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Application of the Arrhenius equation to solid state kinetics: can this be justified?

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Abstract

Application of the Arrhenius equation to the kinetics of solid state reactions has been criticised on several grounds. One of the main theoretical objections has been that the energy distribution amongst the immobilised constituents of a crystalline reactant is not represented by the Maxwell–Boltzmann equation. The detailed band structure of a solid may, however, include interface energy levels (analogous to impurity levels in semiconductors) that participate in the crucial bond redistribution step. Occupancy of such levels would be determined by energy distribution functions based on Fermi–Dirac statistics for electrons, and Bose–Einstein statistics for phonons. For the highest energies, necessary for reaction, both distributions approximate to an exponential energy term, thereby countering the above objection to the application of the Arrhenius equation to reactions of solids. The existence of such interface levels, with a limited range of energies, would also allow for the variation of apparent activation energy with extent of reaction, and also with temperature, reported for many complex solid state reactions.

Keywords: Arrhenius equation; Activation energy; Solid state kinetics; Maxwell–Boltzmann equation; Interface energy levels

1. Introduction

Although the use of the Arrhenius equation [1,2] in homogeneous kinetics normally requires no justification, and values of the pre-exponential term, or frequency factor, *A*, and activation energy, *E*, have been reported for countless chemical reactions of all possible types, serious doubts have been expressed [3–11] about the theoretical justification for the application of the Arrhenius equation to chemical changes proceeding in the solid state. The main reservation expressed [6–10] has been that the energy distribution amongst the immobilised constituents of a crystalline reactant is not represented by the Maxwell–Boltzmann equation that is applicable to a homogeneous gaseous system.

Alternative functions to the simplest form of the Arrhenius equation, many of which introduce additional constants, have been described by Laidler [2] as "theoretically sterile", in that the constants do not lead to deeper understanding of the mechanisms of chemical reactions. The reproducibility of rate data measured for most solid state reactions is usually insufficient to allow conclusions to be drawn regarding the preferred fit to such alternative functions. From a purely practical perspective, values of *A* and *E* provide a convenient comparative measure of reactivity and of the temperature coefficient of reaction rate.

In the terminology of homogeneous kinetics, the activation energy (*E*) is usually identified as the energy barrier (or threshold) that must be surmounted to

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enable the occurrence of the bond redistribution steps required to convert reactants into products. The pre-exponential term, or frequency factor, A, provides a measure of the frequency of occurrence of the reaction situation, usually envisaged as incorporating the vibration frequency in the reaction co-ordinate. An alternative representation, based on a reaction dynamics treatment [12], identifies the activation energy as the difference between the energy of the molecules undergoing reaction and the overall average energy. For low energy reactions, this energy difference may be appreciably different from the threshold value.

In practice, Arrhenius plots, using the rate coefficients, k, measured for reactions of solids, based on application of a limited set of model rate equations $\{g(\alpha) = kt\}$ [4,5] (where α is the fractional reaction), are often acceptably linear (or approximately linear) and the calculated values of E and A are usually regarded as possessing significances similar to those developed in the theory of homogeneous reactions, in spite of Garn's objection [6–10].

2. The Polanyi–Wigner model

An early attempt to explain Arrhenius-type behaviour in solid state decomposition reactions was that of Polanyi and Wigner [13] who derived the expression

$$\frac{dx}{dt} = \left(\frac{2vE}{RT}\right) x_0 \exp\left(\frac{-E}{RT}\right) \tag{1}$$

for the linear rate of advance of the interface, dx/dt, in terms of x_0, the incremental advance from unit reaction, and v, a vibration frequency. Rate control was identified as the dissociation of a particular bond, strength E, within the advancing interface, followed by evaporation of the surface-held species. The linear rate of interface advance is modified by the reaction geometry in deriving the model rate equations, $g(\alpha) = kt$ [4,5].

