A VIEW AND A REVIEW OF MELTING OF ALKALI METAL HALIDE CRYSTALS

Part 3. Melting of solids: theories and mechanisms of fusion

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Theoretical models for the melting of solids are inadequate because relatively little is known about the structures of liquids formed and the factors that control this phase transformation. In the present analysis of fusion phenomenon, usually considered to be a physical change, it is pointed out that, for many solids (e.g., metals and some simple ionic salts) melting involves the redistribution of primary valence bonds. Accordingly, this review includes examination some more chemical aspects of the controls of melting. The available data show that enthalpy and density changes during liquefaction and solidification of the metallic elements and of the alkali halides are small. From quantitative consideration of these values, it is concluded that ordered packing arrangements of atoms, ions, or molecules, comparable with those of crystals, must be extensively retained into the melt.

The energy and molar volume changes on melting are too small to allow significant departure, in the liquid, from the regular, efficient space-filling arrays that characterize crystalline solids. The set/liq model for melting (dynamic equilibria between alternative ordered structures) is proposed to account for the properties of the liquid. A detailed and critical comparison of melting with solid state decompositions considers the kinetics and the mechanisms of the changes that occur during the supply/removal of energy to/from the melt/crystal contact interface. Other relevant aspects of melting are discussed including the factors that determine the magnitudes of the melting points of individual solids.

Keywords: *alkali halides, crystolysis reactions, fusion, melt structures, melting, melting point, metal, solid decomposition*

Introduction

The formulation of a general theory of melting has proved to be particularly intractable, even though the fusion of solids is a very well-defined and familiar phenomenon [1]. At low temperatures, crystalline solids are typically characterized by regularity of structure, coherence and rigidity. Long range order is maintained by constituent interactions through van der Waals, covalent, ionic, metallic and hydrogen bonds, and all realizable combinations of these. For most pure crystalline substances, there is a precise and characteristic temperature, the melting point, T_m, at which a phase transformation, solid- to liquid-state, occurs with discontinuous losses of rigidity and long-range order. Fusion at the T_m is probably the most usual, though not an invariable, consequence of the unrestricted heating of a solid. However, despite the generality and importance of melting, none of the proposed representational models or theoretical explanations has yet found general acceptability or applicability.

Many studies of melting have focussed interest on limited groups of related, often simple, crystals, including metals [2], elements, inert gases, alkali halides [3, 4], etc. In the absence of an accepted comprehensive theory, one implicit objective of such studies appears to be the expectation (or hope) that progress in understanding the properties such a group of melting solids might later be capable of development for wider application. Although progress has undoubtedly been made in the understanding of fusion phenomena, the difficulties in formulating a general theory remain formidable and include the following.

- Melting/crystallization is usually regarded as a physical change, because all constituents of the solid and of the liquid (atoms, molecules or ions) remain chemically unaltered. Fusion is (usually) readily reversible. Many solids melt through redistributions of only weak (e.g., Van der Waals) intermolecular forces: these are physical changes. For other solids, however, melting can be regarded as different from most other physical processes because primary (ionic, metallic or even covalent) chemical bonds may be ruptured and/or redistributed. The present discussion explores some of these more chemical aspects of melting.

- Although melting almost always involves common characteristic features (a precise T_m, long range order loss, reversibility, etc.), the diversity of types of

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bonding forces between constituents in the varied and disparate solids that melt complicates the formulation of a comprehensive model. It may be that there is no single and universally applicable theoretical explanation for fusion.

- The limited information that is available concerning structural order in a melt at its T_m, including the relative dispositions of and types of bonding between the constituents, has been a considerable restriction in the development of a comprehensive theory of melting. This absence of knowledge about melt properties is discussed below and contrasts with the wealth of information available for many solids, that defines structures, properties and premelting changes below the T_m.

- Structures, together with movements of small amounts of mass and energy, are particularly difficult to characterize quantitatively within and adjoining a melting solid/liquid interface. Within the active fusion zone, interactions between juxtaposed liquid and solid condensed phases are effectively inaccessible to precise measurement, highly sensitive to local conditions and likely to be distorted by inserted probes. Minor perturbations may modify interface behaviour.

- Small quantities of chemical impurities and other extraneous effects may exert disproportionately large influences during experimental attempts to characterize interface and/or premelting phenomena, particularly during the onset of fusion.

Research directed towards furthering our understanding of melting has already considered all the obvious theoretical and practical aspects of this phase change, somewhere within the massive range of relevant publications. Nevertheless, the subject generally would undoubtedly benefit from updating by topical, comprehensive and critical literature reviews. The important (1978) survey, by Ubbelohde [1], provides an authoritative perspective of the subject to the mid-1970s. 'The Molten State of Matter' can be recommended both as a reliable information source and as an excellent survey of the literature to that time.

The present article develops, in a widened perspective, the previously proposed representational model for the melting of metals [2] and of alkali metal halides, both pure (Part 1 [3]) and binary, common ion mixtures (Part 2 [4]). Background references are cited in [3]. In the present article, this set/liq model for melting [2–4] is examined further to determine the relationship of fusion with other physical and chemical changes. Most metals and all alkali metal halide crystals are thermally (relatively) stable, high T_m values are ascribed to strong interactions between crystal constituents: these (metallic or ionic) bonding links are primary valence forces. Consequently, the present comparative analyses regard melting phenomena from a more chemical viewpoint than has been customary. Some similarities and differences between fusion and the thermal (chemical) reactions of solids are compared and contrasted. The significance of melting is discussed as one (important) step in the sequence of the several 'Changes that occur during the unrestricted heating of a crystalline solid from 0 K' (forming the penultimate section of this paper). In the context of these behaviour patterns, aspects of the kinetics and mechanisms of melting are critically considered and related to other thermal physical and chemical phenomena. It is hoped that the set/liq model for melting, initially formulated for these relatively simple systems [2–4] and described in the following paragraphs, may find wide applicability.

The set/liq model for melting

The set/liq model for melting was proposed in [2–4]. A description of this theoretical representation of the melt is included here for completeness, to provide the necessary background for discussions below. The essential observations underlying this approach are that, for the metals [2] and for the alkali metal halides [3], the magnitudes of the enthalpy and density changes that occur during melting or solidification, at the T_m, are relatively small. Thus, the possible extents of modifications to component structural dispositions and to their relative mobilities that can occur during the phase change are very limited in extent. This conclusion is based on the (reasonable) assumptions that, at T_m, melting of the substances mentioned are accompanied by no significant changes of component (atom or ion) sizes and shapes, intercomponent bonding, constituent packing controls or of other physical properties. The set/liq model represents the melt at T_m as retaining structural (dense component packing) similarities with the crystal form. The small enthalpies of fusion and concurrent small density changes [2, 3] are ascribed either to minor modifications of bonding and/or structure throughout the substance or to the generation of locally greater disorder within only a small proportion of the melt. Consequently, the melt structure must closely resemble that of the precursor crystal. In the liquid, constituent atoms, ions or molecules are expected to maintain dense and regular packing, controlled by attractive and repulsive bonding forces that are probably identical with those determining the lattice of the crystal precursor. These observations, identifying the loss of structural order at the T_m as being less profound than is often implicitly accepted, are the foundation of the set/liq model for melting [2–4]. The measured [2, 3] small changes in energy and density at T_m can be achieved only by retention of a high degree of struc-

tural order into the liquid phase: appreciable disorder is excluded for stereochemical reasons. It is further suggested that, in liquids at the T_m, there is relaxation of the restriction, applicable to a crystal, that only a single lattice arrangement of constituent particles can be present.

The set/liq model for melting [2–4] contrasts the rigid crystal, which is composed of a single structure that sustains long-range order, with the fluid melt, represented as dynamic equilibria maintained between small (regliq) domains composed of particles packed in alternative lattice arrays. The liquid is portrayed as an assemblage of regliq zones, continually and rapidly interconverting. Each regliq domain consists of a locally regular (crystal-type) structure but is small, below the dimensions capable of reinforcing X-ray diffraction [3] (about 2–10 nm). All possible alternative regliq ordered packing lattices, structures of sufficient stability, participate. Each domain is bounded by less ordered interfaces (irregliq) that maintain coherent, shared contact with all contiguous, surrounding regliq domains. Thus, every individual regliq domain is envisaged as continually undergoing rapid transfer of material to and from its neighbours across the less ordered, shared contact (irregliq) interfaces that are thin, perhaps of monomolecular thickness. The melt might, therefore, be described as a dynamic autoeutectic: on fusion the (static) single lattice structure continually reorganizes itself within an assembly of small regular zones that show a formal textural similarity to a eutectic.

Irregliq bounding, neighbour-contact surfaces are represented as a network of structural discontinuity interfaces, extending throughout the liquid. This mesh can be regarded as analogous to grain boundary systems in crystals. The thermal energy available constantly redistributes components between all the participating regliq domains of the various different structures present, across all irregliq interfaces. In the dynamic equilibria of the liquid, new regliq domains are constantly being nucleated, while others grow and shrink, some disappearing. Within the locally less regular packing of the irregliq material, individual components can be easily displaced, resulting in the constant transfer of atoms, ions or molecules between the contiguous, ordered regliq domains on both sides. Components within an irregliq phase discontinuity are expected to transfer very easily between the contiguous crystal-like zones. Movements, within these locally less ordered contact interfaces also permit the facile relative displacements of neighbouring regliq domains. The components of the transient irregliq contacts provide 'lubrication', for ready relative movements, slipping, of the contiguous regliq domains, thereby accounting for the flow properties of the liquid. Constant movement, realignments of material in irregliq interfaces, means that these cannot withstand shear and their dynamic, always transitory, character permits the movement required to account for the flow properties of the melt. Thus, liquid fluidity is ascribed to the facile displacements that can occur between the neighbouring very small regliq (crystal-like) domains that constitute the greater proportion of the melt.

