

The Thermal Equilibrium Between Ethylene Iodide, Ethylene and Iodine

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In Fig. 2 the values of $\log p$ from Table II have been plotted in the usual manner against an abscissa proportional to $1/T$. The straight line drawn was computed from the same data, assuming a linear relationship. Its equation is: $\log p = 6.99 - 8980/T$. The points obtained fit this line fairly well; the mean deviation from the line corresponds to an error of about 10 percent in the value of p . In computing this equation the values at 750 and 725°C, which will be seen to fit the line quite well, were also included. Actually these temperatures are above the melting point of barium, 710°C.⁷ Hence these points correspond to the vapor pressure over liquid barium and should therefore, strictly speaking, fall on a different line, intersecting the one for the solid at the melting point. Evidently the heat of fusion is so small compared to the heat of evaporation, that the change of slope is far beyond detection with the limited accuracy of these measurements.

⁷ Rinck, *Comptes rendus* **193**, 1328 (1931).

We have also included in Fig. 2 a line representing the vapor pressure of calcium obtained in the previous work by one of us.⁵ It will be seen that the calcium pressures are 2 to 3 times higher than those of barium for the same temperature in this range. From the slope of the barium curve the latent heat of evaporation is 4.09×10^4 cal./mole, a value somewhat smaller than that for calcium, *viz.*, 4.31×10^4 cal./mole. As in the case of calcium the vapor pressures for barium of from 12.5 to 26.5 mm in a small range near 1100°C, obtained by Hartmann and Schneider,⁸ using the boiling point method, are higher than one would expect from these low pressure measurements by the method of molecular effusion. Unfortunately there are no reliable data for the specific heat of barium. It is therefore not possible to compute the heat of evaporation at $T=0$ and the vapor pressure constant from these measurements at present.

⁸ Hartmann and Schneider, *Zeits. f. anorg. u. allg. Chem.* **180**, 275 (1929).

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The Thermal Equilibrium Between Ethylene Iodide, Ethylene and Iodine

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The thermal equilibrium between ethylene iodide, ethylene and iodine in the vapor state has been studied in the temperature range 50 to 125°C. The method devised involved measurements of the iodine vapor pressure by a photometric device utilizing photronic cells in a null-point arrangement. Iodine and ethylene iodide were both present as unsaturated vapors. The measurements gave results

which were found to agree with the extrapolation of Mooney and Ludlam's data for lower temperatures, but to disagree with the same authors' higher temperature determinations. The heat of dissociation of ethylene iodide is 13.4 ± 0.5 kcal. The position of equilibrium is given by: $\log K = -13,400/4.58T + 8.17$, where the equilibrium constant is expressed in atmospheres as units.

STUDY of this equilibrium has already been described in the literature. Mooney and Ludlam¹ investigated the gaseous equilibrium in the presence of solid iodine and ethylene iodide at temperatures from 10 to 65°C. The plot of the logarithm of the equilibrium constant against inverse temperature gave a curve which they chose to interpret as two straight lines. One, with a slope corresponding to a heat of reaction

of 13.4 kcal., was drawn in the temperature range 10 to 45°; the other, with 22.3 kcal. as the heat of reaction, represented the points from 45 to 65°. This second value they considered the more reliable of the two.

Polissar² studied the equilibrium in solution with carbon tetrachloride as the solvent. Between 122 and 152°C he obtained 11.3 kcal. as the heat of reaction. He interpreted the mechanism of the reaction with the aid of chains

¹ Mooney and Ludlam, *Proc. Roy. Soc. Edin.* **49**, 160 (1929).

² Polissar, *J. Am. Chem. Soc.* **52**, 956 (1930).

involving free iodine atoms and from this mechanism deduced an independent value for the heat of reaction equal to 13 kcal.

Combustion data of Berthelot³ alone give 16 kcal. for the reaction between solid ethylene iodide and iodine and gaseous ethylene. Combined data of Berthelot and of Mixer⁴ give 20.4 kcal. for the same quantity.

There is thus a considerable uncertainty about the heat of this reaction, which cannot be accounted for by the different physical state of the components in the several determinations cited. The same uncertainty exists concerning other organic iodine compounds and it seemed to us worth while to redetermine the heat of dissociation of ethylene iodide since this value may be used, at least as a crude approximation, for other iodine compounds also.

APPARATUS AND METHOD

It was intended to study the homogeneous gaseous equilibrium in the absence of solid or liquid condensates since it was their presence which must have caused the uncertainty of Mooney and Ludlam's results. The system chosen was a static one and three determinations were needed to calculate the position of equilibrium. They involved the measurement of the total pressure—with the aid of a quartz spiral gauge as a null instrument; the measurement of the total amount of iodine present (as free iodine or as ethylene iodide), which was accomplished by weighing the amount of iodine or ethylene iodide introduced into the apparatus; and the measurement of free iodine vapor by a photometric method.

