

NUCLEATION STUDIES ON IONIC MELTS

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INTRODUCTION

Previous work on crystal nucleation in one-component melts has largely been confined to molecular liquids or metals. Molecular liquids have been studied in bulk¹, and in the form of clouds of droplets produced by condensation in supersaturated vapour²⁻⁶. Metals have also been studied in bulk^{7, 8}, and as droplets of microscopic size. These were produced either singly by melting small fragments^{9, 10}, or in large numbers in emulsions^{11, 12}. For some purposes it is an advantage, in studying supercooling, to subdivide a sample of melt into a large number of droplets, thereby reducing to a small fraction the number which might contain impurities. In particular, only droplets free from impurities may be relied upon to exhibit phenomena of spontaneous nucleation.

Apart from work on glasses, where crystallization is very slow, little information exists on the spontaneous nucleation of ionic melts. In spite of experimental difficulties due to their high melting points, work on inorganic salts containing simple ions seems likely to prove rewarding, especially in view of the additive properties of the inter-ionic forces. Central, Coulombic force fields are more amenable to theoretical treatment than those in other classes of compounds, as is evident from the considerable success with which they have been used to predict the lattice energies of ionic solids.

A short description is given below of a new technique for studying the solidification of molten salts at high temperatures, together with some preliminary results obtained with alkali halides.

EXPERIMENTAL

Experiments with ionic salts are in progress in this laboratory, using a furnace in which clouds of melt droplets are formed in an atmosphere of salt vapour by intermittent supersaturation. Condensation is induced in an inert supporting gas by raising the temperature of a salt bead above that of the surroundings for a short interval, usually about 0.5 sec. The bead is supported on a small platinum heater coil in the roof of a chamber in the carbon furnace-lining. The chamber takes the form of a horizontal cylinder loosely closed at its ends with windows of transparent silica. Thermocouples embedded in the walls are used to measure the temperature of the gas in the enclosure. The movement of condensed particles by sedimentation and convection can be controlled by judicious use of the supersaturator so that they may be made to grow or evaporate at will while circulating slowly in the supporting gas. The cloud is illuminated by a mercury arc lamp placed opposite one end of the furnace, and the

forward-scattered light is viewed with a telescope at the other end. In this way the light reflected from single droplets can be studied, and their solidification detected by the onset of "twinkling", described below.

The present method, in which light scattered from discrete particles can be observed, has certain advantages over previous techniques²⁻⁴, in which the appearance of the illuminated cloud was examined by the unaided eye. Some doubt exists¹⁴ as to whether failure to observe scintillations in these earlier experiments was a reliable indication of the absence of solid particles. Care is necessary, however, even where variations in the intensity of forward-scattered light can be detected. Thus it has been observed in the present work that dense clouds of droplets under strong illumination show an effect which resembles the twinkling of crystals. This is due to the fact that neighbouring droplets move through critical positions in which light scattered from one reinforces that from the other. A droplet passing through several of these positions is thus seen to twinkle. This effect is nevertheless easily distinguishable from the behaviour of solid, since twinkling of droplets dies away as the cloud disperses, whereas crystals twinkle as they slowly rotate in the gas, even when isolated.

The aim of the present experiments is to measure the maximum supercooling in clouds of various compounds by observing the temperature at which solidification is complete in a convenient interval of time. The choice of this interval is limited by the period for which individual droplets can be identified, and is usually about 10 sec. Before recording the behaviour of droplets at a given temperature any catalyst impurities are removed from the supporting gas by one or two preliminary condensations. Several successive clouds are then examined to ascertain the reproducibility of results.

In all experiments carried out so far it has been possible to measure only the temperature corresponding to the sudden onset of crystallization. The rate of freezing turns out to be so sensitive to temperature that once it becomes detectable at all, the whole cloud solidifies in the observation period. This kind of behaviour is quite a general experience in nucleation studies and provides support for the predictions of theory, while at the same time severely limiting its practical investigation.

The apparently uniform frequency and intensity of twinkles from solidified droplets suggests that they are, in fact, tiny cubes rotating at about one revolution per second. Their rate of fall in the stationary gas indicates a particle size in the range 1-5 microns. Microscopic examination of the fall-out from condensations in various alkali halide vapours confirms this and also shows that the crystals are of roughly cubic form. It seems likely, moreover, that the particles are single crystals since an electron diffraction study by Young and Morrison¹⁵ of sodium chloride particles prepared by condensation of vapour showed that these were monocrystalline with a normal lattice parameter.

