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Thermochimica Acta, 242 (1994) 259-264
thermochimica acta

Note

Magnitudes of Arrhenius parameters for decomposition reactions of solids

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(Received 27 September 1993; accepted 10 February 1994)

Abstract

The Polanyi-Wigner theory of rates of solid state reactions and the transition state theory indicate a preferred value of approx. $10^{12}\ \mathrm{s}^{-1}$ for the Arrhenius reaction frequency factor A. To investigate whether this value is preferred amongst the reported kinetic results in the literature, some 404 similar sets of activation energy (E) and A values have been compared, including results for a wide range of different solid state decompositions. Plots of the relative numbers of reactions having different magnitudes of A showed a slightly preferred value between $10^{11} < A < 10^{13}\ \mathrm{s}^{-1}$. This weak preference did not offer strong support to the general applicability of the Polanyi-Wigner model. Similarly, E values were fairly evenly distributed between 100 and 230 kJ mol^{-1}, without a dominant value. There was no evidence of compensation behaviour.

Keywords: Activation energy; Arrhenius; Decomposition; Solid

1. Introduction

Early theoretical discussions of the magnitudes of Arrhenius parameters for reversible solid state decompositions proceeded through the quantitative considerations of the Polanyi-Wigner model [1]. In this approach, the rate of the interfacial reactions controlling the advance of the rectant/product contact is expressed as [2, 3]

$$\text{Rate} = \nu C \exp(-E/RT) \qquad (1)$$

where ν is the vibration frequency in the reaction co-ordinate (approx. 5-$10 \times 10^{12}\ \mathrm{s}^{-1}$) and C is related to the number of water molecules, or other reactant

SSDI 0040-6031(94)01766-A

species, in the active interfacial zone. The exponential term includes the activation energy E which is calculated using the Arrhenius equation from the variation with temperature of the velocity of interface advance. Much of the early work, intended to provide a theoretical explanation for the magnitudes of the Arrhenius parameters, was measured for reversible reactions and included, in particular, the dissociations of hydrates and carbonates [1].

Many of the earliest (pre-1950) quantitative studies in the field proceeded from the assumption that the magnitude of v was invariably between 10^{12} and $10^{13}\ \mathrm{s}^{-1}$ and, for reversible processes, that the magnitude of E was close to the measured reaction enthalpy. Several of the values considered in these investigations were in accordance with expectations [1–4]. In particular, magnitudes of v were comparable with the factor kT/h (= approx. $10 \times 10^{12}\ \mathrm{s}^{-1}$ at 500 K) which appears from the transition state theoretical analysis. Where the Polanyi–Wigner predictions were applicable, the reaction was described [1] as *normal*, as, for example, for the dehydrations of $CuSO_4 \cdot 5H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$ and $NH_4Al(SO_4)_2 \cdot 12H_2O$. However, where the predictions were in significant disagreement with the determined values, examples being the dehydrations of $CaCO_3 \cdot 6H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$, the reactions were described as *abnormal* because Eq. (1) was inapplicable.

The use of the terms 'normal' and 'abnormal' seems to me to be unacceptable because their use appears to derive from the dogmatic assertion that all such rate processes necessarily and invariably are described by the Polanyi–Wigner expression. I believe that the factors controlling rates of chemical changes within the reactant–product interface of reactions of this type have not yet been so definitely characterized. Such chemically active zones are inaccessible to direct study and the bond redistribution steps participating are inevitably inferred from indirect evidence [5–7]. In the absence of reliable characterization of the reaction mechanisms it is not possible to provide generally applicable theoretical explanations.

From these general considerations, taken together with the wide acceptability of the transition state theory throughout the field of chemical kinetics, I considered it to be of value to determine whether there are obviously preferred values of Arrhenius parameters. Accordingly, I identified two sets of rate studies concerned with a wide range of decompositions of solids for which reliable comparisons of the magnitudes of E and A could be made. Sets A and B together included 404 values of Arrhenius parameters. These two different sets required a slight variation in analytical method, described below, to obtain values of A and of E that could be used in the comparisons. Both sets include a very diverse representation of solid state reactions, overall comprising dehydrations (17%) and decompositions of oxides, hydrides, etc. (11%), azides (4%), carbonates (4%), diverse oxyacids (sulphates, oxyhalides, permanganates, etc.) (37%), carboxylates and other organic acids (20%), and other reactants (7%).

