Thermochimica Acta 375 (2001) 161–167

thermochimica acta

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# Should the melting of ice be represented as a solid state reaction?

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Received 30 October 2000; received in revised form 29 March 2001; accepted 2 April 2001

## Abstract

Ice cubes, held in a flow of water maintained at a constant temperature, melt at a rate that is well expressed by the contracting volume rate equation, familiar from kinetic studies of solid state reactions. The apparent activation energy, $28.5 \pm 3.0$ kJ mol$^{-1}$ between 276.2 and 303.4 K, is close to the strength of the hydrogen bond in ice. From these observations, it appears that this physical change exhibits a pattern of kinetic features that is superficially identical with behavior characteristic of the chemical steps occurring during thermal decompositions of solids. However, careful examination of the rate data at the temperatures closest to the melting point of ice shows that here rates are much slower than is consistent with expectation from the Arrhenius line. It is concluded, therefore, that rate constant measurements are more satisfactorily represented overall by a rate of interface advance, during fusion, that is directly proportional to heat flow; this is directly proportional to the difference between the temperatures of the ice surface and of the flowing water. It follows that the melting rate is most satisfactorily represented as being controlled by heat transfer across a boundary layer of moving liquid, close to the ice surface. These alternative analyses of the same data are presented to emphasize that mechanistic and kinetic interpretations of rate processes involving solids must be based on realistic assessments of conditions within the zone of change. This demonstration that a kinetic expression that is characteristic of solid state reactions satisfactorily describes the data together with an activation energy that correlates with a known bond strength in the reactant does not necessarily prove that a solid state, activated reaction is occurring here. Aspects of the mechanistic interpretations of the kinetic characteristics of many solid state decompositions remain difficult to understand and are incompletely resolved.

*Keywords:* Activation energy; Crystolysis reaction; Kinetic analysis; Solid state kinetics

## 1. Introduction

In some articles reporting kinetic and mechanistic studies of solid state decompositions, it appears that researchers represent rate characteristics through equations based on concentration terms, the rate expressions that are familiar from homogeneous kinetic analyses. However, such reactions are often more satisfactorily, and accurately, represented by rate equations derived from geometric models [1]. These kinetic models are appropriate because many processes involving the breakdown of lattice constituents in crystalline solids occur preferentially, even exclusively, at an active reactant–product interface that advances within the solid particle undergoing change. Rate equations formulated through consideration of the geometric patterns of interface development, originally modeled from microscopic observations of the topology of interface development [2,3] have been widely and successfully applied. The initial generation

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PII: S0040-6031(01)00523-8

of the active interface sometimes occurs at a limited number of surface sites (nuclei) and each advances, usually with expansion thereafter of the active reactant–product contact area within which the chemical change occurs, inwards into the reactant particle. Such reactions give, during isothermal decomposition, sigmoid-shaped fractional reaction–time curves, that are characteristic of many solid state processes. In another type of behavior, reaction is initiated rapidly across all surfaces and the zone of chemical change advances inward from all surfaces of the original particle, reaction is deceleratory throughout. In both groups of heterogeneous reactions, the isothermal rate is represented as being controlled by geometric factors rather than the concentration of participants, as is characteristic of most homogeneous rate processes. Identification of the rate equation giving the 'best-fit' to kinetic data for a solid state decomposition can be used to infer the geometric pattern of interface development, though the reliability of such conclusions is increased significantly by confirming the mechanistic deductions by direct observations, usually through microscopic examinations. Kinetic analysis can be based on either isothermal or programed temperature measurements. There has been some tendency in rising temperature investigations to prefer the use of rate equations based on reaction orders. The great majority of kinetic studies of reactions occurring on heating initially solid reactants include a determination of the activation energy for the rate processes considered.

A set of (about a dozen) characteristic rate equations based on geometric models [2] have found extensive application in mechanistic studies of solid state decompositions [1–3]. Some of those found useful also include due allowance for the influence of diffusion in rate control. A fundamental feature of mechanistic studies of a reaction involving a solid reactant is to determine whether or not melting accompanies the chemical change. For some reactions, involving progressive melting as reaction proceeds, this may be more difficult to recognize than is sometimes appreciated [4]. For this reason, the term "crystolysis reaction" has been proposed [5] for use as a keyword, or index entry to aid literature searches directed towards locating reactions proceeding in the solid state, where words, such as "crystal", "decomposition" and "solid" appear widely and generally in abstracts and other lists, but are highly non-specific. The use of this distinctive term might further encourage authors to state positively the phase (melt or solid) in which reaction occurs, an important mechanistic characteristic that is not always identified.