The vibrational frequency, v, of a crystal constituent at a surface or interface, is expected, from Eq. (1), to be of the order of 10^{13} s^{-1}. Experimental values of the pre-exponential factor, A, have sometimes been compared with this expected frequency and reactions have then been classified (e.g. [14]) as "normal" (when agreement is within a factor of 10 to 10^2, together with an E value close to the enthalpy of dissociation) or as "abnormal" (when both A and E values are appreciably larger than the above criteria). The use of these descriptive terms [15] assumes the universal applicability of the Polanyi–Wigner model, but important aspects of the conditions existing at reaction interfaces and the factors controlling reactivities have yet to be established. Due allowance must be made for the number of precursor species within the reaction zone, the changing area of the reaction interface and the operation of alternative, possibly more complex, mechanisms.

A survey of published A and E values for decompositions of solids [15] showed a slight predominance of A values between 10^{11} and 10^{13} s^{-1}, and a spread of activation energies mainly between 100 and 230 kJ mol^{-1}, with no obviously dominant value.

Young [16] interpreted the Polanyi–Wigner equation in terms of the thermodynamics of the activation process ($\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$) for an irreversible reaction

$$\frac{dx}{dt} = \left(\frac{k_B T}{h}\right)_{x_0} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right) \tag{2}$$

where k_B is the Boltzmann constant and h the Planck constant. The so-called "normal" values for v in Eq. (1) are calculated on the assumption that the entropy of activation ($\Delta S^{\ddagger}$) is zero. Values of A calculated for reactions which did not fit the Polanyi–Wigner treatment ("abnormal" reactions [14]) correspond to values of $\Delta S^{\ddagger}$ of from 200 to 500 J K^{-1} mol^{-1}.

3. Transition-state description

Shannon [17] used transition-state terminology to derive an expression for the rate coefficient, k_r, for the decomposition $A(s) \rightarrow [A(s)]^{\ddagger} \rightarrow$ products

$$k_r = \left(\frac{k_B T}{h}\right)\left(\frac{Q^{\ddagger}}{Q}\right) \exp\left(\frac{-E_0}{RT}\right) \tag{3}$$

where $Q^{\ddagger}$ is the partition function for the activated complex $[A(s)]^{\ddagger}$, with the contribution from motion along the reaction co-ordinate removed, and Q is the partition function for the reactant.

Calculation of Q for the reactant is reasonably straightforward, but the assignment of a value to $Q^{\ddagger}$ requires assumptions about the structure of the activated complex. From published kinetic data, Shannon [17] calculated the ratios ($Q^{\ddagger}/Q$) in Eq. (3). Three patterns of behaviour were considered with (i) $(Q^{\ddagger}/Q) < 1$, (ii) $(Q^{\ddagger}/Q) \sim 1$, and (iii) $(Q^{\ddagger}/Q) > 1$. Two mechanisms of decomposition were distinguished [17]: (i) direct loss of gaseous product from the interface (dissociations of $CaCO_3$ and $MgCO_3$), and (ii) formation of mobile adsorbed material followed by desorption (applicable to some dehydrations where water is the mobile species and $Q^{\ddagger}/Q > 1$). Cordes [18] extended the theoretical analysis to consider intracrystalline reactions, including bimolecular processes.

Burnham and Braun [19] have shown that including a temperature term in the pre-exponential factor has little practical effect on the fit of the empirical form of the Arrhenius equation over a typical 50 °C temperature interval used for experimental measurements (see also [2]). The temperature dependence of the pre-exponential factor becomes absorbed into the experimental value of E with a compensating change in A. Calculation of k values by extrapolation beyond the temperature limits is also not seriously affected by ignoring this temperature dependence.

Garn [6–8] believes that no discrete activated state is generated in decompositions of solids. Vibrational interactions transfer energy rapidly within a crystalline solid so that no substantial difference from the average energy can be achieved or sustained.