The essential feature of the proposed, set/liq, model for melting [2–4] is the continual rapid interconversion of small zones, representing equilibrium between all possible, locally ordered regliq domains. Fusion is portrayed diagrammatically in Fig. 1.
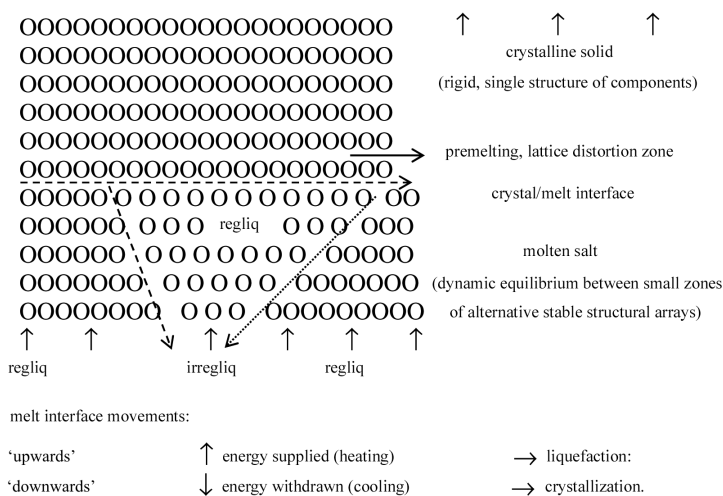
Fig. 1 Diagrammatic representation of melting interface zone for crystal/melt alkali metal halides. Upper – crystalline solid is the rigid lattice with long-range order. This extends 'downwards' on energy removal (cooling) or 'upwards' on energy supply (heating). Lower – molten salt is the liquid phase, composed of different, crystal-like (regliq) domains separated by connective (irregliq) contact interfaces (here identified by dotted arrows) across which components easily transfer between the alternative lattice structures in contact. There may be slight structural distortion of lattice arrays in the immediate vicinity of the phase discontinuities, including the crystal/melt interface

Melting point, T_m

Characteristic T_m values, that are measured precisely and reproducibly for most pure crystalline solids, have attracted much interest. However, attempts to predict T_m, from the physical properties of lattice components, and/or their interactions, have achieved only limited success. Identified trends of variations of T_m with selected physical parameters, for sets of related compounds, are approximate, at best. For example, crystal stabilities have been regarded [5–9] as a function of the strength of bonding between the constituent ionic components in the lattice. For the alkali halides of 6:6 coordination there is only a very approximate trend between T_m and lattice energy [10], Fig. 2 (data from Columns 4 and 8 of Table 1 of [3]). Neither of the lines shown extrapolates through the graph origin, (0,0). Without a theoretical explanation, these correlations remain empirical. Several factors, which apparently influence magnitudes of T_m, are mentioned in the following paragraphs. However, as discussed below, some aspects of the deviation patterns are consistent with the set/liq melting model [2–4].
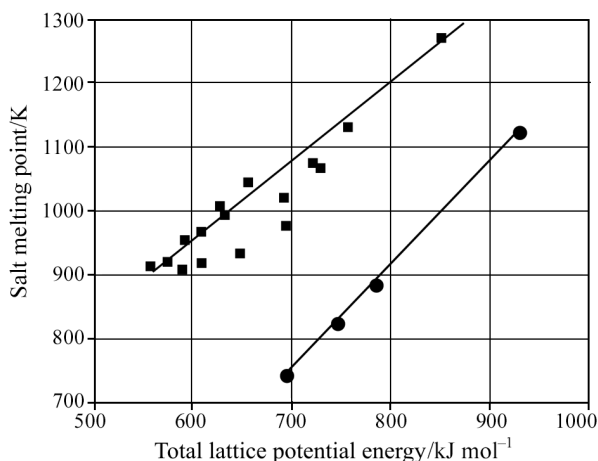
Fig. 2 Plot of calculated total lattice potential energy for 6:6 coordination (U_6/kJ mol^{-1}, Table 1 of [3]) for alkali halides *vs*. crystal melting point (K); • – the lower line represents the four lithium halides and ■ – all other values are close to the upper line: the significances of the variations are discussed in the text

T_m values for the alkali halides

Values of T_m for the four lithium halides are close to the lower line in Fig. 2; T_m magnitudes are 200–300 K below those for the other alkali halides of comparable stability. This significant difference led to the suggestion [3] that these salts should be classified as a discrete sub-group in the formulation of a model for melting phenomena.

Lithium halides

As suggested in [3], melting may result in the formation of a preponderance of the 4:4 structure in the liquid, in accordance with expectation [11] from radius ratio values for LiCl, LiBr and LiI. The calculated [10] crystal lattice energy differences between the 6:6 and 4:4 structures are small, Table 1 of [3], and the T_m values for these three salts are lowest of the all alkali halides, representing the least (thermally) stable crystal structures. Lattice energy values suggest that the 4:4 form is the most stable crystalline LiF but this radius ratio (0.571) favours the alternative 6:6 coordination, characteristic of the solid. LiF has a relatively higher T_m than the other lithium halides, but it is significantly lower than might have been expected from the calculated lattice energy, which is the highest value for all the alkali halides [3].

Caesium halides

Calculated lattice potential energies, Table 1 of [3], show the 8:8 structure to be only slightly less stable than the 6:6 form (by 8.4 to 5.2 kJ mol^{-1}: values progressively diminish from CsF to CsI). The T_m magnitudes for CsBr, CsI and CsCl (in ascending sequence) are relatively low: 908, 913 and 918 K but, nevertheless, are appreciably greater than those of the lithium salts containing the same anions (by 85, 171 and 35 K, respectively). The suggested structures of the melts [3] again involving facile transformations, are here regarded as retaining higher coordination structures in the melt (8:8 and/or 6:6): crystalline CsBr and CsI maintain the 8:8 arrangement to the T_m [11]. The melting point of CsF is only slightly greater, 967 K. Estimated stabilities for the 4:4 forms, considered unlikely to exist for stereochemical reasons, were significantly less: 43.5 to 35.0 kJ mol^{-1} from CsF to CsI.

Sodium, potassium, rubidium and caesium halides

The scatter of points for these solids about the line on Fig. 2 shows that factors other than lattice potential energy exert significant control on T_m magnitudes. For a majority of the salts, the T_m deviations from the mean line on Fig. 2 were less than about ±20 K. However, some salts showed much larger variations: T_m magnitudes for CsF and NaI were about –75 K and RbF, CsCl and NaBr were about –35 K distant from the line. These are the halides which contain the smallest mass ratios [anion/cation or (cation/anion)] for the constituent ion pairs: 0.143, (0.181) [CsF, NaI] and 0.222, 0.267 and (0.288) [RbF, CsCl, NaBr] respectively. These two groups of salts, in which the masses of constituent ions were the most highly disparate, close to 1:7 and 1:4, respectively, are associated with an approximate doubling of the distance

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from the line. It is suggested that there may be characteristic patterns (resonances) of ionic vibration, generated within crystal lattices composed of ions of very different inertia, which is one possible explanation for destabilization of the crystal structure when the thermal energy content approaches that characteristic of melting. The deviations shown by lithium halides are not, however, explained by this influence of disparate mass ratios. A wide range of other possible correlations between T_m and ionic and structural properties and characteristics was examined in detail, but no other consistent trend was found. Parameters quantitatively examined included ionic sizes, radius ratios, dispositions and relative proportions of unit cells occupied by ions (ratios of ionic volumes/unoccupied space; volume of interionic, tetrahedral space between ions within each cell; interionic spacings, etc.).

Except for the approximate trend of variation of T_m with lattice stability, Fig. 2 and [5–9], no other quantitative correlation with any single parameter could be found for any of the wide range of reliably measured physical, structural or energetic features available for this set of particularly well-characterized solids. While this comparative survey cannot claim to be exhaustive, the negative result is consistent with the absence of any theoretical explanation for T_m magnitudes in the literature. In contrast, the evidence suggested that no single (and simple) parameter alone determines the melting points of the solids considered [2–4]. Moreover, it appears that the alkali metal halides do not form a single, strictly comparable crystal set. Lithium halides, in particular, exhibited relatively low T_m values, distinguishing these salts as a recognizable sub-set: one explanation is the facile adoption of 4:4 coordination in the melt [3].

T_m values for the alkali halides compared with T_m for some similar crystals

Crystal lattice energies, similarly calculated [10] for Mg, Ca, Sr and Ba oxides and sulfides (having the NaCl structure), when plotted *vs.* T_m showed a relatively greater scatter than that on Fig. 2. Moreover, extrapolation of the line on Fig. 2 did not pass close to this group of values and no correlation of these data with the alkali halides could be found. Similar comparisons revealed no trends to link T_m values for the alkali halides either with AgF, AgCl and AgBr (NaCl structure) or with TlCl, TlBr and TlI (CsCl structure). A probable reason for these differences is the relatively much higher polarization energies in both Ag and Tl salt triads (about –120 kJ mol^{-1}, [11]).

T_m values for metallic elements

Metallic element melting was recently reviewed [2]. T_m values tend to increase with numbers of bonding electrons and vacant valence orbitals available, though other factors are involved. For the alkali metals, the average T_m is 335 K: enthalpies of fusion, 2.1–3.0 kJ mol^{-1}, are small. Values are larger for the divalent alkaline earth metals, the mean T_m is 1130 K and enthalpies of fusion are 7.1–8.5 kJ mol^{-1}. The mean T_m for Group 3 metals is 1496 K and the highest of all T_m values are for the transition metals with the largest numbers of potential bonding electrons and vacant orbitals [2].