The point of central interest to the investigation reported here is that the set of rate equations applied to reactions of solids are based on reaction models and mechanistic assumptions that are quite characteristic and distinct from those applicable to homogeneous processes occurring in gases and in liquids. It is, nevertheless, often assumed that the theoretical significances of the Arrhenius parameters calculated for reactions of the two types are equivalent. This pragmatic approach is adopted, and widely accepted, as the 'best available' because we know comparatively little about the details of the chemical steps and the controlling parameters of solid state interface processes, which tend to be inaccessible to direct experimental investigation. The fit of rate processes of both classes to the Arrhenius equation implies comparable controls and it may follow that similar deductions can be drawn about the 'energy barrier to reaction' (the calculated activation energy, $E_a$) and the 'frequency factor' (the Arrhenius preexponential factor, $A$). This is unsatisfactory in that the energy distribution function for the reactant precursors to a solid state reaction is not (necessarily) adequately expressed by the Maxwell–Boltzmann treatment, accepted as the (homogeneous) foundation in the theoretical formulation of the Arrhenius equation. Aspects of this fundamental shortcoming, and the application of the Arrhenius equation to solid state reactions, have already been discussed in some detail [6], so this analysis will not be presented again here.

Reactions proceeding exclusively within an active contact zone, located between reactant and product crystalline phases and perhaps of a few molecules thickness, are difficult to investigate directly and to measure the data required to identify reaction controls. In considering simpler systems, capable of giving information about factors determining rates of change at a crystal boundary, it appeared that a kinetic-type study of the rate of melting at the surface of a well-characterized solid at a range of temperatures could be of interest. Solids rarely superheat, so that the rate of transformation of solid to liquid is expected to be determined by heat transfer. Moreover, the rate of product removal by mass diffusion will not influence the apparent kinetics of melting, unlike many solid state reversible dissociations [7,8]. The system that we selected for ease of investigation was the melting of ice because the "reactant" (ice), the "product" (water) and the melting process appear to be simple and well-characterized. The investigation was undertaken to compare quantitatively the apparent kinetic characteristics of the interface advance process (regarded as a solid state reaction) with aspects of the known characteristics of melting.

## 2. Experimental

Melting experiments were carried out in a large bath (capacity, about 40 l) filled with water thermostatted (±0.2 K) at the temperature of interest and constantly circulated by a pump. Ice blocks for study, initial masses 10–12 g, were stored at 273 K in melt water. Each approximately cube-shaped block was weighed before being held in the thermostatted bath within the flow of water from the circulating pump for a measured interval of time between 1–20 min (±0.05 min) before being removed and immediately reweighed. Each step was completed as rapidly as possible to minimize errors. Up to eight successive measurements could be made using a single ice block (of progressively decreasing dimensions) at the lowest temperature investigated (276 K) but fewer (perhaps two or three) could be completed during more rapid rates of melting at higher temperatures (up to 303 K). Over 350 separate mass-loss with time (isothermal) determinations were made at seven selected temperatures within the range mentioned.

## 3. Results

Representative measurements of the rates of ice melting are given in Fig. 1. These are expressed as fractional reaction, $\alpha = (m_0 - m_t)/m_0$, where $m_0$ is the initial mass and $m_t$ mass remaining after time $t$ in the water flow at one of the temperatures (±0.2 K) studied: 276.2, 281.0, 282.5, 289.0, 292.7, 299.2 and 303.4 K. Points shown were obtained for ice cubes introduced into the water flow, after intermittent rapid weighing, on successive occasions until melting was completed. Each line includes results from two or three ice cubes treated identically. Data for the pairs of temperatures (281.0 and 282.5 K = 281.7 ± 0.8 K) and (289.0 and 292.7 K = 291 ± 2 K) overlapped and each pair is represented by a single line. Measured mass losses, from melting, during unit time were