4. Multi-step processes

There is growing and convincing evidence [20] that the expectation that the rate of a complex process such as the decomposition of a solid should be determined by the rate of a single contributing step during the entire course of reaction, or even over a significant proportion of reaction, is probably unrealistic, even for use as a first approximation. The immobility of constituents and intermediates at an interface enables reaction to proceed by mechanisms that cannot occur in homogeneous processes, such as three-body collisions or a linked sequence of steps. In some reactions the chemical change under consideration may be a consequence of bond activation through electronic energy, in others through phonon activation. If any local melting occurs, a restricted volume of liquid becomes interposed between reactant and product. Within this region, reaction may be subject to the usual controls of homogeneous rate processes.

Vyazovkin and Linnert [20] have shown that the observation of systematic variations of values of E with extent of reaction, α, is a good indication of a multi-step process. For example, they showed that the dependence of E on α for measurements of the dehydrations of a number of crystalline hydrates was consistent with a reversible reaction followed by an irreversible step.

Bertrand et al. [21] regard E as a composite function, comprised of contributions from several parameters, including the deviation from equilibrium and the thermal gradient.

5. The reaction interface

For reactions involving solids, chemical change occurs exclusively, or very largely, at a reactant/product interface [4,5]. Established interfaces advance (grow) into unchanged reactant from specialised sites of initiation (nuclei) [22] and the reaction rate is directly proportional to the total area of active contact between reactant and product. The conditions within the interface that are responsible for the enhanced reactivity within this zone are not well understood and such zones are often inaccessible to direct examination, without damage, by microscopic and other techniques.

Reasons advanced [4,5] for the local enhancement of rate include a local decrease in E and/or an increase in A; strain between different juxtaposed crystal structures; catalytic activity of the product surface or a reaction intermediate, or partially irreversible recrystallisation of product.

The reactant/product interface formed during decomposition of a solid, which may be regarded as a complex crystal defect, can be of several general forms, although each sample of a particular solid reactant will have its own individual characteristics [23]. The fact that a fair degree of reproducibility is often observed from sample to sample of one chemical substance, is due to the highly-averaging effects of most of the usual experimental techniques, such as thermogravimetry and accumulated gas pressure measurements, which would mask the fundamental and constantly changing role that these individual characteristics play as reaction proceeds at the molecular level.

One extreme (although unlikely) case of a reactant/product interface would be perfect crystalline reactant in contact with perfect crystalline product. The thickness of such a reaction zone would be of molecular dimensions and gradients of all properties will be steep. Closely related to this extreme would be the case of decomposition to form all gaseous products, with rapid removal of these from the interface

$$R|P \quad \text{or} \quad R|\text{inert gas or vacuum}$$

In topotactic reactions [24,25], orientation and structural features of the reactant are preserved in the crystalline product.

A more likely form of interface is where there is an intervening phase different from both crystalline reactant and crystalline product. The intervening phase could be a melt [26].

$$R|I|P$$

This situation results in two (or more) interfaces: R|I and I|P and reaction could occur at either, both, or within I. The decompositions of several initially solid reactants involve the intervention of liquids [27]: ammonium dichromate [28], ammonium perchlorate [29] and copper(II) malonate [30].

If the reactant undergoes changes [31], such as partial water loss in dehydrations, together with some modification of crystallographic parameters, in advance of the reorganisation that results in the intervening phase, I, the modified reactant intervenes further

$$R|R(\text{mod})|I|P$$

The intervening phase, I, could be regarded as a modification of the final crystalline product

$$R|R(\text{mod})|P(\text{mod})|P$$

The modifications could be formation of intermediates temporarily adsorbed at the solid surfaces of either the reactant or the product [32]. During the thermal decompositions of those metal carboxylates that give the metal as product, anions may be transferred to and become chemisorbed at the surface of the metal. They may then breakdown by a mechanism that closely resembles the heterogeneous breakdown of the acid on the metal [33–35].

Applications of the Polanyi–Wigner treatment [36] apparently assumed a smooth contact interface. Alternatively the interface may be regarded as a complex defect. The role of strain in causing cracking [37] and loss of contact is unpredictable [38]. Different crystallographic surfaces may show different reactivities and reactivity may differ in the vicinity of crystal imperfections.