Energy absorbed by alkali halides to melted salts

Melting can be regarded as a consequence of the accumulation, within a solid, of an amount of energy which exceeds that capable of accommodation within the stable crystal. This results in the loss of both crystal rigidity and long-range order on liquefaction at the T_m. It is of interest, therefore, to consider the steps involved in introducing sufficient energy into the alkali metal halides to complete fusion and the variations in this quantity for the different salts. Characterization of these quantities of energy may enable the parameters that control T_m values to be identified.

On heating a crystal from 0 K to the melt at the T_m, energy is acquired in three steps. (*i*) During the initial systematic rise of thermal capacity to the Debye temperature, θ_D [12, 13]. (*ii*) Above θ_D the specific heat becomes nearly independent of temperature [12–14]. (*iii*) The fusion enthalpy, ΔH_F, required to melt the solid is absorbed at constant temperature, T_m. (In the following analysis, all variations reported as ± are root mean square deviations for each group of salts considered. Some properties of CsBr and CsI differ from those of the other salts because 8:8 coordination is retained to the T_m [11]).

Energy accommodation on heating the crystal from 0 K to fused melt at T_m

Total lattice potential energies, U_6

The most stable crystalline alkali halides, measured by the enthalpy of formation, contain the smallest ions. Values of total lattice potential energy, U_6 (Table 1 of [3]), all decrease systematically from Li→Cs and F→I: the overall variation was from 930.6 to 558.3 kJ mol^{-1} (ratio 1.00:0.60) LiF to CsI.

Specific heat below the Debye temperature

Values of θ_D, and consequently the total energy absorbed on heating the crystal to this temperature [12, 13], all decrease systematically F→I and also Li→Cs (excepting CsBr and CsI).

Heating from the Debye temperature to T_m

The temperature intervals $\theta_D \to T_m$ [13] for the alkali metal halides, other than those containing lithium, were between 753 and 855 K, the mean difference was 799±30 K for the 16 values. No trends of variations with salt constituents could be discerned. The intervals for LiF, LiCl, LiBr and LiI were significantly smaller: 387, 458, 549 and 535 K, respectively.

Specific heats of the alkali metal halides [14] progressively increased, but only by relatively small amounts, across this temperature interval ($\theta_D \to T_m$). Above θ_D, specific heats of solids are (theoretically) $3R$ [12], corresponding to 49.88 J K^{-1} mol^{-1} for these binary solids. The mean value for all 20 alkali metal halides (including the Li salts), representing the mid-point of each temperature interval ($\theta_D \to T_m$), was appreciably greater at 56.4±1.7 J K^{-1} mol^{-1}. All values were between 54.1 (RbCl) and 59.5 (RbF) J K^{-1} mol^{-1}: again no systematic trend of variation with salt constituents was found.

The mean enthalpy required to heat each of the 16 (Na, K, Rb and Cs) halides from θ_D to T_m was (799×56.4=)45.06±2.14 kJ mol^{-1}. Unusually large, but unexplained, deviations were found for RbF and CsBr (50.87 and 41.37 kJ mol^{-1}). All other individually calculated values were much closer to the mean and no trend of variation with either constituent ion could be discerned. Values for the lithium salts were much lower (22.68, 27.02, 29.76 and 29.42 kJ mol^{-1} for LiF, LiCl, LiBr and LiI, respectively), due to the smaller ($\theta_D \to T_m$) temperature intervals for these solids.

Total energy absorbed to T_m

From the above data, the energies required to heat each alkali metal halide (except the Li salts) to the T_m were 52.05±3.88 kJ mol^{-1} [3]. Values for the lithium halides were significantly smaller, from 36.4 to 47.5 kJ mol^{-1}. Minor, composition dependent, diminutions of values were detected in the sequences Na→Cs and F→I, attributable to the contributions from specific heats below the θ_D.

Enthalpy of fusion, ΔH_F

Significant trends were also found in the variations of ΔH_F [15] with salt compositions (Table 1 of [3]). Values of ΔH_F decreased in the sequence F→I, with a less pronounced decrease from Na→Cs. Magnitudes for the lithium salts are relatively low and those for NaI, CsBr and CsI do not conform. Points on a plot of ΔH_F vs. T_m, for all 20 alkali halides were scattered within about 50 K of a mean (straight) line, which intersected the T_m axis in the vicinity of 400 K.

Total energy absorbed on melting

The energy required to melt each salt was obtained from the varying specific heat values within two ranges (0 K→θ_D and θ_D→T_m) together with ΔH_F. For alkali metal halides, the aggregate mean enthalpy to heat from 0 K to melt at T_m was 77.0±6.6 kJ mol^{-1} (overall range 69.7 to 94.6 kJ mol^{-1}), excluding the lower values for the lithium salts, between 51.1 and 74.6 kJ mol^{-1}. For all 20 alkali metal halides, there were systematic diminutions of this composite value from F→I (except CsBr and CsI), with indications of a slight decrease from Na→Cs.

T_m values

The trends identified have been discussed above for Fig. 2. Lithium salt T_m values are relatively lower than is expected from the diminution Na→Cs (except NaI). Values also decrease F→I, with CsI as a slight exception.

Enthalpy of formation of Schottky defects

No trends in variations of the enthalpies of vacancy formation [15] with salt components were discerned. Values are large, compared with ΔH_F (the lowest, LiI, is 129 kJ mol^{-1}, several are 160–180 kJ mol^{-1} and some, mainly fluorides, are above 200 kJ mol^{-1}): it is concluded, therefore, that the vacancy concentrations formed on melting are relatively low [15].

Accommodation of energy within the crystal

T_m values are not determined by a single crystal parameter

The absence of any recognizable trend between T_m and crystal parameters for the alkali metal halides prevents the development of a general theory of fusion. The characteristic properties of the lithium salts and the alternative structures of CsBr and CsI distinguish these as potentially anomalous sub-groups.

Debye temperatures

Magnitudes of θ_D are related to physical properties of crystals by the (approximate) relationship [12]:

$$\theta_D = (Y/M)^{1/2} \tag{1}$$

where M is the atomic mass, here taken as the sum of the masses of the two ions, and Y is Young's modulus, which for a cubic crystal is given by:

$$Y=(C_{11}-C_{12})(C_{11}+2C_{12})/(C_{11}+C_{12})$$

Values of the elastic constants, C_{11} and C_{12}, are available in tabulated data [16]: values for RbF and CsF were not listed and are, therefore, omitted from consideration here.

A plot of θ_D *vs.* $(Y/M)^{1/2}$ is shown in Fig. 3. Data for most alkali metal halides (including those with 8:8 coordination at θ_D, CsCl, CsBr and CsI) are close to the (full) straight line, confirming the applicability of Eq. (1) to these solids. The relatively higher values for the lithium salts are on the dashed line, which, unlike data for the other solids, does not extrapolate through the graph origin (0,0). θ_D values are, therefore, related to the elastic properties of each crystal. For all 20 salts, values of θ_D, and the energy required to heat the crystal to θ_D, show systematic and significant decreases with ionic size increases (F→I and Li→Cs: RbI is the single slight exception).
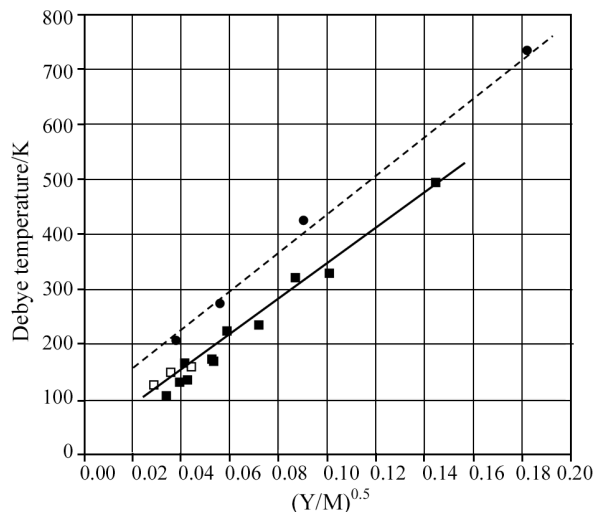
Fig. 3 Plot of Debye temperature *vs.* $(Y/M)^{1/2}$ (arbitrary units) for alkali halides [12, 16] where Y is Young's modulus and M the mass of the constituent ions; ■ – most salts, including □ – three 8:8 coordinated Cs halides, fit the full line; ● – four lithium halides fit the higher (interrupted) line

Variations in energy absorbed to completion of melting

Between θ_D→T_m, specific heat magnitudes for all 20 alkali metal halides show no systematic variations with composition: the average value was 56.4 ± 1.68 J K^{-1} mol^{-1}. For 16 solids, excluding the lithium salts, all temperature intervals, θ_D→T_m, were close to the average value, 799 ± 30 K, and no systematic variations were discerned. Thus, the aggregate heat absorbed by each salt, across this temperature interval, was also close to a constant value, 45.06 kJ mol^{-1}. ΔH_F values (the third enthalpy absorption interval, at T_m) behaved differently, varying with salt compositions, decreasing F→I (except Cs) and also Na→Rb (with minor exceptions) and Li values were generally smaller. These similarities and differences, between the consecutive but cumulative energy-absorbing processes, makes it improbable that any generalized, simple and single crystal property or parameter, applicable to all the salts of the set, controls each T_m value. (A limitation in appraising the significance of these trends is that errors in the tabulated data, including temperature dependent variations of specific heats, are not known.)