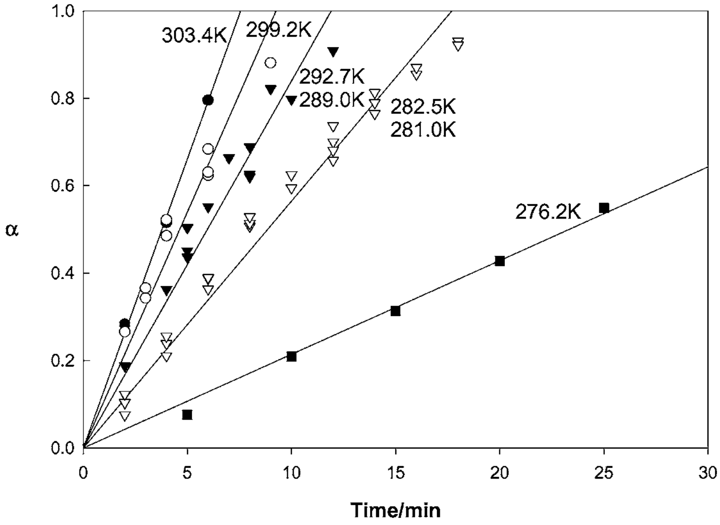

Fig. 1. Measured data for the rates of ice cube melting in a flow of water thermostatted at constant temperatures (±0.2 K), expressed as fractional reaction, α–time plots at seven temperatures in the range 276.2–303.4 K.

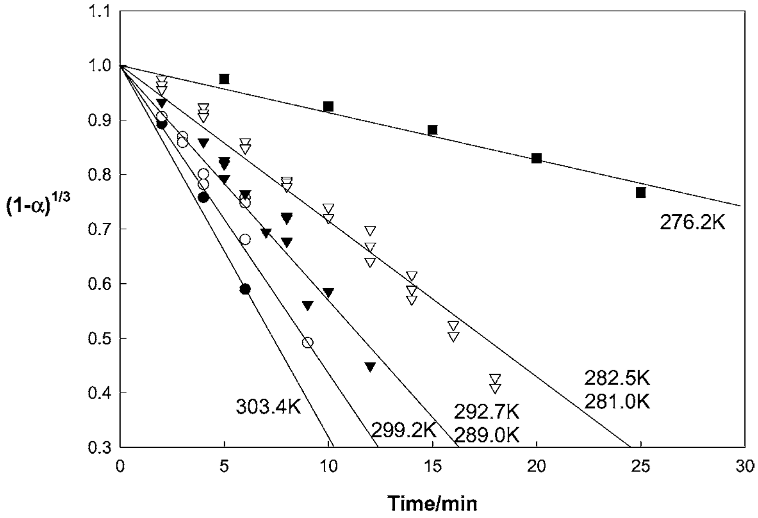

Fig. 2. Kinetic analysis: fit of extent of ice melting against time to the contracting cube equation [1]; these are plots of $(1-\alpha)^{1/3}$ against time for the data given in Fig. 1.

approximately constant in the early stages but later became deceleratory. This is fully consistent with expectation for a fit of the kinetics of melting to the contracting volume equation [1–3]

$$1-(1-\alpha)^{1/3}=\left(\frac{2k}{a}\right)t$$

where $a$ is the linear dimension of the ice cube edge. For cubes of initially equal size ($a$ is constant) plots of $(1-\alpha)^{1/3}$ against $t$ were linear (Fig. 2). While there was some scatter of the experimentally measured data, the ‘contracting cube equation’ [1] provided the best available representation and was consistent with the obvious shrinkage of the cubes, visually observed.

The variation of rate constant, $k$, with temperature is well represented by the Arrhenius equation, Fig. 3, with the significant exception of the lowest value,

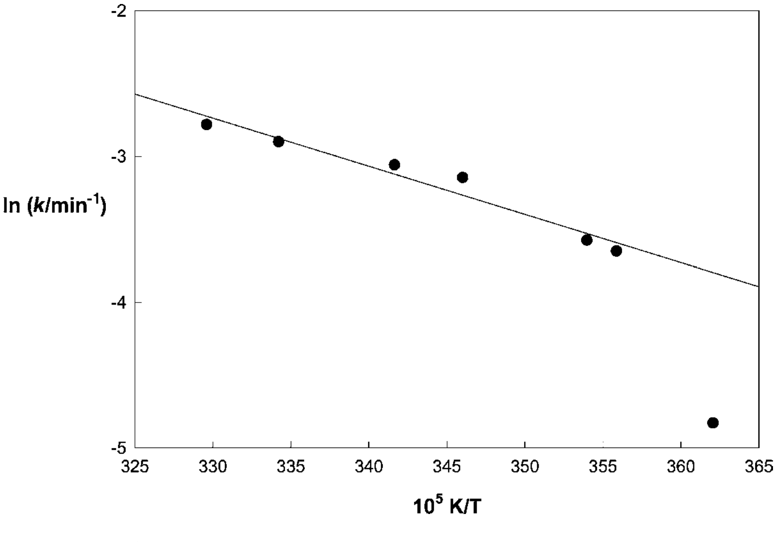

Fig. 3. Arrhenius plot for ice melting in flowing water thermostatted at various temperatures between 276.2 and 303.4 K, using rate constants from the contracting cube equation (Fig. 2).