1.1. Set A

The A and E values to be used in the comparison were calculated for 257 isothermal kinetic studies included in the review by Brown et al. [5]. For each rate study the mean reciprocal reaction temperature $(T_M/K) = 0.5(T_{max}^{-1} + T_{min}^{-1})$ was calculated from the maximum (T_{max}) and minimum (T_{min}) temperatures for the interval across which the kinetic data had been measured. Assuming that the rate constants throughout these investigations were measured for reactions completed in time intervals between 0.1 and 6.0 h (reflecting the approximate limiting values for reaction rates that are conveniently studied isothermally), we conclude that, to a satisfactory degree of approximation, the rate constant of T_M is close to $k/h^{-1} = 1.00$. Accordingly

$$\lg(A/s^{-1}) = (E/RT_M) - 3.56$$

257 sets of A and E values from ref. 5 were listed.

1.2. *Set B*

From a survey of kinetic reports in the author's personal collection, studies were identified in which the temperature (T_T) at which $k/h = 1.00$ could be calculated. The pre-exponential factor was calculated from

$$\lg(A/s^{-1}) = (E/RT_M) - 3.56$$

147 sets of A and E values were listed.

2. Accuracy of kinetic data

The activation energy values that constitute both sets of data were obtained from surveys covering a most extensive range of publications. Magnitudes of E incorporated are, therefore, representative of results reported in numerous refereed journals. It is difficult to provide an overall estimate of the reliability of these results that encompass the best available isothermal kinetic studies for the reactions of solids. Probably most values of E are accurate to better than ±10%, from which we conclude that the trends shown in Fig. 1 are meaningful.

Pre-exponential factors (expressed here as lg A) are inevitably slightly less reliable. Uncertainties arising from those inherent in E are estimated to be ±0.7–1.0 unit in lg A. It is more difficult to assess contributions arising in the calculation method used but it is probably realistic to assess a maximum error of ×4–1/4 in rate or ±0.6 unit in lg A. Values of lg A therefore, are believed to be generally accurate to ±1.5 unit, from which the trends in Fig. 2 are again regarded as meaningful.

3. Distribution of magnitudes of activation energies

The numbers of reactions for which the reported E values occurred within steps of equal increment (30 kJ mol^{-1}) are shown in Fig. 1. The distribution shows a broad flat maximum, for which 65% were between $100 < E < 230$ kJ mol^{-1}, in

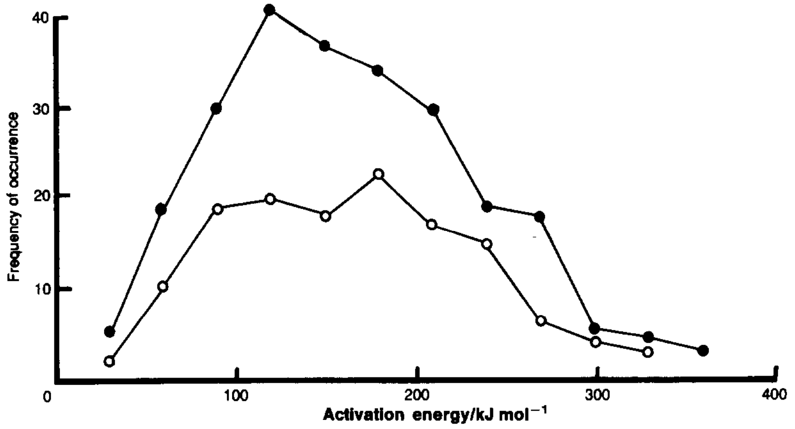

Fig. 1. The frequency of occurrence of activation energy values, in steps of equal increment (30 kJ mol^{-1}), from two sets, including a total of 404 values, from kinetic studies for a wide range of diverse solid state decompositions.

accordance with expectation. No particularly preferred magnitude of E can be identified. The overall mean magnitude of E was 175 kJ mol^{-1}. There was a small proportion (8%) of relatively large E values, >300 kJ mol^{-1}.

4. Distribution of magnitudes of frequency factors

The numbers of reactions for which the reported frequency factors (expressed as $\lg(A/\mathrm{s}^{-1})$) occur within steps of equal magnitude (2) are shown in Fig. 2. There is weak evidence for a preferred value between $10^{11} < A < 10^{13}\ \mathrm{s}^{-1}$ in both sets of data but the distribution peak is not sharp and there is a wide spread of values on both sides. This model generally accords with the theoretical treatment provided by Cordes [8] but does not provide any strong confirmation of the predictions of the Polanyi–Wigner model. We conclude that, in the absence of detailed information concerning the mechanism of the interface reaction, the interface structure and the controlling bond redistribution steps, it is premature to speculate about the physical significance of the magnitude of A values measured for solid state decompositions.