A 'band theory' of melting

The generalization, identified here as being of some potential theoretical interest, is that the total enthalpy absorbed on heating θ_D→T_m is almost constant (45.06 ± 2.14 kJ mol^{-1}), for those alkali metal halides that do not contain lithium. The constancy of specific heats and of temperature intervals θ_D→T_m is unexpected because values of the crystal stabilities, U_6, vary significantly and systematically with compositions (Table 1 of [3]). A possible explanation is that the 6:6 ionic lattice structure is capable of accommodating only this limiting total amount of energy. Represented by a band structure model for solids, this quantity of energy might be regarded as filling all available vibrational energy levels to the stability limit for this ionic arrangement. Further heating would then cause melting, characterized by the appearance of new, but higher, energy levels, separated by a forbidden zone with the gap corresponding to ΔH_F. This representation is proposed to explain the extremely well-defined upper limit for crystal stability, the characteristically precise T_m value and the absence of superheating of solids: these properties are discussed further below. It follows that T_m magnitudes for the alkali metal halides are not constant because the values of θ_D vary significantly within the set of salts compared, Fig. 4. The unit slope of the upper line on this graph shows that T_m increases above 799 K correlate directly with θ_D, but values for the lithium salts are close to a different line, arising from the significantly smaller temperature intervals, θ_D→T_m, for these crystals.

Distinctive character of lithium-containing halides

Throughout this comparative analysis, the four lithium halides have been found to behave differently from the other alkali metal halides, and should, perhaps, be regarded as a distinct sub-set. Either or both of the following explanations may apply. It was concluded [3] that lithium halide melting is accompanied
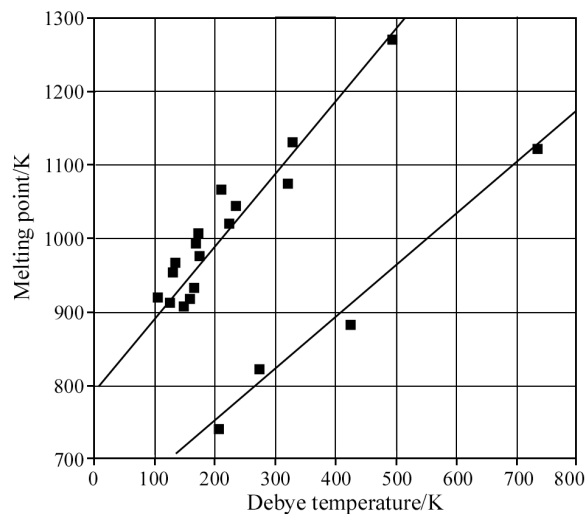
Fig. 4 Plot of T_m *vs*. the Debye temperature, θ_D, for the alkali halides. For the Na, K, Rb and Cs salts there is a direct relationship ($T_m = \theta_D + 799$ K) with some scatter: the slope of the upper line is unity. Values for the lithium salts are (again) significantly lower and the slope is less steep

by changes from 6:6 to 4:4 coordination. The latter structure differs from those believed to be adopted by the other alkali halides [3], identified with the closely similar U_4 and U_6 values for the lithium salts (excepting the fluoride: Table 1 of [3]). Alternatively, the significantly smaller size of the Li^+ ion than the other cations may be a factor in facilitating fusion of these salts. Evidence that small ions exert an important role in influencing melting behaviour of binary mixtures was presented and discussed in Part 2 [4].

Comment

The 'band theory of melting' model, outlined above for the alkali metal halides, is superficially attractive as a possible explanation for T_m magnitudes. However, at present it remains speculative and has restricted value in the absence of support through its demonstrated applicability to a very much wider range of substances. The significant conclusion from the above analysis is that more than a single parameter participates in the control of crystal melting. The approximate trend whereby T_m values increase with crystal stability (lattice potential energy) for the alkali halides is shown in Fig. 2. This approach has been developed and refined by van Uitert [5–9] and by Bosi [17], who have applied it to a wider range of solids. However, the present analyses, with [3], have identified lithium salts as a distinguishable sub-set within this group of chemically similar solids. It was also noticed that other solids of similar structure, but containing divalent ions, were not represented by the line on Fig. 2. The slight evidence that T_m values may be influenced by disparate masses of the constituent ions

has been mentioned. Total lattice potential energy is not the single parameter that determines T_m.

In formulating a theoretical explanation for T_m magnitudes, it may be necessary to recognize that thermal energy is accommodated into the solid in two distinct heating steps. The theory must consider both contributions if total enthalpy uptake is a factor in determining T_m. Up to the Debye temperature, the integral heat absorbed depends on the elastic constants of the individual crystals, Eq. (1). Above θ_D the specific heats of all crystals are close to the common value, $3R$ [12]. Furthermore, this is consistent with the absence of any identifiable or significant correlations between T_m and any one of a variety of possibly relevant crystal parameters mentioned above. There is also evidence [2] that the melting of metals is determined to some extent by available bonding electrons and vacant orbitals. Our conclusion is that no single, simple model or parameter appears capable of predicting T_m magnitudes for simple crystalline solids.

Properties of liquid alkali metal halides between T_m and boiling point, T_b

The temperature interval, across which the liquid is the stable phase for the Na, K, Rb and Cs halides, are all within a relatively narrow range of values, $(T_b - T_m) = 660 \pm 30$ K and the (T_m/T_b) ratios are 0.61 ± 0.02. (Data were incomplete, all values available from [18] were used.) The lithium halides again appear as a distinctive group, with $(T_b - T_m) = 760 \pm 44$ K and $(T_m/T_b) = 0.51$ to 0.58. These (T_m/T_b) ratios are generally greater than values for the metallic elements, for which the mean was 0.489 [2].

The enthalpies of volatilization of the alkali metal halides (based on 16 values, between 115 and 191 kJ mol^{-1}, listed in [14]) are significantly greater than the enthalpy required to heat the crystals from 0 K to the melt at T_m (mean 77.0 kJ mol^{-1}). The mean ratio (enthalpy of fusion at T_m/enthalpy of volatilization at T_b) is 0.14 ± 0.05. Magnitudes of the specific heats of the melts are often 15 to 20% greater than values for the crystalline alkali metal halides [14]. The relatively small magnitudes of the fusion enthalpies, compared with the other changes that occur during heating, provide further evidence that the loss of order during fusion is limited in extent.

Melting and chemical reactions: similarities and differences

Melting, a first-order transformation [19], is conventionally regarded as a physical change of state because the individual constituents of the solid/melt (atoms, molecules or ions) undergo no chemical change

during the (usually) facile, reversible liquefaction/solidification processes. For the metallic elements and the simple ionic salts, with which this comparative analysis is predominantly concerned, the electrostatic interactions that stabilize each ionic crystal can be regarded as primary valence forces. Consequently, the structural changes that accompany melting [3, 4] represent modifications to chemical (metallic or ionic) bonding, and fusion can be regarded as exhibiting features of a chemical change. It may be of value, therefore, to explore the kinetic characteristics and to discuss possible mechanisms of melting [2–4] through the theory developed to apply to solid state thermal decompositions [20, 21].

As mentioned above (starting this article), melting is a well-defined and familiar phenomenon. It is probably the most commonly observed change caused by heating a crystalline compound. However, liquefaction without chemical reaction is not the only possible consequence of raising the temperature of a pure solid, many undergo thermal decomposition in the solid state (crystolysis reactions [20–22]): chemical processes that transform the reactant into different compounds below the T_m. There is an extensive literature on these reactions [20–22], in which characteristic common features, and theoretical concepts, have resulted in this group of (solid state) chemical changes being effectively recognized and treated (almost) as a distinctive discipline. Currently, this subject is in a state of discord due to disagreements about the applicability of the alternative theories that are available (some are mentioned below and in [22]). Nevertheless, specific features of crystolysis reactions may be useful in developing a theory for melting and a relevant outline of the subject is given in [22].

Theoretical models and principles that have found applications in investigations of crystolysis reactions [20, 21] are extended to the consideration of melting phenomena below. Nomenclature, concepts and terminology borrowed from this distinctive subject area are found to be suitable for use in discussions of melting and in examinations of its behavioural similarities with and differences from thermal chemical reactions involving solids. These comparisons are, however, less easily achieved than might have been expected because the field of thermal reactions of solids has become a specialist research topic in which there are currently important areas of disagreement. Nevertheless, significant overlaps of interest with crystal melting can be identified, which merit exploration and are incorporated into the discussion below. In the first draft of this paper, those aspects of the theory of crystolysis reactions, identified as providing the necessary background for this review were presented as an Appendix. A helpful Referee expressed his opinion that: 'Appendices

are not a good idea in a review of this length. Much more likely to be read and appreciated would be a separate paper on «Comparisons between melting and crystolysis».' Appreciative of this generous counsel, I am pleased to take his advice and present the same material as an associated paper [22] (although with the different title: 'Melting and thermal decompositions of solids: an appraisal of mechanistic interpretations of thermal processes in crystals.').

Kinetics and mechanisms of melting

As generally accepted (and emphasized here), the melting of a pure crystalline solid is both initiated and completed, without sensible change, at a characteristic temperature, T_m, cited as the melting point. The present discussions compare and contrast melting with other physico-chemical processes for which rates and sometimes extents (e.g., equilibria) vary with temperature over significant intervals. Such comparisons are intended to provide insights that may extend understanding of fusion phenomena.

