coefficient calculations introduced by the use of inaccurate and inadequate thermal data. A subsequent communication will describe the application of these dilution measurements to some freezing point determinations recently made in this Laboratory.

Summary

Differential heats of dilution to be used with cryoscopic data for the evaluation of activity coefficients of sodium chloride in aqueous solution have been obtained (by the chord-area method) from appropriate calorimetric measurements at 0, 12.5 and 25°.

These dilution data have been combined with those of Gulbransen and Robinson (extrapolated to infinite dilution by the method of Young and Groenier) to demonstrate that the apparent molal heat capacity of sodium chloride in aqueous solution is not a linear function of the square root of the molality. Many of the discrepancies between various precise measurements of the heat capacities of electrolytes, and the limiting law derived from the Debye–Hückel theory arose from linear extrapolations. Others are probably due to extrapolations which are too nearly linear. The theory is in agreement with measurements of the heats of dilution of aqueous sodium chloride solutions.

CHICAGO, ILL. RECEIVED SEPTEMBER 8, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 374]

The Normal Vapor Pressure of Crystalline Iodine[1]

BY LOUIS J. GILLESPIE AND LEWIS H. D. FRASER

The normal vapor pressure of iodine is the pressure of the pure vapor in equilibrium with pure solid or liquid iodine when this is subjected to the pressure only of the pure vapor. But few attempts have been made to measure it directly. Ramsay and Young[2] appear to have determined the pressure of air necessary to stop the sublimation of iodine at various temperatures from 58 to 113°. Haber and Kerschbaum[3] used a vibrating quartz fiber as manometer below 0 to −48°. They report some data by Naumann[4] from 19 to −40°. The precision of none of this work is within the theoretical uncertainties of the better indirect methods.

These uncertainties are due to the assumption, necessary in the indirect methods as ordinarily practiced, that iodine vapor behaves as an ideal gas—more particularly, that a mixture of iodine vapor and a permanent gas behaves as an ideal gas mixture. Gerry and Gillespie[5] showed how the uncertainties may be removed by applying thermodynamic corrections. They derived the corrections from the extensive data of Braune and Strassmann[6] and applied them to the precise indirect results of Baxter and co-workers.[7] They applied to these corrected results the rational equation of Giauque,[8] which has only one adjustable constant—the coefficient of the reciprocal temperature—and found the following equation to fit the corrected results very well

$$\log p = -3512.8/T - 2.013 \log T + 13.3740 \quad (1)$$

where p is the vapor pressure of the solid iodine in atmospheres, log is to the base 10 and $T = 273.1 + t°$.

The present paper deals with some direct measurements of the normal vapor pressure of solid iodine, of relatively high precision, made by means of a flexible metallic diaphragm to restrain the iodine vapor and devices for measuring precisely the low pressures of dry air on the opposite side of the diaphragm when the position of a pointer on the diaphragm, observed with a microscope, indicates a state of balance.

Apparatus

Corrosion experiments showed that platinum is not attacked by iodine, and gold becomes slightly tarnished, but the tarnish disappears on standing in air. These metals and glass were used to contain the iodine.

Figure 1 shows the diaphragm A, a disk of platinum-rhodium foil (4% Rh) 0.01 mm. thick with an effective diameter of 5.7 cm. It is mounted between two brass

---

(1) From a thesis submitted by Mr. L. H. D. Fraser in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

(3) Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

(4) Naumann, Dissertation, Berlin, 1907.

(5) Gerry and Gillespie, *Phys. Rev.*, **40**, 269 (1932).

(6) Braune and Strassmann, *Z. physik. Chem.*, **A143**, **225** (1929).

(7) Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907); Baxter and Gross, *ibid.*, **37**, 1061 (1915).

(8) Giauque, *ibid.*, **53**, 507 (1931).

rings B and B′. Through six holes in these rings screws pass into the block C. By tightening these screws the diaphragm is stretched over the curved surface of C like a drumhead and free from wrinkles. All brass surfaces against which iodine vapor may come are gold-plated. The tube D is of glass. It is ground well to the gold-plated conical hole in C, and the annular space at the bottom is tightly packed with gold dental moss and sealed with deKhotinsky cement, protected in turn with several coats of shellac.