which is much lower than is consistent with the other data. The apparent activation energy, $E_a$, was 28.5± 3.0 kJ mol$^{-1}$ between 276.2 and 303.4 K. The frequency factor, $A$, was calculated as $8 \times 10^9$ s$^{-1}$ from the rate of interface advance and the density of water molecules at the ice surface. A further measurement (insufficiently accurate to include on the graph), for the melting of ice in water at 273.5 K, was similarly far below the line [approximately: $\ln(k/\text{min}^{-1}) = -5.4$ at $(10^5\,\text{K}/T) = 365.6$].

Similar plots, drawn using further measurements of rate constants across the same temperature interval, gave values of activation energies between 28.5 and 35 kJ mol$^{-1}$ and values of the frequency factor between $8 \times 10^9$ and $1 \times 10^{11}$ s$^{-1}$. Those Arrhenius plots from which the apparently relatively higher values were calculated tended to be slightly curved and magnitudes of all rate constants measured below 278 K were significantly below the line defined by the other data.

## 4. Discussion

The pattern of rates of ice block melting, described above, across the temperature interval 278–304 K, based on more than 350 mass melted/time measurements, appears (superficially) to characterize the kinetics of fusion as a solid state decomposition proceeding at an advancing water–ice interface. The isothermal yield (loss of mass from the ice cube), represented as $\alpha$–time data, are acceptably described by the contracting volume rate expression (Fig. 2) which is based on a geometric model [1–3]. The apparent magnitude of $E_a$, although small, 28.5 kJ mol$^{-1}$, is slightly greater than the strength of the hydrogen bond in ice (about 21 kJ mol$^{-1}$ [9]) and appreciably greater than the latent heat of ice melting (6.01 kJ mol$^{-1}$). Thus, the rupture of an oxygen to hydrogen, non-covalent link (hydrogen bond), might, from these data and following usual theoretical practice, be identified as rate limiting. The frequency factor ($8 \times 10^9$ s$^{-1}$) was somewhat below the value characteristic of the (so-called [10]) 'normal' interface processes participating in reversible solid state dissociations, $5 \times 10^{12}$ s$^{-1}$, but not significantly outside the range generally reported for reactions of this type [10–13].

This mechanistic interpretation of the measured rate data, identified as conforming closely with expectation for the behavior pattern of a solid state decomposition (crystolysis reaction [1]), is not acceptable, however, for two main reasons. First, melting rates measured in water at 276.2 K (Fig. 3), and also at 275.5 K, are significantly below the Arrhenius line. Moreover, values must diminish further, effectively to zero rate, at 273.15 K. Second, it is generally accepted that melting cannot be treated as an activated process. Immediately below the melting point, the rate of change is zero, or negative (representing solidification), whereas above this temperature, the rate is finite (probably controlled by heat transfer at the solid/liquid contact). Across a narrow temperature interval, traversing the melting point, the value of $E_a$ is large or perhaps (theoretically) infinite.

In the context of these reservations, the kinetic data are alternatively (and more realistically) interpreted by considering that the melting rate is controlled by the transfer of heat to the ice surface (at 273.15 K) from the warmer water with which it is in contact. The trend shown in Fig. 4, a plot of rate constant, $k$, against temperature (assuming control by temperature difference rather than the activation process underlying the Arrhenius expression), supports the view that melting rate control is by heat transfer. Rate constants, providing a measure of the interface advance (melting) rate, increase in direct proportion to the magnitude of the temperature discontinuity at the solid–liquid contact. Significantly, the low temperature values are now no longer anomalous and all points are close to the line, with the rate constant, $k$, reaching zero, in accordance with expectation, at 273.15 K. From the slope of this line, the latent heat of ice melting and the thermal conductivity of water, we estimate that the rate of melting corresponds to the flow of heat across a static water layer, approximately 2 mm thick. This, however, can only be an approximate representation of the dynamic, perhaps turbulent, movement of water flowing past each ice surface at about 2 m s$^{-1}$. Heat distribution within this viscous fluid, suffering drag in the layers adjoining the static solid, must be inhomogeneous, with the transfer of energy being opposed by water cooled as a result of melting (the latent heat of ice melting is approximately 80 times the specific heat of water).