In practice, experimental measurements of fusion rates are usually effectively impossible. Reversible melting (solidification) is so facile that progress appears to be determined by rates of energy diffusion to (from) the solid/liquid melt interface. Fusion rate characteristics appear, therefore, to be predominantly determined by heat transfer processes; presumably these are effected by the relatively more mobile constituents of the liquid phase. In practice, such behaviour eliminates the use of the versatile and valuable kinetic approach to the mechanistic investigation of melting, which has found innumerable applications in elucidating controls for many and diverse types of chemical reactions [20–23].

The problems that arise in applying, to melting, the kinetic methodology originally developed to investigate the rate controls of simple homogenous reactions [24] present an interesting paradox. Enthalpies of the facile fusion process are often relatively small [3]. However, in comparison with values for many chemical reactions, the (apparent) magnitudes of typical, conventionally calculated, activation energies (E_a, the kinetically measured energy barrier to reaction [24]) for melting are evidently very large, perhaps even infinite. The melting rate of a crystal is zero (or infinitely slow) at temperatures immediately below the T_m. However, at and immediately above the T_m, the rate of melting becomes appreciable (though it may be difficult to measure). Conventional calculation of E across such a discontinuous change of rate, from zero to appreciable after an insignificantly small temperature rise, implies a large (potentially even infinite) apparent E_a value, conventionally calculated. This inherent feature of fusion contrasts with

the characteristic behaviour of other thermal processes, where rates of chemical reactions (also, evaporation, sublimation, etc.) almost invariably increase systematically (usually exponentially) with temperature rise across significant intervals, and are usually expressed by the Arrhenius equation. For such rate processes, the applicable theory is based on a reaction model in which the energy barrier to change is overcome by a thermal activation step [24]. A large apparent E_a is, however, inconsistent with the facile and easily reversible melting process that is observed immediately above the T_m. Thus, fusion is not obviously, simply or usefully represented by an activation model.

An advancing interface model for melting

The concept that fusion occurs preferentially at a crystal/melt contact interface [22] provides a suitable model for discussion of this readily reversible phenomenon. Crystals (almost never) superheat so that a melt is (almost invariably) readily formed at and above T_m. On cooling, crystallization is usually initiated at, or immediately below, the T_m though, in the absence of solid, it may be necessary to introduce seed crystals into the melt but, thereafter, once the solid is present, crystal growth proceeds readily.

Melting as a surface initiated process

Melting has long been regarded as a surface-initiated phenomenon, a suggestion attributed [25] to Tammann (1920) [26], though others [27] find an earlier association of T_m with surface energy (1909) [28–32]. This identification of the onset of melting with the peripheral material is consistent with diminished thermal stability within the outermost crystal layers. Those components (ions, atoms or molecules) forming the particle boundary surfaces are necessarily incompletely coordinated, with unsymmetrical bonding that results in local crystal strain. The magnitude of such distortion must progressively diminish inwards across a few (perhaps several) lattice planes below the outermost array. As the crystal temperature approaches its T_m, this relatively less stable boundary layer is the first to become modified, progressing towards the premelting crystal reorganizations or 'liquefaction nuclei' that characterize the structural modifications that increase on the approach to fusion. Premelting, the development of superficial disorder, effectively initiates comprehensive surface 'nucleation' [33] near the T_m [27, 30, 31]. At the T_m, all crystal faces readily undergo liquefaction, the transformation only requires supply of the enthalpy of fusion and no activation step is necessary to enable the phase change. Comprehensive surface premelting changes are the precursor steps analogous to effec-tively complete surface nucleation and lead to superficial fusion on achieving T_m.

This portrayal of the facile initiation ('nucleation') of melting contrasts with the nucleation processes in crystolysis reactions. The latter show [20–22] the characteristics of activated chemical processes, sometimes infrequent and difficult, that are required to enable the bond redistribution steps to take place within the reactant components undergoing modification. Nucleation may be followed by further (again, usually activated) modifications of primary valence forces during chemical changes of reactant constituents and reorganization/crystallization of the residual phase. The initial steps are regarded [20, 21] as generating the (germ) nuclei [33], which are usually represented as very small volumes of solid product, possibly of molecular dimensions. The product/reactant contact boundaries of germ nuclei then become transformed into the active reaction interfaces, which advance into the reactant. This contact is identified as a zone within which the activated chemical changes of the reactant components occur preferentially. Those solid decompositions, for which the energy barrier to nucleation is small, leading to rapid and dense nucleation from the start of reaction, show a formal geometric similarity to melting. Change is initiated at all boundary surfaces from which an interface advances inwards towards the crystal centre: 'the contracting cube model'.

Advancing liquid/melt interface

The facile reversibility of melting and solidification processes is consistent with the phase change occurring preferentially at the liquid/solid contact interface [22]. Melting is initiated readily by changes that start below T_m. Crystallization does not invariably occur so easily and the solid, a seed crystal (nucleus), may be required to provide the initial surface on which growth from the melt proceeds. The solid and liquid phases (composed of the same components) must inevitably be chemically compatible so that the melt phase adheres to and spreads across the wetted solid surfaces, rather than the liquid separating as distinct droplets. It is common experience that a molten salt adheres strongly to the crystal from which it was formed. Little is known about the interfacial surface free energy at the solid/melt boundary [1], though the surface free energy of a liquid may be greater than that of the solid [34]. 'Premelting' changes in the solid, as mentioned in the previous paragraphs, probably also occur in melting crystals, close to retreating/advancing crystal/melt contact interfaces. Thus, unless control is dominated by rapid rates of heat supply or withdrawal, interface advance (retreat) will preferentially take place at solid/melt contacts, estab-

lished across all existing crystal boundaries, and the 'contracting cube' (geometric) kinetic equation is expected to express the rate characteristics [20, 21].

Superheating

The existence of a superficial 'premelting' zone, of diminished order and coherence below T_m, adequately accounts for the rarity of superheating in solids. The evidence is that the 'nucleation' step [22] in fusion is extremely facile, it is not detectably activated and it occurs across all surfaces in the approach to the T_m. The proliferation of 'prenuclei' is regarded as removing any effective energy barrier, activation step, to onset of the phase change and ensures that superheating of solids is exceptional. The few known examples [29] have been reviewed by Peppiatt [31]. In one instance, As_2O_3 [31], significant superheating (60 K) was ascribed to structural differences between liquid and solid phases, so that activation was required to effect the bond rearrangements that must occur during melting and crystallization. The articles [27, 31] also discuss the participation of the superficial liquid layer in relatively diminishing T_m values observed for very small particles of some metals and the role of structural imperfections in solids during liquefaction at a melting surface.

Supercooling

In contrast with the exceptionally rare occurrence of crystal superheating above the T_m, supercooling of melts is relatively familiar. In the absence of the solid, many substances are capable of remaining in the liquid state at tens, even hundreds, of degrees below the T_m [35]. For some systems, crystal nucleation is difficult and viscosity increase during cooling results in glass formation, delaying crystallization indefinitely. In those melts that supercool below T_m, the generation of a sufficiently large structurally ordered zone, a template of suitable crystal to initate growth (nucleation), or the ability to disperse excess energy, through nucleation, is believed to be difficult. The crystallization of a supercooled melt is usually readily promoted by seed crystals, where existing solid surfaces appear to act as templates for the ordered deposition of components resulting in crystal growth. The solid particle may also act as a thermal sink, temporarily accepting, and dispersing, excess enthalpy from the immobilized material newly added to the developing surface. As with nucleation in solid state reactions, little is known about the minimum conditions and precise properties necessary for a seed crystal to initiate crystallization.

There is diminution of order in crystals, particularly at the boundaries, as the T_m is approached, this premelting disorder has already been mentioned. Thus, any crystal capable of sustaining growth must be sufficiently large, and stable, to maintain the regular lattice that can be extended. It has been shown for some particular systems, e.g., metals [27], that the T_m can diminish with particle size. Second, the excess energy ($+\Delta H_F$) above the T_m, greater than that which can be accommodated in the crystal, must be withdrawn or dispersed from the solid/melt contact zone to permit crystal growth. Because melts are stabilized relative to the solid, $+\Delta H_F$ (ascribed in [2–4] to alternative structures, imperfections, species mobilities, etc.), growth is possible only when the seed crystals are sufficiently large and stable to persist in the solid state. Investigations of the essential characteristics and properties, including minimum size, of seed crystals for growth nucleation could contribute to increasing understanding of melting controls.

Theories of melting

Two strongly presented models for melting ascribe loss of the crystal long-range order at the T_m to a sudden and considerable proliferation of crystal imperfections [36], identified alternatively either as point defects/lattice vacancies [15, 37, 38] or as line defects or dislocations [39]. Generation of either type of imperfection [20] in a stable crystal requires considerable energy absorption, particularly at low concentrations. However, increasing crystal modification, initiated during premelting, reduces the structural coherence of the solid: one consequence is that the energy constraints on continued imperfection formation are thereby diminished. Consequently, defect formation within increasingly disordered material becomes progressively easier with temperature rise. In the immediate approach to the T_m, this might be regarded as a cumulative process, leading eventually to removal of the requirement for appreciable energy input. At a threshold concentration for each crystal, defining the T_m, energy barriers to continued imperfection proliferation become effectively zero, resulting in a discontinuous large rise in their concentration on fusion. This causes a catastrophic loss of order [29], melting, which is completed within a negligible temperature interval. One possible interpretation of these models is that crystal-like order must be present in the liquid phase (also a feature of the set/liq model [2–4]), albeit with a much increased imperfection concentration. (An 'imperfection' is recognizable only as a departure from a regular structure, which here must (presumably) be assumed present in the melt.)

