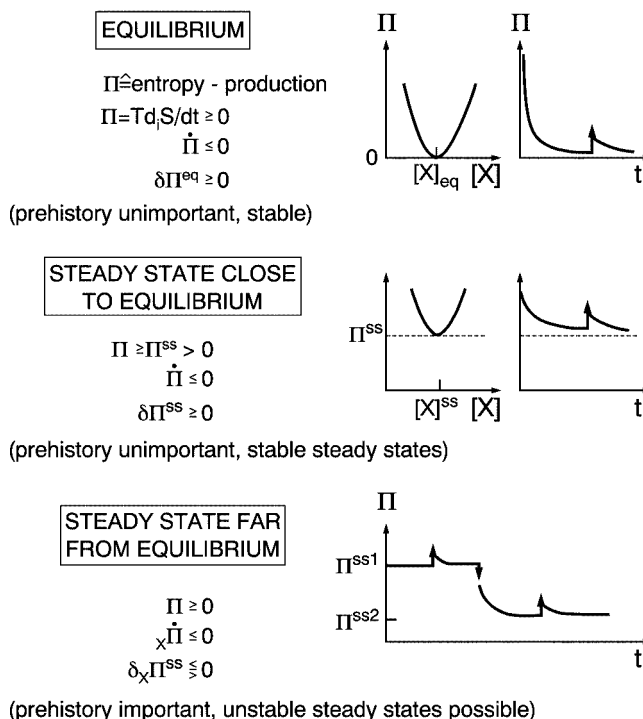


Fig. 9 Dissipation and stability of steady states. From Ref. [5].

as non-equilibrium phase transformation, oscillations, pattern formation and chaotic behavior [31], we analogously expect “negative differential reactivities” [3] to be the major culprit in terms of reaction kinetics. Before we consider this in more detail let us recapitulate some fundamentals of nonlinear irreversible thermodynamics [5, 28–32] (see Fig. 9).

Closed systems at equilibrium exhibit a maximum entropy. Thus, in equilibrium the entropy production (dS/dt) or the dissipation ($\Pi = T^{-1}dS/dt$) is zero. Outside equilibrium, entropy is produced; in stationary states (with fixed forces) close to equilibrium, Π is necessarily non-zero but at minimum. Far from equilibrium this is only so for those changes in Π that are due to the forces (\mathcal{A}). As an immediate consequence [28], stationary states close to equilibrium are, as the equilibrium state itself, stable; i.e. perturbations are ironed-out. Far from equilibrium perturbations can be amplified and lead to new situations, a prerequisite for many characteristic nonlinear phenomena and in particular for the occurrence of life. A decisive mechanism is the case of autocatalysis. A representative reaction may be [33]



in which F describes the “food” whose consumption leads to a growth process. Following Ref. [33] we analyze the two stationary states ($d[X]/dt = 0$), viz. the initial state with $[X] = 0$ and the equilibrium state with $[X] = [\hat{X}]$. In the first

case any fluctuation leading to a trace of X is amplified. It has been shown by Prigogine that the condition for such an instability is

$$\delta\mathcal{A}\delta\mathcal{R} < 0. \quad (26)$$

Recognizing that $\mathcal{A} = RT\ln K[F]/[X] = \text{const} - RT\ln[X]$ and hence $\delta\mathcal{A} \propto -\delta[X]/[X]$ while $\mathcal{R} \propto [F]/[X]$ and $\delta\mathcal{R} \propto \delta[X]$, this is indeed the case. (At equilibrium the negative feedback overwhelms because of the back reaction that is quadratic in [X]; it is easy to show that then $\delta\mathcal{A}\delta\mathcal{R} > 0$ as it should be close to equilibrium.) Interestingly, the above condition (Eq. (26)) is indeed equivalent to having a negative differential reactivity [3].

If – following *Eigen* [33] – we couple Eq. (25) with a decay reaction, i.e. far from equilibrium for a set of species X



the initial development is given by $d[X_j]/dt = [X_j](k_{1j}[F] - k_{2j})$. The bracketed value (let it be termed W_j) decides upon growth or death. This value is different for different species X_j and depends on [F]. In other words: tuning of [F] leads to non-equilibrium phase transitions. If F is not present in excess as assumed above, but if the different species have to compete for it, the bracketed term W_j is not invariant and only that species with the most favorable kinetic parameters survives; the others die out. If by fluctuations other X_j species are generated, it depends on their kinetic parameters whether they die out as well or suppress the surviving species. These extremely simple kinetic scenarios already introduce such elaborate processes as competition and selection. Slightly more complex schemes can lead to oscillation or deterministic chaos [28–33]. The coupling of rate equations with diffusion processes, according to the continuity equation

$$\partial c_j / \partial t = D_j \nabla^2 c_j + v_j \mathcal{R}^{(j)}, \quad (28)$$

opens the possibility of forming of spatial non-equilibrium patterns.

A mechanism of fundamental importance is the Gierer-Meinhard mechanism [34] which involves the interaction between short-range activation (a = activator concentration) and long-range inhibition (h = inhibitor concentration). A simple, plausible kinetic ansatz is

$$\begin{aligned} \dot{a} &= \alpha + \beta a^2 / h - \gamma_a + D_a \nabla^2 a \\ \dot{h} &= \epsilon a^2 - \mu h + D_h \nabla^2 h \end{aligned} \quad (29)$$

where α , β , γ , ϵ , μ and the diffusion coefficients D_a , D_h are constant parameters [34]. Typical solutions generate periodic patterns such as marking of animal coats, development of nerve networks or thorn production in plants.