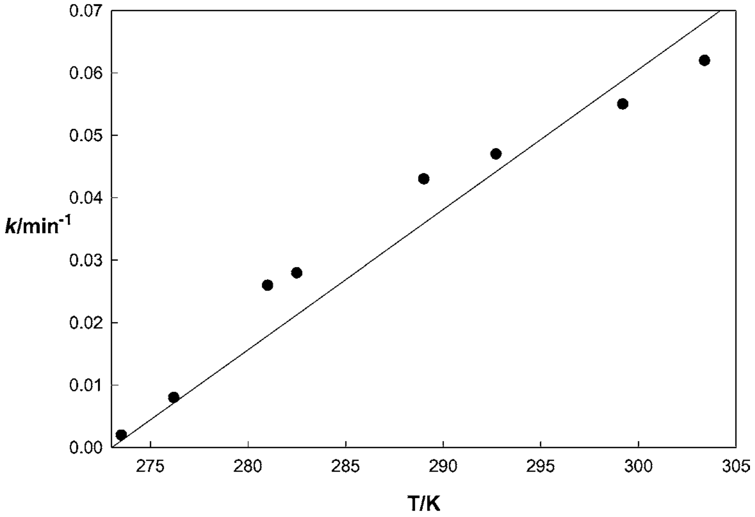

Fig. 4. Plot of contracting cube rate constants, $k$/min$^{-1}$, for ice melting against water bath temperature.

The principal objective of this paper is to point out that for this (apparently) most simple of rate processes, the kinetic data conform, in almost all respects, to a behavior pattern that can be regarded as being characteristic of solid state decompositions, crystolysis reactions, that are rate controlled through an activated step, represented by the Arrhenius model. Kinetic data capable of distinguishing between these possibilities through the preferred fit of data to alternative functions that express the variation of rate constants with temperature [6,14] would require measurements of considerably greater accuracy than can usually be achieved.

We consider that the interpretation in which the fusion rate is controlled by heat transfer provides a considerably more realistic representation of the melting process investigated here. This conclusion is apparent for this system, selected to examine the simple change which is readily observed and no primary bond redistribution step is involved. However, the interpretation of data obtained for less familiar and/or more complicated processes, where the participation of chemical, bond redistribution steps may be involved, is very much less straightforward. Interpretations of rate measurements must be based on the widest possible experimental base and all contributory influences must be critically considered. Some reactions appearing, from limited study, to be solid state decompositions may involve melting which may be local and temporary [4,15–17] or extensive and complete [18,19]. In many other reactions, rate may be partially, or completely, determined by mass and/or heat transfer [7,8,20–22]. It follows, therefore, that the positive identification that a reaction proceeds in the solid state must be based on a realistic appraisal of possible contributions from alternative mechanisms involving melting. Interpretation of kinetic data can be most usefully supported by visual, or microscopic, observations. A current trend, accepting that a decomposition can be reported as a crystolysis process on limited isothermal and/or non-isothermal kinetic observations, also used to calculate magnitudes of $E_a$ and $A$, often yields reports of doubtful reliability and value.

## 5. Conclusions

We conclude that the answer to the title question is ‘no’.

We regard the similarities, described above, of the kinetic behavior pattern measured and reported for the melting of ice with the characteristics of solid state decompositions to be unexpectedly close. This example is presented to demonstrate that kinetic analyses methods routinely accepted in rate and mechanistic investigations of the changes that occur on heating initially crystalline reactants are more difficult to interpret than is perhaps generally accepted. Indeed many kinetic studies, sometimes including mechanisic interpretations, define the initial reactant (usually solid) but do not discuss whether the rate processes described take place in the crystalline state or investigate whether there is melting before or accompanying reaction. We believe that the establishment of the phase within which the chemical change occurs should be a fundamental and essential feature of any reaction mechanism proposed, yet this important characteristic of such changes is not always defined or even discussed. The present work emphasizes that great care must be exercised in identifying the mechanisms, and the parameters controlling rate, that determine the course of reactions that may (or may not) proceed in a crystalline reactant.

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