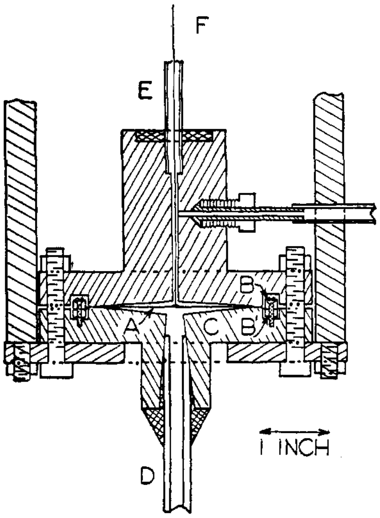

Fig. 1.—Diaphragm pressure balance.

The pointer F is a very light fiber of blue glass cemented to the diaphragm. The pointer and the tube E extend well up out of the thermostat. The top of the pointer is cut off square and is observed through the flattened wall of the top of the tube E through a microscope with the aid of a scale in the ocular.

The sensitivity of the diaphragm has been from 0.001 to 0.004 mm. of mercury pressure, depending on the initial stretch given the foil.

The portion of the apparatus shown in Fig. 1 is well immersed in the oil of the thermostat.

Figure 2 shows a manometer used by Professor F. G. Keyes in unpublished research and kindly lent to us. The arms A and B are 3.2 cm. in diameter. A vacuum is maintained over the mercury in B. The pointer P is operated by a 12.7-cm. dial D through a mercury-protected packing gland G. This can be tightened at any time by means of a special wrench. The periphery of the dial has 200 equal divisions; the thread of the screw is about 1 mm. in pitch, and the position of the screw can easily be estimated to 0.001 mm.

The manometer and the compression chamber C are in an air-bath. By means of the compression chamber the pressure of the dry air can be multiplied about 7 times before measurement with the manometer.

Experience showed that the zero reading of the dial (for equal pressures on both sides) varies with time, particularly because of necessary retightening of the packing. Hence in many cases it was preferred to find the pressure without the zero reading, by measuring in turn the dial reading for the original pressure and for the pressure after compression in the chamber C, and dividing the difference of the two dial readings by a number equal to the compression ratio diminished by unity. The pitch of the screw has been carefully calibrated by means of a good cathetometer with invar scale and found to be uniform. From the temperature of the air-bath and the value of gravity at Cambridge, pressures in international millimeters of mercury were calculated from the dial readings. These pressures are those of the dry air in the apparatus. When the vapor pressure of mercury is added we obtain the total pressure which balances the iodine pressure across the diaphragm.

A portion (not shown) of the tube D in Fig. 1 is bent to give elasticity and communicates through two special stopcocks either to a tube containing the supply of pure iodine or to the vacuum line, which includes condensing trap, gage and mercury and oil pumps. The stopcocks are operated under the oil of the thermostat but are protected by shields so that no oil can touch the plugs. By means of these cocks the tube D can be evacuated for a null-point determination of the diaphragm or connected with the iodine reservoir for a vapor pressure measurement. These cocks are lubricated with a mixture of meta- and pyrophosphoric acids obtained by heating two parts by weight of 85% ortho- with one part of metaphosphoric acid to various temperatures and for different lengths of time.[9] The mixtures used are very viscous and the cocks readily freeze if not turned frequently. The volume of the tubing D and its ratio to the volume of the system including the McLeod gage are known, so that any permanent gas present with the iodine after an experiment can be determined.

The pressure of the air used to balance the vapor pressure is steadied by means of a large bulb in the thermostat.

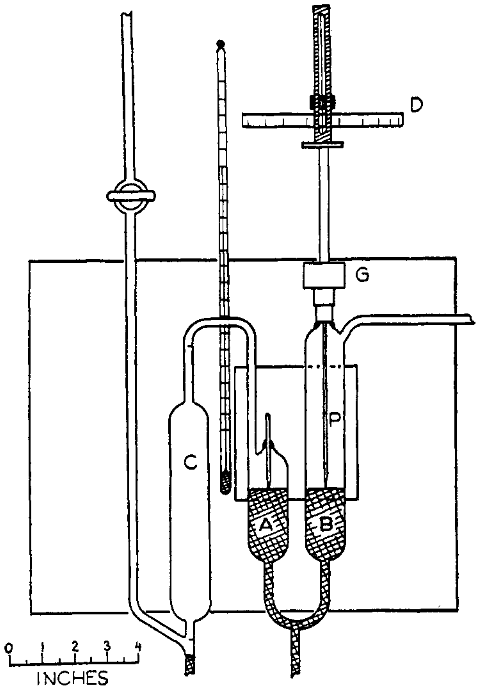

Fig. 2.—Low pressure manometer.