The all-glass apparatus, placed into an air thermostat with automatic temperature regulation, consisted of the photometer tube, with plane-parallel windows, 40 cm long; a magnetically operated all-glass pump for circulation of the gases; the quartz manometer; a magnetic hammer for breaking the glass ampules containing weighed amounts of iodine or ethylene iodide and a system for introducing ethylene, which was sealed off from the rest during the runs.

³ Berthelot, *Ann. Chim. Phys.* (7) **21**, 296 (1900).

⁴ Mixer, *Am. J. Sci.* (4) **12**, 347 (1901).

The pump, of the Lind⁵ design with some minor improvements, was found necessary because otherwise, even after twenty-four hours, the diffusion of iodine throughout the apparatus was not completed and no consistent readings could be obtained.

The photometer utilized two photronic cells and worked by the null method. Light from a small projection lamp was made parallel by two short-focus lenses. One beam passed through the absorption tube in the thermostat and on to one cell; the other passed through two Nicol prisms and on to the other cell. The cells were opposed and connected to a L & N high sensitivity galvanometer. One of the Nicol prisms could be rotated and was provided with the usual circular scale. It was adjusted, in taking readings, until the galvanometer gave a zero deflection; the lamp was turned on several minutes before taking the readings, to age the photronic cells. We found it most essential to keep the temperature of the cells constant and equal as otherwise considerable variation of the zero point was the result. It is well known⁶ that the absorption of iodine depends to some extent on the presence of foreign gases. This is true of the banded region of absorption and therefore light filters were used to cut off all light above *ca.* 5000Å in both light beams. They consisted of a 5 mm Corning lantern blue glass and of 2 mm medium cobalt glass. It was found that with the filters in place (but not without them) an addition of a full atmosphere of air made no measurable change in the absorption of iodine vapor. Since the effect on absorption of iodine is due chiefly to paramagnetic molecules, such as oxygen, while ethylene is diamagnetic, we feel justified in concluding that ethylene also has no effect on iodine absorption, under our experimental conditions, although such an experiment was not performed.

The calibration of the photometer was obtained by measuring the light absorption of iodine vapor of known pressure, in the presence of solid iodine in an otherwise evacuated apparatus; the temperature of the thermostat was carefully measured and the Giauque⁷ data on

⁵ Porter, Bardwell and Lind, *Ind. Eng. Chem.* **18**, 1086 (1926).

⁶ Loomis and Fuller, *Phys. Rev.* **39**, 180 (1932).

⁷ Giauque, *J. Am. Chem. Soc.* **53**, 507 (1931).

the vapor pressure of iodine used. Such calibrations were made over the entire range of iodine pressures used in the present investigation. An objection may be raised against this procedure because the calibration and the observations in the several runs were made at different temperatures. We have found, however, that the change in absorption of a fixed amount of iodine vapor over the small temperature range covered in these experiments is well within our experimental errors which amounted to about 0.3 percent of the maximum light transmitted.

The zero point of the photometer did not remain sufficiently constant over the periods of several days needed for a run, and therefore the absorption tube was attached to the rest of the apparatus by means of flexible glass tubing spirals so that it could be swung out of the light path. Thus a zero point of the photometer could be determined at frequent intervals.

To calculate the pressure of iodine from the weighed amounts introduced the volume of the apparatus had to be determined. This was done with the aid of a gas burette and pressure readings. A determination of the iodine pressure by the photometer, after a known weight of iodine, not enough to give saturation pressure, was introduced into the evacuated system, showed the correctness of this determination and also the absence of more than negligible adsorption on the glass walls.

In the temperature range covered in this work, 50 to 125°C, the equilibrium is very far on the side of dissociation and when approximately equal pressures of iodine and ethylene iodide, not too far from saturation, are desired, a large excess of ethylene is needed. This was introduced by decomposing purified ethylene iodide made by the method of Semenov.⁸ Vapor of ethylene iodide, from a heated trap, was passed through a tube heated electrically to about 300°C, where it decomposed to more than 75 percent, then through two traps filled with glass wool and cooled by solid carbon dioxide and into the apparatus. When sufficient pressure was built up, the preparative unit was sealed off. Previously, of course, the entire system was thoroughly evacuated with a high vacuum pump

and then sealed off from it, while the ethylene iodide for generation of ethylene was kept cold. No iodine or ethylene iodide passed through the traps as tested by the absorption measurements. After ethylene was introduced into the system, one of the ampules containing the iodine was broken magnetically and the temperature of the thermostat adjusted a few degrees above or below that one at which it was desired to determine the equilibrium. After allowing the equilibrium to establish itself approximately, the temperature was changed to the final setting and accurate readings were begun.