6. Energy and energy transfers

Energy is present in solids in the form of phonons (vibrational interactions between atoms, ions or molecules, together with internal vibrations) and electronic energy represented as a distribution in the band structure of the solid. There may also be additional strain energy locally associated with imperfections. Mobility of chemical species is far from that upon which the collision theory of homogeneous reaction rates is based. The factors controlling energy distributions in liquids and solids may, however, not be as different as has sometimes been assumed in kinetic considerations [39]. Interatomic energy transfers for both are achieved largely by vibrational interactions between neighbouring atoms, ions or molecules.

7. Band theory representations

Within the interfacial zone the species are probably more ordered than in a liquid, but less ordered than in a crystal. The energies of reactants in a liquid or solution are usually regarded as being associated with each individual molecule, whereas, in solids, band theory considers the distribution of energy within the whole crystal. The band structures for a crystalline reactant and its crystalline decomposition (or oxidation) product will generally be, at least, recognisably different. Except possibly for a very small number of highly topotactic reactions [24,25], where structure is extensively conserved, and some dehydrations which are not accompanied by recrystallisation, it is unlikely that continuity of reactant-product bands is preserved across a reaction interface.

The band structures portraying the transition between ‘p’ and ‘n’ zones of a semiconductor are a good model for representing the consequences of

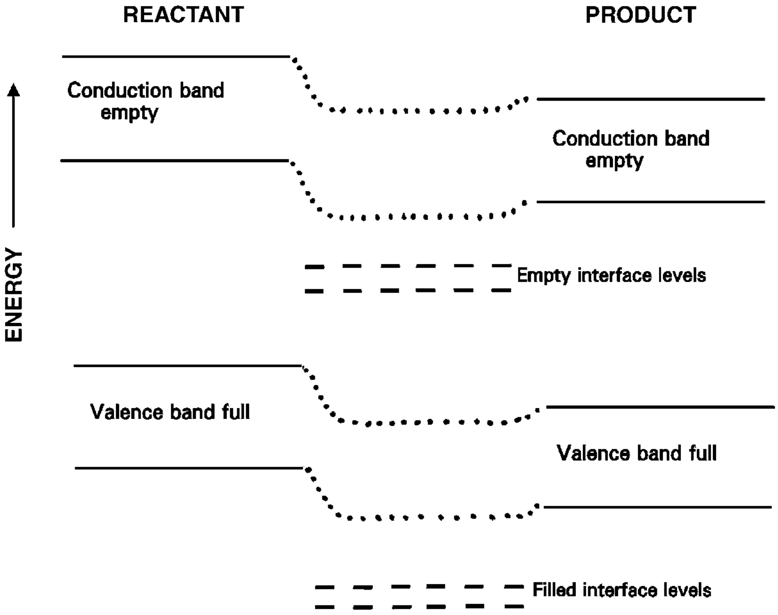

Fig. 1. Suggested band structure across the reaction zone [39].

small changes in concentrations of imperfections within a dominant regular crystal structure. Reaction species are situated, with associated interface levels, in the locally modified environment between the band structures characteristic of both the reactant and the product phases. These interface levels (analogous to impurity levels in semiconductors) differ from the levels of contiguous crystals, see Fig. 1 [39]. The electron transfers or bond redistribution steps that are essential for reaction, occur within this zone and involve the interface levels.

Band structures of solids in the vicinity of surfaces have been described by Cunningham [40]. Energy levels for both conduction and valence bands are distorted in the zone adjoining the crystal boundary and these may also occur as discrete levels associated with specific imperfection sites.

Gray and Waddington [41] have calculated the thermal energy required to excite an electron from an azide ion to the conduction band as 166 kJ mol^{-1} in AgN_3 and 224 kJ mol^{-1} for KN_3. These values are slightly larger than the measured activation energies for the decompositions: 150 kJ mol^{-1} in AgN_3 and 203 kJ mol^{-1} for KN_3. These data are consistent with the participation of interface levels that have energies somewhat below the band energy differences in the reactant crystal.