It has also been observed that particles at the threshold of solidification do not twinkle immediately on formation, delays of up to several seconds being typical. As practical limits to the range of observable twinkling frequencies are set on the one hand by the persistence of vision and on the other by the observation time, it would be possible in the absence of

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further evidence to attribute the lack of twinkling either to very slow or to very fast rotation. However, calculations of the influence of particle size on rotation frequency, based upon the exchange of energy between the rotational inertia of the particle and the Brownian motion of the gas molecules, show that twinkling of crystals should be detectable for all particles visible with the present method. Furthermore, a stroboscopic technique, in which the early stages of drop life were examined in a periodically interrupted light beam, failed to produce evidence of rapid twinkling. It therefore seems that twinkling is a reliable indication of the presence of crystals, and that in the early stages of their existence particles at the threshold temperature are partly or wholly liquid.

In addition to the onset of twinkling, further indications of the freezing of droplets are provided by changes in the rates of growth and evaporation. Whereas, for example, a large proportion of liquid droplets may evaporate entirely during the period of observation, especially at temperatures above the freezing threshold, twinkling particles are lost mainly through sedimentation. This behaviour forms the basis of a useful method for roughly locating the critical temperature of solidification, since at slightly higher temperatures the drop size changes so rapidly that the period of observation is materially shortened by distillation and fall-out.

The observed difference in growth rates of liquid and solid particles is not entirely attributable to the higher vapour pressure of the liquid. Droplets probably have an accommodation coefficient approaching unity, but this is not necessarily true for solid particles. The probable monocrystalline nature and cubic habit of the crystals obtained in the present experiments suggests that the predominant growth mechanism is one involving two-dimensional nucleation. Further growth of a crystal, once it has been formed by the solidification of a droplet, therefore depends on the maintenance of marked vapour supersaturation.

RESULTS

Some preliminary results for alkali halides are given in *Table 1*. In columns 2, 3 and 4 are listed the melting points T_f , the nucleation threshold T_n , and the critical supercooling θ . Salts of "analytical reagent" grade were normally used, without further drying or other purification. The supporting gas was usually argon, although its replacement by nitrogen made no measurable difference to the results for potassium iodide. Saturation of the argon at room temperature with moisture had no effect

Table 1. Data for homogeneous nucleation in molten alkali halides

<i>Salt</i>	$T_f^{(20)}$ (°K)	T_n (°K)	θ (°K)	$\sigma_{(001)}$ (erg/cm ²)	γ (dyne/cm)	λ^*/d	N^*
NaF	1265	985	(280)	252	230.4	8.9	700
NaCl	1074	911	163	102	125.7	8.8	680
NaBr	1023	862	161	85.5	117.6	9.0	740
KCl	1045	877	168	78.5	109.5	9.1	750
KBr	1013	850	163	69.5	100.2	9.1	750
KI	958	804	154	57.0	88.2	9.1	750
RbCl	988	845	143	51.8	110.6	9.9	980

on the critical supercooling of potassium iodide, neither was this influenced by using a supersaturator bead containing about 10 per cent of potassium hydroxide. Material obtained from large monocrystals of sodium chloride and potassium bromide, of the quality used in the manufacture of prisms for infra-red spectrometers, gave results which were indistinguishable from those obtained with commercial reagents. It is concluded that partial hydrolysis does not significantly affect the nucleation mechanism for these salts. Insensitivity to impurities has also been observed by Staveley^{2, 3} in nucleation experiments with various molecular compounds. Some difficulty was experienced with sodium fluoride in inducing condensed particles to grow to appreciable size. This may have been connected with the fact that clouds were noticeably polydisperse in this case. Also the onset of twinkling was less distinct for sodium fluoride.

DISCUSSION

The critical supercoolings recorded in *Table 1* are quite large, that for sodium fluoride being especially so, although there is reason to believe that for this salt the recorded result is somewhat too high (see below).

The interpretation of critical supercoolings in terms of the theory of homogeneous nucleation involves certain assumptions. The first and most important of these is to regard the formation of a three-dimensional crystal nucleus within a droplet of liquid as the rate-controlling factor in the solidification process. This enables one to identify the temperature of sudden freezing with the threshold of nucleation. The observations of Turnbull and Cech¹⁰ on the freezing of metal drops indicated that this was plausible, and further support is provided by our own observations with alkali halides. Formation of single crystals in our experiments suggests growth from single three-dimensional nuclei, and it follows that the growth rate in the liquid greatly exceeds the rate of nucleation at the temperatures concerned.

A basic postulate of the more recent theories is that the observed nucleation rate is governed by a stationary distribution of embryos of all sizes up to and including that of the critical nucleus itself^{16, 17}. Approximate theoretical estimates for the condensation of vapours^{18, 19} indicate steady-state relaxation times of 10^{-5} or 10^{-6} sec. Growth and decay of embryos in condensed systems are, however, activated processes and associated relaxation times may be much longer¹⁹. Calculations show that under the conditions of the present experiments droplets can cool by radiative heat loss through several hundred degrees to the end temperature (the furnace temperature) in a few milliseconds. For relaxation times appreciably longer than this, therefore, it is the furnace temperature which governs the rate-determining process of nucleation.