---

(9) Stephens, THIS JOURNAL, 52, 635 (1930).

The stirrer of the thermostat and its motor are hung on a separate support to avoid vibration.

The Experiments

The iodine used was purified and dried by subliming it *in vacuo* from a mixture of resublimed iodine, anhydrous potassium iodide and phosphorus pentoxide. Sublimation was between temperatures of about 45 and −78° and required about three days. The bulb containing the pure product was brought into communication with the rest of the apparatus by breaking a glass tip *in vacuo* by a solenoid arrangement.

Before admitting iodine vapor to the tube D of Fig. 1 for a measurement, it was necessary to find the reading of the pointer on the scale in the ocular of the microscope when equal pressures were on either side of the diaphragm. Zero pressure was chosen for this. The null-point of the diaphragm should not vary with the small pressures in question at constant temperature, because of the simple and symmetrical geometry of the strong metal apparatus.[10]

Iodine vapor was then admitted to the tube D from the reservoir, dry air being admitted to the air system on the other side of the diaphragm, and by use of a mercury injector the diaphragm was again brought to the null-point. When equilibrium had been reached the pressure of the dry air was measured as described above, and the vapor pressure of mercury at the temperature of the gage of Fig. 2 added to obtain the vapor pressure of iodine. After a series of such measurements the null-point was observed again and the results discarded if a significant change had occurred during the series.

No effort was spared to obtain the greatest precision of which the apparatus was capable. Thus twenty-four experiments involving over 500 settings of the dial were performed to determine the two compression ratios used in the multiplication of the pressure (about 7, in each case). The corrections for deviations from Boyle's law were negligible. Eighty-one vapor pressure measurements involving over 1600 settings of the dial were performed at four temperatures from 30 to 60°. Of these, 32 were discarded either because the null-point of the diaphragm had changed or because equilibrium seemed not to have arrived. At each temperature the exact value of the temperature varied slightly from run to run, and the mean reciprocal temperature was found for the mean value of the logarithm of the pressure. This calculation is slightly better than direct averaging of the pressure and temperature but gave practically the same results, because of the smallness of the temperature variation.

At the end of the experiments at 30 and 40° no partial pressure of permanent gas was found in the iodine chamber. When the pressures of permanent gas found at the end of the groups of experiments at 50 and 60° were divided by the time elapsed since the previous evacuation, the rates of air leakage appeared to be constant at each temperature, and from these rates corrections were applied to each result according to the time elapsed, Dalton's law being used for the small corrections. At 50° the correction was 0.3% of the final value of the presssure on the average, and reached about 1% in a single case. At 60° it was about 1% on the average and reached 3% toward the end of one series.

The results are shown in Table I. A thermodynamic check for consistency is given by calculating from each result the value of ΔE_0° in the following equation of Giauque

$$\Delta F^\circ = -RT \ln p_{\text{atm.}} = \Delta E_0^\circ + 429 + 4.0T \ln T - 61.186T \quad (2)$$

TABLE I

VAPOR PRESSURE OF SOLID IODINE IN MM. AND ΔE_0°

Temp., °C.	29.967	40.017	50.154	60.119
Pressure, mm.	0.46709	1.02614	2.21318	4.30723
ΔE_0°	15643.29	15645.56	15630.91	15644.50

The value of ΔE_0° at 50° is inconsistent with the others, pointing to too high a value of the vapor pressure (by about 0.045 mm.). At this temperature the same inorganic stopcock lubricant was used as for the two lowest temperatures, and it proved too fluid, finally failing altogether. We believe that this was associated with a perceptible vapor pressure of water which caused the high results. In any case, a stiffer batch of lubricant was prepared and used at 60°, and the results here are consistent with those at the lower temperatures. From the mean result for ΔE_0°, excluding the value for 50°, the latent heat of sublimation of iodine at 25° is found to be $\Delta H_{298.16} = 14880.8 \pm 0.8$ cal.$_{15}$ per gram mole. In the above calculations 273.16 was used for the ice point and 1.98690 cal.$_{15}$ for R.