Defect or lattice vacancy formation

The theory of melting formulated by Ksiazek and Gorecki [15, 37] is based on the 'hole' theory of liquids, proposed by Frenkel almost seven decades ago. This concept was developed to account for the changes of some physical properties at the T_m for various metals and rare gases. More recently the alkali metal halides have been investigated leading to the conclusion that the melting of these salts commences when the concentration of Schottky defects reaches the critical value, 0.0017. At the T_m, values of the estimated rates of vacancy formation are sufficient to account for the change in defect concentrations believed to occur on fusion, approximately $\Delta c = 0.15$. This model is regarded as explaining [15, 37, 38] the changes of many physical properties at the T_m, including enthalpy of fusion, molar volume, volume thermal expansion coefficient, molar heat capacity, etc. We note, however, that the scatter of data points on a plot of T_m *vs.* energy of formation of Schottky defects, Fig. 1 and Table 1 of [15], is not significantly better than the correlation of T_m with some other crystal parameters. It is not entirely clear (at least to this author) why the vacancy concentrations mentioned represent critical and characteristic values, how this approximately constant value relates to the melting of other types of crystals and to the ionic packing structure of the vacancy-rich melt. If Schottky defect formation is the dominant feature of melting, it might be expected that the ionic components of these melts would retain the lattice structure of the precursor solid (this representation shares some common features with the reg/liq model). We also note that the generation of vacancies in a regular crystal requires the absorption of appreciable energy: the mean heat of melting is estimated as 12.7±1.7% the formation energy of Schottky defects [15]. Therefore, it seems highly probable (again, in the opinion of this author) that activation steps associated with defect formation, identified as controlling the progress of fusion at T_m, would be a kinetic process with a detectable, presumably measurable, E_a value. Such a mechanism of fusion would be closely comparable with a crystolysis reaction [22] and does not appear to account for the facile, reversible melting process that is observed. (Enthalpies of formation of Schottky defects are listed [15] as between 129–255 kJ mol^{-1}, such energy barriers are comparable with activation values measured for many crystolysis reactions [20, 21].)

Dislocations or line defect formation

An alternative approach is through the dislocation, line defect, model and this has been reviewed and discussed by Cahn [36]. Progressive absorption of energy, at the T_m, results in spontaneous generation of increasing numbers of dislocation loops [40], with the destruction of crystal order. Kuhlmann–Wilsdorf [39] has concluded that, at the T_m, the free energy of the cores of glide dislocation become negative and there is the unrestricted formation of such dislocations. These fill the crystal to capacity, order is lost and the liquid is formed.

Comment

Both of the above models are consistent with particular features of melting but, hitherto, neither appears to have been generally accepted as providing a quantitative, comprehensive or general theory of the phenomenon. Moreover, it is obvious that these alternative and distinct proposals cannot both possess equal validity. Similarly, other explanations advanced to account for specific aspects of melting [1] have not achieved widespread acceptance, despite the prolonged interest in the topic. Reasons include the difficulties of making meaningful (accurate) experimental measurements that characterize melt structures, including concentrations and distributions of the different types of imperfections that are present. Moreover, there is the possibility that the controls of melting (including generation, annihilation, interactions between and the movements of point and/or line defects) are more complicated than can be represented by a single, simple model. The perennial scientific problem is to design experiments that are capable of distinguishing between the strengths and weaknesses of the rival alternative theories available.

Structures and dynamics of melts

Many discussions of the controls and mechanisms of melting focus on the discontinuous nature of the phenomenon: onset and completion invariably occur at a precise T_m. This distinctive behaviour has been emphasized by use of the descriptive term 'catastrophe' [29, 32, 36], whereby the theoretical explanations proposed focus on the sudden removal of barriers that inhibit imperfection generation or multiplication precisely at the T_m. However, since none of the available theoretical models for melting has received general acceptance, some aspects of the dynamic character of melts (sharing features with the above models) are considered further here.

Order in melts

The dynamic melt model proposed in [2, 3] is based on the assumption that all possible alternative (stable and regular) structures can contribute to the dynamic equilibria, through facile exchanges of material between

the participating domains across less ordered contact zones. This approach recognizes the strengthening evidence that, close to the T_m, melts retain order. The following articles appear to offer some general or indirect support for this view. Oxtoby [41], considering liquid structure models in the vicinity of the T_m, mentions that molecular fluids form transitional phases in the liquid/crystal transformation. Berry [42] discusses the complexity of interactions between atoms that result in formation of large clusters that can rapidly interconvert between numerous possible positional isomers. Jardet *et al.* [43] have identified the local order of liquid clusters in totally molten alloy mixtures of Al–Ga–Zn. The structure of liquid water is largely determined by the (relatively weak) hydrogen bond and the 4-coordination structure between neighbouring molecules that is stable across the considerable temperature interval from below 0°C to the normal boiling point [44]. Molecular clusters in liquid water have been studied by infrared spectroscopy [45].

Assemblages of comparable components in a condensed phase demonstrate a strong inherent propensity for 'self-ordering', spontaneously generating arrays having regular dispositions. The outstanding examples are the extended regular structures of constituents in crystals. This is ascribed to attractive and repulsive bonding forces that dominate the packing of closely spaced species in condensed phases but is opposed by increasing thermal energy (see below). Somewhat weaker electrostatic interactions are identified as appreciably reducing the random spatial distributions of dissolved solute ions, as shown by the Debye–Huckel recognition of 'ionic atmospheres' that account for the departures of solutions from ideal behaviour [46]. It also appears probable that there are parallels between the set/liq melt model discussed here and the structures of 'crystals' in the 'dusty plasmas' recently investigated by Thomas *et al.* [47, 48] (see also [49]). Ordering in these dilute suspensions of particles arises through relatively long-range electrostatic interactions so that the phase structures of certain assemblages (under specified conditions) are described as exhibiting 'flow and floe' properties. These regular dispositions of particles may be regarded, in some respects, as 'dilute' versions of the melt ordering proposed in [2, 3].

Martensitic transformations in the melt

The set/liq melt model described in [2, 3] identifies equilibria as being maintained through rapid transfers of individual ions between zones of the different participating regular structures, across less ordered interfacial regions. There is, however, the alternative possibility that transformations between the different stable regular ion-packing arrangements could equally well be achieved by extended structural reor-

ganizations, involving synchronized concurrent redistribution of the components within many neighbouring crystal units. The martensitic transformation [50] is a cooperative shearing displacement within a crystal structure that involves concurrent multiple, but small, bond/component movements and results in the rapid change of lattice for relatively large numbers of unit cells. This structural modification may be repeated, with little or no variation, through multiple cycles and changes can be nucleated by local textures that may not be significantly modified by the occurrence of the transition [51]. This type of extended restructuring event, involving large groups of components, is well-known [52] from metallurgy. Each such change could convert a single regular domain, within the melt, to an alternative domain of one of the other possible stable crystal-type structures. In any melt, either or both of these different mechanisms of phase transformations (ion movements across interfaces and/or cooperative martenistic events) are potentially capable of sustaining overall equilibrium between the coexisting contributing domains.

Features of the martensitic transformation, described by West [52], are entirely consistent with the type of phase change envisaged in the set/liq model of melting. This recrystallization process is completed very rapidly because no diffusion processes or changes of chemical compositions are involved. The bond repositioning steps required, and (presumably) any activation energies, are expected to be relatively small. Moreover, martensitic transformations exhibit hysteresis, consistent with the ability of liquids to undergo supercooling: crystallization does not necessarily occur at the T_m. For the most extensively studied alloy systems, it has been shown that martensitic transitions may involve the retention of specific structures in the product and the changes are not necessarily completed at a constant temperature. Such delays are not expected to influence the onset of melting in pure crystals because premelting processes (described above) ensure that the omnipresent 'nuclei' effectively prevent solid superheating. It seems probable that martensitic transformations would be promoted mainly by vibrational energy, translation and rotation are strongly inhibited in the condensed phases. This provides a link with the Lindemann theory of melting [53, 54].

Changes that occur during the unrestricted heating of a crystalline solid from 0 K

Melting is considered in the context of the several other changes that contribute to the progressive, cumulative diminutions of regular structure and order that occur during continued, unrestricted heating of an initially crystalline material. It is appropriate to

emphasize that the increases in irregularity that appear on fusion are relatively small compared with the systematic rise in disorder that occurs as the temperature of an initially solid substance is raised, without limit, above 0 K. The following characteristic types of changes are observed, though all do not necessarily occur for every substrate and sequences may vary somewhat with both substance and conditions.

- Debye temperature: the specific heat of a simple solid increases with temperature above 0 K according to the Debye formula [13], reaching approximately $C_v=3R$ at the θ_D, when every mode of oscillation participates. Increasing vibration of its components diminishes crystal order.
- Above the Debye temperature: the specific heat remains approximately constant at $C_v=3R$. Values for the alkali metal halides appreciably increase with temperature [14] and the aggregate total heat energy absorbed to the T_m is close to a constant value. The vibration of immobilized crystal constituents increases.
- At the melting point: long-range order is lost and there is limited mobility of components in the fluid formed. Possible structural changes are discussed in [2, 3]. Components freed from crystal constraints acquire limited freedom of movement.
- The liquid above the melting point: C_v values increase somewhat and rise further with temperature. Increasing thermal energy progressively diminishes the structural order that has been retained in the melt above T_m. Continued progressive loss of component order through increased vibration and ease of movement with heating.
- Volatilization and above: heating a liquid increases its vapour pressure: the volatilization enthalpy absorbed results in a discontinuous, and large, increase in the freedom of component movement. Unrestricted heating of the gas diminishes all molecular interactions, leading to the eventual dissociation of all compounds. The ultimate consequence of unrestricted heating is the virtually free movement of individual atoms within the space available, towards the theoretical 'perfect gas'. At high temperatures there is continued progress towards the ultimate freedom of movement of individual atoms.