The stationary embryo distribution specified by theory might not, in fact, be entirely realized in the present type of experiment, since the rapid solidification of a droplet could terminate the relaxation process as soon as a critical nucleus appears. In applying the theory it is therefore necessary to assume that the first effective nucleus forms at a late stage in the relaxation process. Some justification for this assumption is provided by the results of the calculations now described.

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Using the supercooling data of *Table 1* critical free energies of nucleation ΔG^* were calculated from the expression of Turnbull and Fisher¹⁷ for the rate I of homogeneous nucleation in pure liquids. This may be written

$$I = (kT/h)(V/v_m) \exp(-\epsilon/kT) \exp(-\Delta G^*/kT) \text{ sec}^{-1} \quad (1)$$

where V is the volume of liquid, v_m the volume per molecule in the liquid, and ϵ an activation energy for the assimilation of liquid molecules by the growing embryos. A value of 0.1 sec^{-1} was assigned to I at the nucleation threshold. As there appear to be no data on the activation energy for viscous flow in supercooled alkali halide melts, which is the parameter usually employed for ϵ , a middle value of 10 kcal/mole was chosen after considering viscosity data for the salts above their melting points^{22, 23}. This seems justifiable since for uni-univalent salts ϵ is not very sensitive to temperature. Moreover, values of the liquid-solid interfacial free energy σ , calculated from ΔG^* , are insensitive to ϵ . The liquid volume V was taken as 10^{-11} cm^3 , corresponding to a droplet diameter of 3μ . A cubic nucleus was assumed and $\sigma_{[001]}$ was obtained from²⁴

$$\Delta G^* = 32 \sigma_{[001]}^3 (v_m/\Delta g)^2 \quad (2)$$

where Δg is the difference in free energy per molecule between the bulk liquid and solid phases. An approximate value for this quantity is obtained from the expression

$$\Delta g = \Delta H_f \theta / (T_f \mathcal{N}) \quad (3)$$

where ΔH_f is the molar heat of fusion and \mathcal{N} is the Avogadro number. Equation (3) is deduced by assuming that the heat content and entropy changes at T_n are equal to those at the melting temperature.

Where the necessary heat capacity data are available enthalpy changes may be corrected to T_n , and Δg calculated from

$$\Delta g = (\Delta H_f/T_f - \Delta C_p) \theta / \mathcal{N} \quad (4)$$

In view of the shortage of data¹⁸, reliable corrections can only be made for some of the salts studied. The values given in the table for $\sigma_{[001]}$ were calculated using equations (2) and (3), and may be as much as 10–20 per cent too high.

With these reservations, the resulting interfacial free energy σ may be compared with the surface tension γ of any melt at its nucleation temperature. The values of γ listed in *Table 1* were obtained by extrapolating the curves of Jaeger²¹ to T_n . On the view that the free energy of an interface is a measure of the extent of structural change across it, it is to be expected that γ will exceed σ . Results in *Table 1* show that this is indeed the case for all the compounds examined excepting sodium fluoride. Heat capacity corrections using equation (4) in place of equation (3) would probably remove this discrepancy. It is also possible, as stated above, that the supercooling for this compound has been over-estimated.

Also tabulated are values for the ratio of the length λ^* of an edge of a critical nucleus to the distance d between nearest-neighbour ions in the crystal. λ^* was calculated from the thermodynamic expression for a cubic nucleus²⁴:

$$\lambda^* = 4 \sigma_{\{100\}} v_m / \Delta g \quad (5)$$

both equations (2) and (5) being derived on the assumption that edge and corner free energies are negligible in comparison with the total interfacial free energy.

Although the values obtained for λ^*/d are plausible it must be emphasized that they merely illustrate the order of nuclear size, since the assumption that the nuclei are cubic may not be justified.

The same objection does not apply to the values in the final column of the table, which refer to the total number N^* of ions in the critical nucleus. This is given by

$$N^* = 4 \Delta G^* / \Delta g \quad (6)$$

and is calculated using equations (1) and (3). Some restriction on nuclear shape is involved in calculating N^* , however, since equation (6) is derived by assuming that σ is uniform over the whole surface of the growing embryo. Values of N^* so calculated are also subject to inaccuracies in Δg , and it is estimated that for this reason absolute values of the tabulated results may be too low by as much as 30 per cent. Nevertheless, relatively, the sizes of nuclei are the same to within an order of magnitude for all the salts studied. A mean radius of about 25 Å is indicated.

At present, the only other evidence about the structure and size of nuclei in ionic melts stems from X-ray studies by Zarzycki²⁵. This author suggests that in alkali halide melts at temperatures slightly above the melting points there are regions about 8 Å across in which the order is much the same as in the crystal. However this may be, present findings indicate that to be effective in producing observable crystallization rates, nuclei for alkali halide melts must be considerably larger.

Direct calculations of the free energy of nucleation from first principles would be very useful as a check on the experimental findings, but for the large sizes of nuclei now found such calculations are not at present practicable.

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