



Fig. 1. The solid-liquid equilibrium data for the ice polymorphs—ice I (●), ice III (○), ice IV (×), ice V (△), and ice VI (□).

ice IV (D_2O) but found that it could only be formed in an apparatus which had not previously contained ice V (D_2O).

The nucleation of ice I presents no problem, for a large number of organic compounds are known which facilitate the nucleation of ice I.³ However, good organic nucleators for the high-pressure ices are extremely rare, partly because below 0°C there is a strong tendency for organic surfaces to adsorb water in the form of a two-dimensional layer of ice I.⁴ On such an adsorbed layer, the high-pressure ices have difficulty in growing epitaxially, therefore a considerable supercooling is generally required. Nevertheless the present study shows that certain organic compounds do exhibit a preference for nucleating a particular phase of ice, even though the required supercooling is relatively large. By using these nucleators each phase has been crystallised from the liquid at pressures outside the range of thermodynamic stability, and by measuring the equilibrium freezing point during crystallisation the solid-liquid equilibrium curves have been extended beyond the pressure range investigated by Bridgman.

Apparatus: A droplet of water about 2 mm in diameter is suspended on the tip of a platinum/platinum-rhodium thermocouple contained in a high-pressure cell fabricated from beryllium-copper. Pressure is generated by a hydraulic pump via a 10:1 intensifier and separator, the limiting pressure being 6000 bar. The working fluid in the cell is petroleum ether, b.p. = 60°–80°C. The cell is cooled at a steady rate of about 4°C/min and the amplified signal from the thermocouple is recorded continuously. When crystallisation begins the temperature of the thermocouple rises abruptly to the equilibrium freezing point of the phase of ice which is crystallising, and remains at this "plateau temperature" until crystallisation is complete. Where two phases have the same equilibrium freezing point the phase which is crystallising is identified by raising the pressure slightly during crystallisation thus obtaining, from the step in the plateau, the derivative of the equilibrium freezing point with respect to pressure.

If the phase which has crystallised subsequently transforms to a more stable phase the transformation is signalled by a temperature spike resulting from the abrupt release of the heat of transformation. Similarly, if during the crystallisation of the first phase, a second phase begins to crystallise, a stepped plateau is formed. The phase which is finally formed is confirmed by heat-

TABLE I. Nucleators for high-pressure ices.

Nucleator	Preferred ice phase	Supercooling (°C)	Pressure range (bar)
α -phenazine	I	4	1–3200
phloroglucinol dihydrate	I	6	1–3200
8-hydroxy-quinoline	III	18	2800–4800
benzoin	III	21	3000–4600
<i>p</i> -amino hippuric acid	IV	13	3800–4200
<i>l</i> (leucine	IV	11	3200–4000
phenol tetra-bromo-phthalein	IV	14	3800
tetra-chloro-phthalic anhydride	IV	7	3200–4000
<i>l</i> -asparagine	VI	5	4400–4800
benzamide	V	14	2600–4200
	V	21	3200–3600
	IV	16	4200–4600
adipic acid	V	22	3400–4600
2,4 dinitro-diphenylamine	VI	13	3800–5000
haematoxylin	VI	10	4000–5000
cholic acid	VI	11	3800–4600
anisoin	VI	16	5600

ing the cell and noting the melting point, this being the temperature at which an arrest appears in the trace of temperature vs time.

The accuracy of the thermocouple-recorder system is shown, by calibration, to be $\pm 0.5^\circ C$. The plateau temperature for ice I at atmospheric pressure is $0 \pm 0.5^\circ C$, thus establishing that in spite of the relatively small size of the water droplet and heat leakage along the thermocouple wires, the thermocouple measures the true melting point. Pressures accurate to ± 50 bars are measured on a 7-kbar Budenburg gauge.

To test a particular organic compound as an ice nucleator the compound is freshly crushed under water and a drop of the resultant slurry is placed on the thermocouple.

Results and Discussion: As reported by Bridgman,¹ ice V is difficult to nucleate from the liquid in the absence of a specific nucleator, the experience being that between 2400 and 4000 bar ice III is obtained, whereas above 4000 bars ice VI is generally obtained.

No evidence has been found for Bridgman's alleged "memory effect" for ice V, i.e., the ability of ice V (but not ice VI) to nucleate from the liquid once ice V had been previously formed in the apparatus. However it is known that memory effects arise from adsorbed films⁴ or from the retention of ice in crevices⁵; therefore one expects the phenomenon of "memory" to be a function of apparatus rather than being an intrinsic property of ice V.

When selective nucleators are present in the water droplet it is possible to nucleate, at will, all the phases of ice except ice II and ice VII, the former being notoriously difficult to nucleate from the liquid,² the latter requiring pressures beyond the limit attainable in the present apparatus. In Table I are listed the most selective of the organic nucleators together with the pressure range in which selectivity is found. Of particular interest is the confirmation of Bridgman's claim that a wholly unstable phase, ice IV, exists within the stability region of ice III and ice V. The melting-point curve of ice IV is depicted in Fig. 1 together with the extension into regions of instability, of the melting-point data of ices I, III, V, and VI.

The melting-point data of all the ices except ice I are, on the average, about 1°C lower than the data reported by Bridgman, but taking into account the uncertainty of pressure and tem-

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