

### Requirements of an Ice Nucleus

THE ability of a substance to nucleate ice is thought to depend on two factors, the first being the fit<sup>1</sup> between the ice lattice and the lattice of the nucleator, the second being the nature of the chemical bonding between the ice and the nucleator. The importance of the latter factor has been proved experimentally by showing the dependence of nucleation on the surface charge of silver iodide under conditions which did not alter the fit<sup>2</sup>. However, the role of fit remains in doubt because, although some good nucleators do exhibit good fit, there are exceptions which cast doubt on the theory<sup>3</sup>, and some authors have suggested that only chemical factors are of importance<sup>4,5</sup>.

To provide unequivocal proof of the role of fit requires a system in which the fit can be varied without, at the same time, altering the chemical factor. This clearly precludes the comparison of nucleators of widely different chemical composition although there would be less objection to the comparison of closely related members of an isomorphous series. The problem can be circumvented by nucleating different phases of ice by the one nucleator, thus keeping the chemistry of the system constant while, in effect, varying the fit. In the present work this has been accomplished by freezing aqueous suspensions of silver iodide under pressures up to 3,000 bars (one bar = 0.987 atm.), thus giving silver iodide the opportunity to nucleate ice in the stability ranges of ice I and ice III (Fig. 1). Up to 3,000 bars silver iodide has a hexagonal structure similar to ice I (ref. 6), the fit between the two lattices being within 2 per cent in all directions. Ice III has a tetragonal lattice in which the hydrogen bonds are distorted by as much as 15 per cent from the normal tetrahedral direction<sup>7</sup>. An examination of the crystal model of ice III has revealed no spacings which correspond to the spacing of the silver iodide lattice.

The nucleation of ice under pressure was carried out by suspending a droplet of water on a fine thermocouple which was itself suspended in a high-pressure vessel filled with heptane. After bringing the vessel to the appropriate pressure, the vessel was cooled, whereupon the temperature of the thermocouple fell steadily to the nucleation temperature, then rose abruptly to a 'plateau' temperature which represented the melting point of the phase which was

solidifying. The vessel was then warmed and a second check on the solid phase was obtained by noting the 'arrest' in temperature as the phase melted.

When doubly distilled water was frozen, ice I formed up to a pressure of 2,060 bars, while above this pressure ice III formed, each phase nucleating approximately 20° C below its melting point curve (that is, along lines AB and CD, Fig. 1). Inadvertent nuclei were evidently responsible for the freezing of ice I, since it is well established that homogeneous nucleation of ice I requires a supercooling of at least 35°. There is no experimental evidence to show whether the same is true for ice III.

When aqueous suspensions of silver iodide were frozen the nucleation of ice I was greatly facilitated, the necessary supercooling being only 4° (EF, Fig. 1), but the nucleation of ice III was not improved. Thus a droplet of suspension, cooled at a pressure between 2,060 bars and 2,750 bars (for example, 2,500 bars), nucleated at point X on the extrapolation of EF. The phase which solidified was not ice III but ice I, as shown by the fact that both the 'plateau' temperature and the 'arrest' temperature coincided with point Y, on the extrapolated melting point curve of ice I, and not with point Z.

Phonazine, another nucleator which closely fits ice I, also induced ice I in the region where ice III is the stable phase, thus confirming that the effect is not a peculiarity of silver iodide.

Thus, in a situation where the chemistry is not a variable factor it has been shown that the phase which best fits the nucleator is preferentially nucleated even though this phase has the lower stability—a clear demonstration of the importance of fit in ice nucleation.

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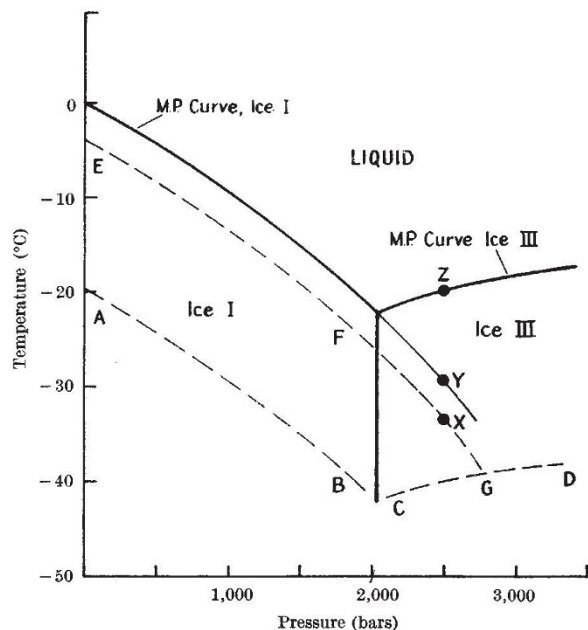


Fig. 1. Full lines denote phase boundaries between ice I, ice III, and the liquid as a function of temperature and pressure. Dashed lines denote nucleation levels. AB, ice I in pure water; CD, ice III in pure water; EFG, ice I in silver iodide suspensions

### Heterogeneous Exchange between Chromium (III)-oxide and Chromate

Andersen and Maddock<sup>1</sup> have doubted whether Libby's hypothesis, that the transition metal oxyanions in the Szilard Chalmers reaction yielded fragments containing the metal in its original oxidation state, is still tenable. From their experiments and results published by Libby<sup>2</sup> and Harbottle<sup>3</sup> I suggest that the oxidation state of the chromium fragments must be determined in the crystal and not by reaction taking place on dissolution.

As a consequence of this postulate the question arises whether the fragments of lower oxidation state undergo exchange reaction with the chromate matrix and especially whether exchange takes place in the solid state between chromate and tervalent chromium. At first sight, measurable exchange effects might seem improbable, for it has been shown by Burgus and Kennedy<sup>4</sup> and other authors<sup>5,6</sup> that exchange between chromium in tervalent and hexavalent state is negligible in aqueous solution. The exceptional stability of the ion  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , as demonstrated by exchange experiments with  $\text{H}_2^{18}\text{O}$ , causes chromic ion to be relatively inert in an aqueous medium. It has been shown, for example, that in the solid state, where the chromic ion is unhydrated, reaction occurs with diphenyl-carbazone<sup>7</sup>, whereas in aqueous solution the chromic ion does not react. Thus it seemed reasonable to look for exchange effects also in the solid state.