To the above (generalized) thermal properties of matter, represented and often regarded as mainly physical in character, the following chemical processes should be related.

- Chemical reactions: the ability of atoms to form chemical links with one another generates molecules, thereby introducing local order, which consists of smaller or larger atomic groupings. Molecules, sustained by strong chemical bonds, primary valence forces, can be regarded as a form of local

order superimposed on those physical characteristics of matter that are briefly summarized above. Chemical reactions may either increase or decrease order and often dominate the properties of matter at low temperatures. All such groupings are, however, eventually replaced by physical interactions at sufficiently high temperatures.

- Solid-state phase transitions: various types of structural modifications can occur in the solid state, some examples are mentioned in [22]. Such transformations have not yet been comprehensively characterized and their precise relationships with melting and decompositions of solids are not yet adequately established. For some solids, crystal transitions (with some loss of order) occur below the T_m.
- Crystolysis reactions: for crystals that undergo decomposition below the T_m, the chemical constituents are changed, through activated thermal breakdown or other reactions of, or between, components: some examples are discussed in [22]. Chemical reactions may increase the freedom of movement of crystal components if gaseous and/or liquid products are given.

Melting and melts

At the T_m, mobility of the vibrating, but hitherto effectively immobilized crystal components (atoms, ions or molecules) is increased. Fusion is an important, but limited, step in the progressive diminution of order/introduction of disorder on heating, by initiating limited relative movements of the components. On melting, only the intercomponent bonds are modified, to a greater or lesser extent, while intracomponent links remain effectively unchanged: fusion occurs at a precise T_m, without detectable activation. This is the first thermal change that permits relative component mobility.

In the above list of distinguishable thermal processes, two major step changes that occur during unrestricted heating of a solid are: (*i*) at T_m relative spatial movement of all components becomes possible and (*ii*) at T_b the relative freedom of movement of individual components is massively increased. The evidence further suggests, for the systems considered here [2–4], that the order retained in the melt at T_m is progressively diminished as the liquid temperature is systematically raised (specific heats tend to increase [14]). Moreover, on heating, intercomponent bonding may undergo (perhaps discontinuous) modification because the linkages that stabilize the extended crystal finally become transformed into those present in whatever molecule evaporates at T_b. In the alkali halides the 6:6 (etc.) coordinated ionic bonding structure appropriate to the solid is changed into the relatively strongly bonded [55] diatomic molecules, M–X, some of which may be present in melts below

the T_b. On such a model, the liquid phase is the transition between solid and gas, as judged by component mobility. However, and equally importantly, liquids exist in the temperature interval between which bonding is modified from the extended forms characteristic of many (macromolecular) solids to more localized groupings found within the individual (smaller) molecules that are capable of independent existence and free movement in the gas phase.

Discussion

Literature comments: limitations in our understanding of melting are revealed, even stressed, by the choice of terms, appearing only rarely in the physical sciences, that are used in discussions of this well-known phase change. Examples are that melting is a 'mystery' [29], an 'obscure phenomenon' [30] and 'that most familiar and most recalcitrant of processes' [56]. The use of the expressive term 'catastrophic' [29, 32, 36] might even be interpreted as a hint that theory breaks down by failing to portray fusion adequately. No satisfactory descriptive theory or representational model of melting has yet received general acceptance, though many have been proposed [1, 15, 37–39]. The set/liq model for melting [2–4] has been described in the 'Introduction'.

The interface in melting

Melting at surfaces

Fusion is predominantly, perhaps invariably, initiated at surfaces, as has long been recognized [25–32]. The melt is conformable with the crystal and surface tension promotes superficial liquid spreading. In a pure substance, only crystal constituents are present and diffusion of (reactant) components does not control the melting rate. Incomplete coordination of surface components may facilitate boundary wetting [31] and its coverage by the liquid phase. The role of premelting changes at crystal outer layers, relaxing surface order immediately below the T_m, was mentioned above: this parallels the tendency for decompositions to nucleate at surfaces [22, 33]. Moreover, any external heat supply almost inevitably warms the surface first and, because solids do not superheat [27, 29, 31], this enhances the propensity towards initiation of fusion here.

Kinetics of melting: geometry of advance of the interface crystal/melt contact

Measurements of the kinetics of melting do not feature in the literature. The following qualitative discussion attempts to identify some of the factors which control,

or influence, rates of melting/solidification and to account for aspects of the patterns of behaviour that are observed. Because no significant activation barrier to melting or to crystallization is detectable, it is concluded that the phase changes in both directions are facile and rates are, therefore, controlled by the transfer of energy to/from the crystal/melt ('wetted' [26]) contact interface. Both processes are easily reversible and are completed at a constant T_m. Because the melt is composed of the same constituents as the crystal only, components are always available at 'maximum' concentration at the interface, no diffusion or participation by a solvent influences the rate of crystallization. The ease of diffusive movement of heat within a melt/crystal system, by conduction and/or by convection (possibly also by radiation), depends on the physical properties of both liquid (viscosity) and solid (thermal conductivity). The more mobile components of the liquid probably predominantly determine the rates of energy transfer within melting mixtures. Overall melting and crystallization rates must also be sensitive to the distances and the spatial relationships between the solid/liquid contacts and the distributions of the heat sources/sinks, together with the local temperature deviations from T_m throughout the system. Moreover, as the phase change advances, these may vary with time, as will the distribution of solid particles within the liquid and the ratio of liquid/solid present. Consequently, the (time- and geometry-variable) movements of heat energy within both melt and crystal are neither readily amenable to control nor accessible to quantitative experimental measurement. Nevertheless, every minute temperature discontinuity, deviation from T_m at the interface, is expected to be eliminated rapidly by melting or by solidification (through $\pm\Delta H_F$). During melting, heat transfer will occur mainly by conduction and/or convection within the relatively more mobile melt, between the solid present and the heat source. On cooling a liquid below its T_m, solid may form preferentially on container walls in the vicinity of the heat sink, or other nucleus (seed crystal) present. Continued solidification, through melt cooling, may necessitate diffusive removal of heat by thermal conduction across a progressively increasing thickness of crystal.

With facile solidification/melting at an advancing interface and considerable experimental difficulties involved in the characterization of heat flows and distributions of small, local temperature deviations from T_m throughout any liquid/solid mixture, rate measurements of melting are effectively impracticable. Thus, the kinetic approach to mechanistic investigations of melting must remain unsuitable until sufficiently sensitive detection techniques for its observation are developed. Ideally, it might be expected that, in a symmetrical system subject to slow temperature

changes, crystal melting might be expressed by the 'contracting cube equation' [20, 21]. The evidence is that fusion is initiated across all crystal faces [26], by 'nucleation' due to premelting changes within the superficial layers. The solid/melt interface, once established, would be expected to advance into the solid thereafter. Confirmation of this suggested geometric representation offers a considerable experimental challenge but it seems that this model of interface advance [20, 21] may, at least qualitatively, be consistent with the information currently available. (Problems encountered in an attempt to measure the kinetics of ice melting are described in [57].)

Kinetics of melting: the interface processes

Properties of, and changes occurring at, a crystal/melt interface can be explained by the operation of two types of control, which are discussed here with reference to the set/liq melting model [2–4]. The absence of solid superheating means that all energy, in excess of the limiting amount required to heat the crystal to its T_m, is immediately absorbed as the enthalpy of fusion through melting of an appropriate quantity of solid. T_m cannot be exceeded by the crystal which, above its melting point, is destabilized by thermal energy. Portraying this behaviour by an energy band model, there is a forbidden zone or 'gap', between the maximum 'solid T_m level' and the minimum 'liquid' energy level. The second control is the absence of any appreciable energy barrier to the facile structural transition: crystal to melt. On the set/liq model, the stable structure of the solid is one of the components participating in the dynamic equilibrium and thus the crystal melting interface can readily exchange material, rapidly and reversibly, with the contiguous ordered regliq domains of the liquid that wets the solid surface. These are suggested as being closely similar to the transfers occurring across the irregliq zones between all the other regliq domains throughout the liquid. An individual atom or ion, leaving the edge of one ordered region (either melting crystal or regliq domain) to enter another, may change coordination during the transfer step. Local displacements of an atom/ion during its movements relative to several closely spaced neighbours are expected to distort rather than rupture its bonding within the condensed phase. This will require much less activation than the bond making/breaking steps involved in chemical changes such as crystolysis reactions [20] and, perhaps, also for the creation of defects.

If the energy investment (E_a), activation, required to transfer crystalline material into or from its melt is sufficiently small, it will be undetectable by kinetic measurements and rates of such processes are determined by the ease of energy movements (diffusion, etc.) within the system. Moreover, if all the ions (atoms or molecules) that form the crystal/melt interface contact are potentially capable of undergoing the phase transition, then the frequency factor (expressing the rate of the process by kinetic nomenclature) has a maximum value. Large A and small E_a values for changes in both directions accounts for the rapid, facile occurrence of the reversible melting/solidification processes. The total amounts of reactant species participating (recognizing the different significance of the term 'concentration' in solid state changes [20]) do not influence the kinetic characteristics of interface processes that depart little from equilibrium. The discontinuous 'energy band and band gap' representation, the existence of a limiting energy level that controls the temperature, T_m, below which melting does not occur, accounts for the apparent high, anomalous and meaningless, values of E_a calculated by conventional methods. These dominant mechanistic controls of melting differ in form and function from those applicable to other physical and chemical changes of solids. Thus, the fundamental difference between melting [1] and crystolysis reactions [20–22] is identified here as facile equilibration between alternative lattice structures in the former, through steps of low (negligible) energy barrier, in contrast with a single dominant activation process that controls the rate of the chemical reaction in the latter.