8. Energy distributions

If all components within the interface are confined within a regular lattice-type structure, the distribution of electronic energy may be represented [39] by the Fermi–Dirac statistical approach [42] which derives the probability (F) that a discrete and non-degenerative energy state E_e is occupied by an electron as

$$F = \left(1 + \exp\left\{\frac{(E_e - E_f)}{k_B T}\right\}\right)^{-1}$$

where E_f is the Fermi level and k_B is the Boltzmann constant. When E_e exceeds E_f by several times the magnitude of $k_B T$ (about 2.5 kJ mol^{-1} at 300 K and 5 kJ mol^{-1} at 600 K), this approximates [42] to an expression having the same form (but derived from a different energy distribution model) as the Maxwell–Boltzmann distribution

$$F = \exp\left\{\frac{-(E_e - E_f)}{k_B T}\right\}$$

If the interface zone is occupied by a crystalline intermediate, and/or includes species bonded as in a solid, this type of electron distribution function is applicable.

Assuming [43] that the phonons in the crystal are mobile, that their random-walk migrations extend without restriction into the bonds of the surface-held species, and that Bose–Einstein statistics are applicable, the energy distribution function, $n(\omega)$, can be expressed

$$n(\omega) = \left\{ \exp\left(\frac{h\omega}{2\pi k_B T}\right) - 1 \right\}^{-1}$$

where ω is the angular frequency of the lattice mode. At higher energies, $h\omega \gg 2\pi k_B T$, and the function decreases exponentially [44]

$$n(\omega) \approx \exp\left(\frac{-h\omega}{2\pi k_B T}\right)$$

This relationship is analogous to the Maxwell–Boltzmann equation.

If a melt is present, there is no band structure and chemical changes can be expected to proceed in the liquid as a homogeneous reaction.

9. Distribution of activation energies

Burnham and Braun [19] have discussed the problems of characterising the range of reactivity inherent in complex materials such as polymers, minerals, fossil fuels and biochemical materials. For such systems, the distributed reactivity caused by the complexity of the reaction can be modelled by a set of concurrent reactions, each with its characteristic pre-exponential factor and activation energy. One extreme of the model would be where there is no relationship at all between the values of A and of E. Simplifying assumptions include: (i) a compensation-type of relationship with $\ln(A)$ being a linear function of E; (ii) a single common value of A and a continuous distribution of activation energies; and (iii) a single common value of E and a continuous distribution of pre-exponential factors. The second simplification has been most used [19]. Burnham and Braun discuss [19] with examples, the types of distribution, which may be continuous (e.g. Gaussian, Weibull or Gamma distributions) or discrete. They report that the most versatile model for distributed reactivity has a discrete distribution of activation energies and they suggest that, for greatest accuracy over the initial and final stages of the reaction, the assumption of a uniform pre-exponential factor be replaced by $\ln(A)$ being a linear function of E.

Vyazovkin [45] has reviewed the factors that can cause the activation energy to vary significantly, even for reactions that involve a single step. He distinguishes two types of effect: those where properties of the medium result in the existence of different energy barriers for reaction; and those where there are diffusion limitations on the rate of a chemical step. He quotes, as examples of the first type, the work of Chandler et al. [46] on reactions in solution involving large polyatomic clusters, where the potential energy surfaces reveal numerous transition states of different energy; and treatments by Constable [47] of the non-uniform catalytic activity of solid surfaces. Vyazovkin [45] also points out the interesting similarity between temperature-programmed desorption studies and thermal decompositions of solids.

10. Reliability of Arrhenius parameters reported in the literature

A recent report on the results of the ICTAC project: "Computational Aspects of Kinetic Analysis" [48] presents the "kinetic triplets", the parameters E and A, and the conversion functions, $g(\alpha)$ or $f(\alpha)$, obtained independently by the participants, using the computational methods of their choice applied to the same sets of thermoanalytical data. The magnitudes of the Arrhenius parameters reported, and to a more limited extent, the conversion functions, identified as giving the 'best fit', showed significant and important variations for all eight sets of data considered. Examination [49] of the pattern of the reported magnitudes of A and E for each data set [48] showed that most, but not all, values were close to the line on a compensation plot (i.e. exhibited a kinetic compensation effect, KCE, a linear relationship between $\ln(A)$ and E [50]). Reasons for this divergence of kinetic conclusions have not yet been established but the differences must be a consequence of the alternative calculation procedures used by different researchers.