5. Compensation behaviour

Because so many groups of related reactions exhibit compensation behaviour, a linear correlation of $\lg A$ and E [9], it was considered appropriate to test this possibility here. However, in this instance (almost unusually) there was very considerable scatter on plots of E against T_{M} or T_{T} and no significant trend could

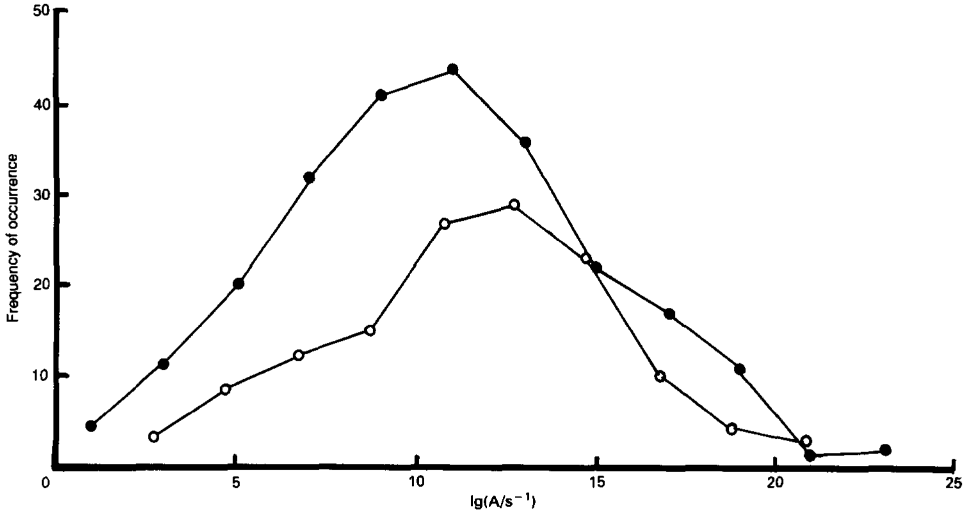

Fig. 2. The frequency of occurrence of Arrhenius pre-exponential values, expressed as $\lg(A/\mathrm{s}^{-1})$ in steps of equal increment (2) for the same kinetic studies as in Fig. 1. There is no strong preference for the Polanyi–Wigner value, A = approx $10^{12}\ \mathrm{s}^{-1}$.

be discerned. There was only the slightest indication that some conventionally calculated values of E increased with reaction temperature. This is clearly consistent with the evidence above that there is no characteristic magnitude for A for solid state reactions. It also emphasizes the difficulties that are inherent in the meaningful determination of the significance of A.

6. Conclusions

The magnitudes of many pre-exponential factors for solid state decompositions were within the range $10^8 < \lg(A/\mathrm{s}^{-1}) < 10^{14}$, some 50% of the present set of representative values. However, because about half of the set are outside this interval, it is concluded that the spread is too large to accept that the Polanyi–Wigner value (approx. 10^{12}) should be regarded as 'normal'. Similarly, values of E showed no preferred magnitude: most were $100 < E < 230\ \mathrm{kJ\ mol^{-1}}$. These sets of reactions did not exhibit compensation behaviour.

References

[1] W.E. Garner, in W.E. Garner (Ed.), Chemistry of the Solid State, Butterworth, London, 1955, Chapter 8.
[2] B. Topley and J. Hume, Proc. R. Soc. London. Ser. A, 120 (1928) 211.
[3] R.S. Bradley, Phil. Mag., 12 (1931) 290.

[4] W.E. Garner and T.J. Jennings, Proc. R. Soc. London. Ser. A, 224 (1950) 460; 189 (1947) 508.
[5] M.E. Brown, D. Dollimore and A.K. Galwey, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
[6] A.K. Galwey, R. Spinicci and G.G.T. Guarini, Proc. R. Soc. London. Ser. A, 378 (1981) 477.
[7] A.K. Galwey and G.G.T. Guarini, Proc. R. Soc. London. Ser. A, 441 (1993) 313.
[8] H.F. Cordes, J. Phys. Chem., 72 (1968) 2185.
[9] A.K. Galwey, Adv. Catal., 26 (1977) 247.