RESULTS

Table I gives the results of all experiments performed with the final form of apparatus. It was found to be more convenient to use iodine in the weighed tubes and in order to be certain that true equilibrium was reached, it was approached both from the side of higher and the side of lower temperatures of the thermostat. The first procedure means an initial excess of iodine, the latter an excess of ethylene iodide. The adjustment of the temperature of the thermostat took several hours as a rule and in that time the equilibrium was usually established. However, it was followed for a whole day. Several temperatures were studied with the same sample of iodine and ethylene and then more iodine from another tube added and higher temperatures investigated before the apparatus was opened and an entirely new filling made. In the first column of the table the capital letters

TABLE I.

		<i>T</i> ° Furnace	<i>P</i> (mm) (C ₂ H ₄)	<i>P</i> (mm) (sample)	<i>P</i> (mm) I ₂	<i>K</i>
<i>C</i>	<i>i</i>	50.3	107.3	2.31	1.17	110.1
<i>C</i>	<i>e</i>	50.2	107.9	2.31	1.17	110.7
<i>A</i>	<i>e</i>	70.0	384.5	7.17	3.39	345
<i>A</i>	<i>i</i>	69.7	385.3	7.17	3.39	345
<i>C + De</i>		76.1	120.4	10.38	8.19	449
<i>A + Bi</i>		88.0	406.3	17.38	11.72	841
<i>A + Be</i>		90.6	410.0	17.52	12.20	940
<i>A</i>	<i>e</i>	90.8	401.2	7.60	5.84	1331
<i>A + Be</i>		99.6	421.5	17.94	14.07	1532
<i>E</i>	<i>i</i>	107.6	672.0	52.70	40.08	2134
<i>E</i>	<i>e</i>	125.0	709.0	55.11	49.20	5902

⁸ Semenov, *Jahr. Fort. Chem.*, 483 (1864).

indicate the sample of iodine, while the letters *e* and *i* show whether the approach to equilibrium was made from the side of lower temperatures (and excess of ethylene iodide) or from the side of higher ones (and excess of iodine). The next column gives the temperature of the thermostat, the following one the pressure of ethylene calculated as the difference of the total pressure and that of the other two constituents of the mixture. The fourth column gives the total pressure (as free iodine plus ethylene iodide) of iodine and ethylene iodide introduced, while in the fifth are recorded the pressures of free iodine from the photometric measurements. The difference of these two columns gives the calculated pressure of ethylene iodide. The last column gives the equilibrium constant of the reaction in mm mercury as units:

$$K = P_{C_2H_4} \cdot P_{I_2} / P_{C_2H_4I_2}$$

In Fig. 1 the logarithms of the equilibrium constants of Table I have been plotted against inverse temperature. It will be observed that the points fall on a straight line with the exception of the value at 90.8°C. In this experiment very little ethylene iodide was present and a relatively small error in iodine pressure will result in a large error in the equilibrium constant. Fig. 1 contains also the data of Mooney and Ludlam and it will be observed that not their high temperature constants, but only those obtained in the low range fall on the continuation of the straight line obtained in the present work. It appears thus that some source of error which Mooney and Ludlam failed to avoid distorted the measurements in the upper temperature range. We are uncertain as to how this error crept into their measurements, but a formation of solid solutions of iodine and ethylene iodide present in their experiments seems to be not out of the question, although it is doubtful whether in this way the entire discrepancy can be accounted for.

The heat of the reaction obtained from our measurements is found to be 13.4 kcal. and if one includes the low temperature determinations of Mooney and Ludlam in deciding upon the slope of the line in Fig. 1, the estimated error is

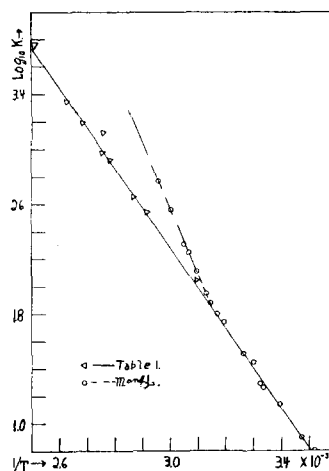


FIG. 1.

of the order of 0.5 kcal. The new measurements alone give a considerably larger error, because of the shorter temperature range covered.

The heat of dissociation here presented is in good agreement with Berthelot's figure from the combustion data, which, upon correcting to gaseous state of all participants,^{1, 7} is found to be 15.5 kcal. The use of Mixer's data for the heat of combustion of ethylene, which leads to a value of more than 20 kcal. for the heat of dissociation, is certainly not justified because, in conjunction with reliable values for the heat of combustion of ethane, it gives a decidedly wrong heat of hydrogenation of ethylene.⁹

Also the results of Polissar are consistent with the present determination, considering the errors involved, and it appears thus that no well founded objections to the value of 13.4 kcal. can be found in the literature. The method described in this contribution is capable of being used with higher homologues of ethylene, no stable diiodides of which are known. It should be of some interest to determine whether the decreased stability is due to a lower heat of dissociation or to the less favorable entropy change in reaction. Such work is being planned now.

⁹ Kistiakowsky *et al.*, J. Am. Chem. Soc. **57**, 65 (1935).