[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE FREEZING POINTS OF THE TWO FORMS OF METHYLENE IODIDE

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The freezing point of methylene iodide was determined as the guide to the purity of a sample of the substance which was to be used as a solvent for selenium. The irregularities found, led the writer to investigate this property thoroughly.

The substance exhibits the unusual characteristic of having two transition points between the liquid and the solid state which are less than half a degree apart. A further unusual feature of this compound is that the solid form, which has the lower transition temperature, is the unstable one. Published values of these freezing points for the same form differ by more than a degree centigrade. Experimental work indicated that the most trustworthy value was 0.3° too low.

When liquid methylene iodide is immersed in an air-bath surrounded by ice water the unstable form having the lower freezing point usually separates at a definite temperature. An unstable equilibrium between this form and the liquid has been maintained for several hours despite stirring. It is said to be unstable because sudden cooling of the equilibrium mixture or seeding with the stable form causes the temperature to rise to the freezing point of the more stable form. The stable form may be prepared by immersing the liquid iodide directly in the ice water cooling bath without the intervening air-bath. This causes the material to cool more rapidly and results in the separation of the stable form. These facts agree with what one would expect of a substance showing a monotropic change such as is diagrammed by Ephraim.[1]

Values for the freezing points of these two forms of methylene iodide taken from the literature together with values obtained by the writer are given in Table I.

TABLE I

FREEZING POINTS OF THE TWO FORMS OF METHYLENE IODIDE IN DEGREES CENTIGRADE

Author	Unstable	Stable
Beckmann[a]	4	4.47
Bruni and Callegari[b]	5.23	5.7
Tammann and Hollmann[c]	..	5.73
This Laboratory	5.54	6.01

[a] Beckmann, *Z. physik. Chem.*, **46**, 853 (1903). [b] Bruni and Callegari, *Atti Roy. Acad. Rome*, Series 5, **13**, 481 (1904). [c] Tammann and Hollmann, "Kristallisieren und Schmelzen," Barth, Leipzig, **1903**, p. 278.

[1] Ephraim, "A Text-Book of Inorganic Chemistry," Gurney and Jackson, London, **1926**, p. 49, Figure 19.

Purification of Methylene Iodide.—The red color due to iodine, which methylene iodide always develops on exposure to the light, was removed by treatment with sodium thiosulfate which had previously been dried for about twenty hours in an oven at 120°. This decolorized material was shaken and allowed to stand overnight with anhydrous calcium chloride. It was then distilled from a water-bath at about 86° and 30 mm. pressure. These conditions of distillation were not determined accurately but frequent observation during the course of a distillation showed no material change. The samples so prepared were clear and of a light yellow color and remained so while protected from the light. Samples taken at different stages of the distillation showed excellent agreement in freezing points.

It was found that when a single sample was used repeatedly for freezing point determinations, there was a gradual lowering of the freezing point to a limit of about 0.05°. Two samples which approached this limit became cloudy on cooling as though an emulsion were being formed. It was found that by shaking a 25-cc. sample with an excess of water (one drop gave an excess) both the approximate lowering of 0.05° and the emulsion like cloudiness could be duplicated. Because of these facts the observations reported were made on freshly distilled samples and these used for but one set of determinations.

Calibration of Thermometers.—The Fahrenheit thermometer (Bureau of Standards No. 32818) was certified in February, 1924, to have a correction of minus 0.10° when the reading was 32.00° and a correction of minus 0.22° when the reading was 60.00°. An ice-point determination agreed exactly with this calibration. Interpolation gave a correction of minus 0.14° to be applied to the observed freezing points of the unstable modification of methylene iodide and a correction of minus 0.15° to be applied to the observations of the freezing point of the stable modification.

The Centigrade thermometer bore the Bureau of Standards No. 39197. The certificate was dated July 8, 1926. A zero ice-point correction and one of 0.07° at a reading of 10.00° was certified. An ice-point determination indicated an error of minus 0.06° which, together with the minus 0.04° obtained from the interpolation of the Bureau of Standards figures, gave a total correction of minus 0.10° to be applied to the observed readings over the range of both the unstable and the stable forms of methylene iodide.

Method of Freezing Point Determination.—The methylene iodide in a glass tube surrounded by an air-bath was immersed in an ice-water bath. A stopper supporting the thermometer and a glass stirring rod was placed in the tube containing the methylene iodide so that the thread of the mercury was completely immersed when the readings were taken. These were taken through the air-bath and ice water with a thermometer magnifier. Work was carried out in a partly darkened room so that the samples showed no color change such as accompanies exposure to light.

TABLE II

FREEZING POINTS OF METHYLENE IODIDE

Thermometer Number 32818

Sample number	Unstable form Corrected value	Unstable form Convert. to °C.	Stable form Corrected value	Stable form Convert. to °C.
103	41.96	5.533	42.77	5.983
106[a]	41.99	5.544	42.87	6.040
107[a]	41.95	5.527	42.80	6.000
107[b]	41.98	5.545	42.82	6.011
Average		5.537		6.008
Thermometer Number 39197				
101		5.54		5.98
102		5.54		6.02
104		5.52		6.01
105[a]		...		6.02
105[b]		5.52		5.99
107[c]		5.55		6.02
Average		5.534		6.007

Eight determinations with a Beckmann thermometer of the difference in the freezing points of the two forms varying between 0.468 and 0.477 gave an average value of 0.473°. The close agreement of this with the difference obtained by the less precise calibrated thermometers is further evidence for the trustworthiness of the determinations. It may also be noted that this difference agrees with that given by the other workers quoted in Table I.

Conclusions

A method of obtaining the two forms of methylene iodide is given.

The unique relations between the two forms with respect to transition points and stability have been confirmed. It appears to be a monotropic dimorphous substance.

The close accord in the values obtained by the use of two independent standards is such as to establish the values for the freezing points of the two forms of methylene iodide as 5.54 and 6.01°, respectively. These values are probably correct within 0.02°.

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