Possible explanations include application of, or different weightings given to, kinetic fits to different

α intervals for complex reactions and/or the consequences of approximations introduced to simplify the calculations. Better characterisation of the reasons for these inconsistencies is essential so that problems inherent in present methods of kinetic analysis can be identified and the reliability of calculated Arrhenius parameters can be assessed. The inconsistency of the Arrhenius parameters revealed by this project introduces doubt into the significance of all reported values of A and E obtained for crystolysis reactions, either by isothermal or programmed temperature techniques.

11. L'vov's evaporation theory of crystolysis reactions

L'vov [51] has recently proposed a model for solid state decompositions based on the Hertz–Langmuir prediction of the dependence of reactant evaporation rate on the equilibrium vapour pressure, which depends exponentially on temperature. This model represents decomposition as proceeding through congruent dissociative evaporation of the reactant with redistribution of the energy released on recondensation of the low volatility products equally between reactant and residual product phases. The primary products of the initial volatilisation step can be different from those representing final equilibration. This model is presented in detail, with supporting references, in a forthcoming review [52] and will not, therefore, be described in detail here. The theory developed accounts for several important features of crystolysis reactions that are currently not fully explained, including: nucleation and growth reactions, the role of volatile products in influencing reaction rates, the magnitudes of both Arrhenius parameters and the estimation of temperatures of onset of reactions.

This novel contribution represents a considerable stimulus to theory development in a topic presently lacking unifying features, by drawing attention to the urgent need to reappraise the fundamental assumptions and should be warmly welcomed. The relatively simple concept, i.e. amenable of quantitative treatment, has already been successfully applied to account for the thermal properties of over 100 substances of many different chemical compositions. Most of these examples are relatively simple compounds but the recent extension to oxalates [51] means that it has been demonstrated as being relevant to an important class of solid state decompositions. The work has already classified several behaviour patterns in changes observed on heating solids that have identified relationships which had not hitherto been recognised. This fundamental reappraisal of the basic principles of the thermal reactions of solids represents a challenge and a promising opportunity for subject advance at a time that the limitations in existing theory are becoming increasingly constraining.

12. Conclusions

The Arrhenius equation has been widely accepted and successfully applied to numerous reactions involving solids. No realistic alternative capable of expressing the form of the $k - T$ relationship or providing an explanation of this pattern of behaviour has gained acceptance. The Maxwell–Boltzmann energy distribution function provides the starting point for a theoretical explanation of Arrhenius behaviour in homogeneous reactions. Although this model is inapplicable to the immobilised constituents of a solid, the energy distribution functions for both electronic energy (Fermi–Dirac statistics) and phonon energy (Bose–Einstein statistics) approximate [39] (for values significantly above the Fermi level) to the same form as that in the Maxwell–Boltzmann distribution and hence are capable of explaining the fit of $k - T$ data to an Arrhenius type equation.

Interface levels, capable of accommodating electrons (analogous to impurity levels in semiconductors, imperfection levels in crystals, etc.) are proposed [39] to be present within the interfacial zone wherein chemical changes occur. These energy levels can be located within the forbidden range between the energy bands of the crystal. The actual energies of these levels will be sensitive to the particular species involved and energies distributed within a limited range are more likely than uniform energies. The realistic model is, thus that of Vyazovkin's [45] first type. Such levels are involved in the crucial bond redistribution steps and account for the increased (but probably variable) reactivity at the reactant/product interface relative to more perfect crystalline regions. The occupancy of these levels is governed by distribution functions similar in form to that of the Maxwell–Boltzmann equation. The band model of solids may thus be extended to accommodate the bond redistributions during conversion of reactant to product.

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