The mean result for the coefficient of $1/T$ in the simple equation of Giauque for the vapor pressure is 3512.859, nearly the same as that in equation (1) above derived by Gerry and Gillespie. The following table affords a comparison between the observed vapor pressures and those calculated by equation (1) and by equation (1) but with the modified value of the coefficient (marked 0.859). All pressures are in international millimeters.

TABLE II

OBSERVED AND CALCULATED VAPOR PRESSURES OF SOLID IODINE

Temperature, °C.	Observed	Calcd. Eq. 1	Calcd. 0.859
29.967	0.4671	0.4663	0.4661
40.017	1.0261	1.0284	1.0279
50.154	2.2132	2.1682	2.1673
60.119	4.3072	4.3107	4.3089

The agreement of the results with the calculated values is very good, with the exception of the data for 50°, which are excluded from all further

---

[10] Mr. Joseph E. Goossens found in this Laboratory that a glass diaphragm with a flattened working surface may change in null-point as the pressure is changed on both sides at constant temperature.

averages and calculations. The average percentage deviation from equation (1) is only 0.16, the greatest deviation being 0.0035 mm. and the greatest percentage deviation being 0.22. (The excluded value at 50 differs tenfold.)

The agreement of the data with equation (1) derived from the gas-stream data of Baxter and collaborators is noteworthy. The mean deviation (observed minus calculated) taken with respect to sign is only −0.044%. Now, in the reduction of these data by Gerry and Gillespie, the values of px_1 received corrections for nonideality of the gas of 0.58, 0.51 and 0.37% at the temperatures 30, 40 and 60°, respectively, as may be found from their Table III. The agreement is therefore within the magnitude of the correction for failure of the ideal gas laws in the gas-stream method.[11]

The average percentage deviation of the results from the equation using the modified value of the coefficient of $1/T$ is 0.14%. The improvement (over 0.16) is not great. The use of a mean value (or of either) should afford very good vapor pressure values, probably from 0 to 100° or higher. Below 0° the equations do not agree well with the data of Haber and Kerschbaum and of Naumann—thus at −48.3° the observed pressure is only 72.7% of that calculated from equation (1) (or 72.3% of that calculated from the original equation of Giauque), and the true vapor pressure is in turn estimated by Haber and Kerschbaum to be about 12% lower than that observed (at room temperature), by reason of the Knudsen effect.[12]

The equations also disagree somewhat at 90° and above with the data of Ramsay and Young, the calculated values becoming progressively greater than the observed, the difference reaching 6.4% of the observed pressure at 113.8°.

These facts suggest that equation (1) is perhaps too simple in form for such a range of temperature as from −48 to 114°.

Nevertheless, the best values at present available for the normal vapor pressure of iodine are probably those calculable from equation (1) with the value 3512.830 for the coefficient of $-1/T$, which averages the results of Baxter and collaborators and the present work. Table III gives such values for even values of the temperature.

TABLE III

NORMAL VAPOR PRESSURE OF SOLID IODINE IN INTERNATIONAL MILLIMETERS OF MERCURY

t, °C.	0	10	20	25	30	40	50	60
p, mm.	0.0307	0.0814	0.201	0.309	0.467	1.027	2.144	4.276
t, °C.	70	80	90	100	110	114.15 (m. p.)		
p, mm.	8.175	15.04	26.73	45.97	76.76	94.18		

Summary

The normal vapor pressure of solid iodine has been measured directly by means of a flexible metallic diaphragm at 30, 40 and 60° with a precision of better than 0.004 mm. of mercury, or better than 0.22%. The results agree with the equation deduced by Gerry and Gillespie from the data of Baxter and collaborators, as corrected for failure of the ideal gas laws, within the magnitude of these corrections. A table is given of vapor pressures derived from a combination of the new data with the corrected older data, as embodied in the modified equation of Giauque

$$\log_{10} p_{\text{atm.}} = -3512.830/T - 2.013 \log T + 13.37400$$

The corresponding value of ΔH for the sublimation of iodine at 25° is 14880.7 cal_{15}/mole.

CAMBRIDGE, MASS. RECEIVED AUGUST 12, 1936

---

[11] Air was the inert gas in this case. The corrections depend in part on the nature of the inert gas.

[12] The calculated pressure at −48.3° is only 7.84 × 10^{-5} mm.; the observed, 5.7; the observed after Knudsen correction, 5.0 × 10^{-5} mm.