The language used so far also betrays that these considerations stem from biophysical chemistry and synergetics but

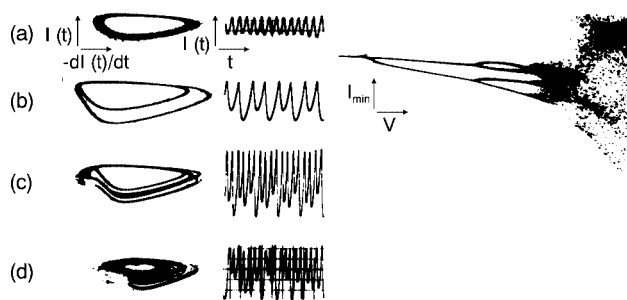


Fig. 10 Characteristic nonlinear behavior in Ge as a result of voltage variation in the nonlinear range (I : current, V : potential). The l.h.s. shows the phase portraits (I vs. I) of the current oscillations, the center (I vs. t , center). The r.h.s. depicts the evolution into a deterministic chaos (by plotting the current minima vs. t). From Ref. [31].

are also valid for defect chemistry. (Needless to mention that genetics is non-linear defect chemistry indeed).

Not so many examples are known in the field of defect chemistry of inorganic materials so far. Exceptions include the Liesegang phenomenon [35] and resistance oscillations involving Ag^+ and H^+ conductors [22]. Phenomena dealing with electronic charge carriers are more thoroughly investigated (see e.g. [31]). Here many of the above mentioned anomalies occur in the context of impact ionization, whereby a high energetic electron uses some of its energy to create an electron hole pair, written as an autocatalytic reaction of the form



Fig. 10 shows a few examples from that field.

4 Complications and Validity Range of Simple Chemical Rate Equations

A significant increase in complexity is achieved if interfaces can vary their structures or are even generated / annihilated which is rather the rule than the exception in solid state kinetics (for details the reader is referred to [36]). One important point addressing what we just discussed, is morphological instability [37] (Fig. 11). Instability occurs if a fluctuation of a positive definite function $L > 0$ is amplified, i.e. $\dot{L} > 0$ (or more generally $L\dot{L} > 0$). (In the previous section Π played the role of such a so-called Ljapunov function [38].) At interfaces L may be the deviation from the planar shape. If by some fluctuation a protrusion (L) occurs, the initial kinetics decide upon whether this is enhanced ($\dot{L} > 0$) (in the limit even dendrites may form) or if the fluctuation is ironed-out. Only in the latter case the planar surface is morphological stable. Arguments like this were used to explain the reaction morphologies of the solid state reaction between $(\text{Fe}_x\text{Mn}_{1-x})_3\text{O}_4$ and $(\text{Fe}_y\text{Cr}_{1-y})_2\text{O}_3$ [39]. It has to be stressed that this is a local analysis; the high degree of complexity prevents usually an explicit numerical (let alone

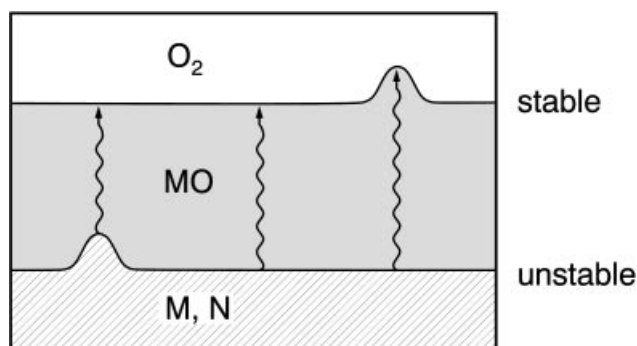


Fig. 11 Referring to local morphological stability of the interface. If the transport through the oxide MO is rate determining a protrusion at the oxide/O₂ interface will be ironed out while at the metal/oxide interface it will be augmented [37]. From Ref. [5].

analytical) prediction of such processes (cf. kinetic potentials [28]).

A very serious point is that chemical kinetic laws such as Eq. (9) are mean field approaches. The atomistic situation is not homogeneous. Nonetheless a mean concentration is used for the description. As far as the validity of simple kinetic equations is concerned, neighbor effects however may in some cases seriously question the validity of mean field approaches. Fractals are extreme cases of deviations in terms of morphology. In such cases reactions of the type of Eq. (9) can only refer to very local situations (cf. percolation processes). Also in structurally homogeneous environments the mean field character of such equations is limited in its validity in particular if the reaction center introduces inhomogeneities such as depletion zones around it. For a detailed analysis the reader is referred to Ref. [40].

Furthermore, if the reactions between species are no longer fast compared with the relaxation processes around [1], the k 's become formally time dependent, a phenomenon that is well-known in transport processes and has e.g. been observed in the frequency conductivity behaviour of disordered materials [41, 42]. In some cases also the Markovian character of the simple rate equations may be violated, i.e. the memory of preceding states is not erased by thermal motion and reacting atoms or clusters are "bouncing dynamically through a series of states" [43].

Conclusions

A variety of kinetic examples are considered with different complexity and different distance from equilibrium showing that simple kinetic rate laws do good service for defect chemistry in many cases but have to be used with care. The correlations of the solid state and connected inhomogeneities and heterogeneities many introduce serious limitations in some cases. To a great degree, however, they allow for the treatment of defect chemical kinetics even far from equilibrium (as necessary if interfacial reactions are to be described) and are very helpful to find out the validity range of linear irreversible thermodynamics that is usually applied

for the description of transport. In all cases however the explicit role of point defects has to be taken seriously.

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