Magnitudes of T_m

The absorption of energy in two distinct steps during heating of the alkali metal halides, $0~K \rightarrow \theta_D$ and $\theta_D \rightarrow T_m$, accounts, in principle, for the apparent absence of a simple relationship between T_m and any single physical property of the crystal and/or its constituents [5–9, 17]. The necessity to classify the lithium halides as a distinctive subset has already been mentioned. Although also forming cubic crystals, the halides of silver and thallium show further differences and some cubic divalent salts provide yet other groups. The metallic elements gave evidence [2] that T_m values rise with numbers of bonding electrons and orbitals available. It is not surprising, therefore, that no simple theoretical model has yet been found capable of accounting quantitatively for these several sets or patterns of T_m values, despite our ability to measure this parameter precisely. The use of more complicated relationships, involving several parameters, to provide a theoretical explanation for the magnitudes of melting points, introduces additional uncertainties including the relative significances of the various contributions. No simple theoretical explanation for T_m magnitudes was found in the present comparative analyses and it seems unlikely that this situation might be easily resolved.

Theories of melting

The formulation of a theoretical model for melting has been impeded by the lack of information about melt structures close to the T_m. The set/liq model represents such 'cool' melts as being predominantly composed of regular arrays of relatively densely packed components that show structural similarity with the precursor crystals. This portrayal is intended to emphasize realistically the limited extents and types of stereochemical changes that can take place within the energy and density changes that characterize the melting of metals [2] and of alkali metal halides [3]. If (as seems reasonable) the sizes, shapes and ionic characteristics of crystal constituents remain essentially unchanged across the phase transition at T_m, the permitted (from energy and density changes) increases in disorder on liquefaction must be very limited in extent. This representation includes features in common with the melting models based on proliferation of Schottky defects [15, 38] or of dislocations [39] where (presumably) order must be extensively retained within the material containing these defects. The set/liq model melt differs from these models in two ways. First, and unlike a crystalline solid, more than a single lattice structure may be present: all possible stable regular arrays are regarding as participating in the equilibria. Second, diminished order and coherence at dynamic irregliq interfaces permits facile relative displacements of contiguous regliq domains that introduces fluidity: stress is not sustained in the liquid.

Melts that form a eutectic

The formation of solid double alkali metal halides was identified [4, 58] in mixtures having components of small cation volume ratios (CVRs [4]): Li/Cs – 0.0943 and Li/Rb – 0.125. This condition for crystal stability also includes the double alkali metal (acid) fluorides, $MF \cdot nHF$ [59, 60]: the (unlisted [61]) proton radius (H^+) is undoubtedly 'small'. Phase diagrams for the systems NaF/HF, Rb/HF and others [59, 60] give evidence of double salt formation, including the 1:1 combinations $MF \cdot HF$. Packing structures may (possibly) include the ion H_2F^-, though characterization of these systems is complicated by the facile volatilization of HF, on heating. On the set/liq model, the participation of further stable ordered structures is identified as introducing additional equilibration possibilities between regliq domains of alternative structures enabling the liquid phase to be maintained to lower temperatures. For example, although the T_m for RbF is 1066 K, a small amount (about 5.5% molar RbF) depresses the much lower T_m of HF (190 K) by up to 8 K. Very similar behaviour

patterns are found in the LiF/HF and NaF/HF phase diagrams [59, 60]. T_m values for the double alkali metal acid fluorides ($MF \cdot HF$) are higher than the T_m of the pure acid and are difficult to study due to HF volatility. The observation that addition of a thermally very stable crystalline salt, e.g., RbF, reduces the melting point of the mixture below the T_m of the much more readily fusible component, HF, supports the set/liq melting model, as described in [4].

The suggestion [4] that double salt structures, which contribute regliq phases to the dynamic equilibrium but have not been found to have independent existence, appears capable of further investigation. For example, extremely rapid (quench) chilling of molten equimolar mixtures of Li/K halides [4] might be used to investigate the possible existence of double salts, for example, $LiKX_2$, though without growth of the small regliq sized domains, the double salt phase might not be detected by X-ray diffraction.

Comment

Hitherto, no adequate or comprehensive theoretical explanation for melting has achieved general support. In this situation, it is appropriate to examine the acceptability of the alternative models that are consistent with the evidence, outlined above. We conclude from the present comparative analysis that the set/liq model for melting [2–4] provides a suitable foundation (or nucleus) for theory development. This is based on the existence of greater degree of structural order in the melt close to the T_m than has hitherto been generally approved. Relaxation, at the (solid→liquid) transition, of the extended packing regularity (single lattice) that is characteristic of the crystalline condensed phase up to the T_m, is regarded as being less profound than might appear from the discontinuous abolition of rigidity, the dominant feature of melting. The highly ionic character of intercomponent interactions in the alkali metal halide melts at T_m is unlikely to be significantly different from the forces responsible for the coherence of the solid immediately below the T_m. The energy and density changes that characterize the phase transformation [3] at T_m are apparently too small to accommodate significant structural modifications, including appreciable loss of order. Similar generalizations apply to the metallic elements [2]. Detailed insights into the ordered structures of solids have lead to widespread understanding of diverse properties of crystals in ways that were hardly imaginable when the first X-ray patterns were interpreted. Similarly, the set/liq concept may be capable of making a significant contribution towards extending our understanding of melts at T_m: the essential features are as follows. (*i*) Ordered constituent packing is

largely maintained in the melt immediately above the T_m, but the size of each regular domain is very small. (*ii*) A dynamic equilibrium continually transfers material between all participating domains.

The present survey of melting has included comparisons with crystolysis reactions, to identify the similarities and differences between these alternative types of changes that occur when solids are heated. It must, however, be emphasized that care must always be exercised before uncritically accepting theoretical and mechanistic conclusions based on kinetic studies of decompositions of solids. The theory of crystolysis reactions is currently in a state of controversy and there remain unresolved disagreements between active authors about the relative merits of the different theories available [22, 62–65]. A fundamental problem is an (often implicit) acceptance that models and concepts, specifically developed for homogeneous rate processes, are applicable to solid state reactions, without adequate confirmation that their underlying assumptions remain valid. It is important to avoid introducing these uncertainties into the theory of melting, although it still may be profitable to explore the possibility that crystolysis reactions and fusion may exhibit similarities of properties, controls or behaviour.

Melting and crystolysis reactions of solids apparently exhibit the common feature that both types of change may be represented as occurring preferentially at an advancing interface. Two aspects of the kinetics of such rate processes can be distinguished.

Kinetic rate equations, describing both changes, may be based reaction geometry: both types of rate processes are usually initiated at outer crystal faces and thereafter the active interfaces advance inwards: the 'reaction interface geometry' model [20–22] may, in principle, describe these rate characteristics. Nucleation of crystolysis reactions may be facile or difficult, resulting in different characteristic shapes of isothermal yield-time curves for various reactants. Melting, however, is (almost) invariably rapidly initiated across all surfaces and its progress is probably well described by the 'contracting volume' rate expression, developed in solid state kinetics [20, 34]. This has not been adequately confirmed by kinetic studies for melting/solidification processes due to experimental difficulties in obtaining the necessary and precise information about interface and temperature distributions throughout solid/liquid, 'reactant', mixtures and their systematic changes with time.

Rate processes at the reaction interface: a fundamental difference distinguishes the two types of change. Thermal decompositions are activated chemical reactions, whereas the magnitude of any energy barrier to melting is undetectably small. (Solids do not superheat and E_a values are probably not signifi-

cantly larger than the vibrational quantae within the crystal.) Without chemical changes, fusion is extremely readily reversible whereas activated decompositions do not always, or easily, reverse.

Crystolysis reactions: the overall chemical changes are usually regarded as being adequately represented as an activated process (E_a), because rate data fit the Arrhenius equation. The interface steps may not be simple, but possibly involve a sequence of contributory participating changes that have not, however, been characterized for most (perhaps all) decompositions of interest. Aspects of the detailed mechanisms and controls, which may involve volatilization or interface strain, have not been agreed [22, 62–66].

Melting: solid fusion is adequately represented as a readily reversible equilibrium, involving no appreciable activation barrier to the change. Concentrations of species participating in transformations to/from liquid and solid phases vary only marginally, through the density differences [2, 3]. Displacement of the interface equilibrium (by solidification or melting) is driven by the addition or withdrawal of energy and is facile, occurring immediately, because the solid↔melt transition is subject to no kinetic barrier (E_a). The rate of change is determined by the ease of heat transfer within the solid/liquid system (by diffusive, convective or conductive transport). These interfaces are not capable of supporting strain.

The present survey identifies melting (at least for the solids mentioned, though the conclusions may have wider applicability) as a relatively minor step in the progressive loss of order when the temperature of a crystalline solid is continually raised. The proposed set/liq model for melting emphasizes the similarities between the melt at T_m and the crystal (ordered packing of components, 'grain boundaries', etc.). This simplified portrayal of ('catastrophic' [29, 30, 36]) melting is intended to remove some of the 'mystery' [29] from this 'obscure phenomena' [30] and 'most recalcitrant of processes' [56]. The representation proposed here [2–4, 22] explains the specific characteristics of this important phase change using behaviour models that are familiar throughout chemistry and physics.

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