6. No evidence was found that common lead is composed either wholly or in part of isotopes of different atomic weight.

We are very greatly indebted to the Carnegie Institution of Washington for generous assistance in the pursuit of this investigation.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

# THE VAPOR PRESSURE OF IODINE BETWEEN 50° AND 95°.

BY GREGORY PAUL BAXTER AND MERRITT ROY GROSE.

Received March 1, 1915.

Some years ago the vapor pressure of iodine was determined in the Harvard Laboratory[1] by the "air current" method throughout the temperature range 0° to 55°. This earlier research was interrupted by the end of the college year during attempts to continue the work at still higher temperatures. In the present investigation the difficulties met at the close of the earlier work were overcome and the method has been extended to cover the temperatures up to 95°.

The procedure in general was to pass a measured volume of pure, dry air, first over the pure iodine, and then into a solution of sodium carbonate to absorb the volatilized iodine. From the carbonate solution, after acidification and reduction of the liberated iodine by means of hydrazine, the iodine was precipitated as silver iodide, which was collected and weighed. In the experiments below 55°, sodium sulfite was used to absorb the iodine, but at higher temperatures this proved too easily oxidized by the oxygen of the air current. An aqueous solution of hydrazine did not reduce the iodine rapidly enough, while sodium hydroxide, attacked the glass apparatus very rapidly.

The purification of the iodine was carried out by methods which have been found effective in earlier researches.[2] Commercial iodine was dissolved in aqueous potassium iodide and distilled from a retort into a Jena flask cooled with running water. The product was several times rinsed with water, and was then suspended in water and reduced to hydriodic acid by means of well scrubbed hydrogen sulfide gas. After being boiled for some time to remove hydrocyanic acid which might have had its source in cyanogen impurity in the iodine, the solution was filtered to remove coagulated sulfur, and was then oxidized in a retort with a slight excess of potassium permanganate. In the latter process there is set free only five-eighths of the iodine, which was then distilled from the solution of potassium and manganous iodides as before. Although this second distillation from an aqueous iodide must have eliminated every trace of

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[1] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907).

[2] THIS JOURNAL, **26**, 1577 (1904); **27**, 876 (1905).

chlorine and bromine, the product was again reduced with hydrogen sulfide and the hydriodic acid solution was oxidized with recrystallized permanganate. The final product was thoroughly rinsed with water, drained on a perforated porcelain funnel and superficially dried over sulfuric acid for some time.

During the course of the work the tube containing the iodine was several times broken so that the contents were wet with the thermostat water. After such an accident the iodine was redistilled from the final solution of potassium and manganous iodides obtained in the purification of the iodine, which was carefully saved for the purpose. Naturally, rinsing and drying of the iodine followed in each case.

Since iodine which has been dried over sulfuric acid still retains water, the partially dried material was finally distilled in a current of dry air in a hard glass tube. The tube was constricted at three points and the iodine was distilled from porcelain boats into the first section, then into the second and third and finally from the tube into a Jena glass retort. The iodine was gently scraped from the walls of the retort.

Sodium carbonate and silver nitrate were both twice crystallized, the latter from nitric acid solution, in order to remove chlorides.

In order to prepare hydrazine, the sulfate was treated with a solution of a large excess of sodium hydroxide in a platinum retort, and the hydrazine was distilled through a platinum condenser. The product was then redistilled. The approximate concentration of the solution was found by comparison with a standard solution of iodic acid in the presence of sodium acetate.

The air used for the sublimation of the iodine was first passed through a tube filled with hot copper oxide, then through a series of towers, one of which contained beads moistened with a solution of potassium hydroxide containing potassium permanganate; one, silver nitrate solution; and three, concentrated sulfuric acid. The last traces of moisture were removed by resublimed phosphorus pentoxide. The apparatus was constructed wholly of glass. The air used in the vapor pressure experiments was not passed over hot copper oxide, but otherwise was similarly purified.

The apparatus used for saturating the air with iodine and for absorbing the iodine was constructed in very much the same way as that used in the earlier research. A spiral glass tube, of about 1 cm. internal diameter, contained the iodine, which formed a column about 30 cm. long. Air was passed through a ground joint from the purifying train into one end of this tube. The other end of the tube was connected by means of a ground joint with the first absorbing tube containing a concentrated solution of sodium carbonate. A second absorbing spiral containing sodium carbonate solution was fused to the first, and in some experiments a third absorbing tube was attached to the first two by a ground joint.

Since, however, no iodine was ever found in the third absorber, in later experiments it was omitted. During a run, the iodine tube and first absorbing tube, including the connecting joint, were immersed in the water of the thermostat. It was necessary of course that this joint should be both tight and dry. Both results were secured by covering the joint completely with a piece of rubber tube securely wired in place. Since the joint was at the temperature of the thermostat it was to be expected that no iodine would condense between the saturating and first absorbing tube, and this was invariably the case, except in two of the preliminary experiments where a very small amount of solid iodine was found in the joint. The outlet of the iodine tube was constricted to 2 mm. to prevent diffusion into the absorbing bulb.

From the second absorbing tube the air passed into the large aspirator bottle used to produce the air current. This bottle, which had a capacity of more than 8 liters, was provided with a thermometer, an open tube mercury manometer, and an outlet tube through which the water content flowed into a carefully standardized bottle of about 8 liters volume in the experiments at the lower temperatures, of about 5 liters volume in the experiments at the higher temperatures. The rubber stoppers in the upper and lower tubulatures of the aspirator bottle were made tight with grease and in addition were wired in place and covered with shellac. The aspirator bottle was also jacketed with plumbers wool to secure constancy in temperature, and the temperature of the water at the outset was adjusted to that of the room so that no appreciable change in temperature of the water occurred during an experiment. The temperature of the room itself was controlled within a very few degrees by a thermostat.

The thermostat had a capacity of 25 liters, and was jacketed with an inch of plumbers wool. The greater part of the necessary heat was furnished by a burner under the thermostat tank, but the fine adjustment of temperature was secured by an incandescent light bulb controlled by a mercury-toluene regulator in the usual way. A mechanical stirrer proved very efficient in preventing variations in temperature in different parts of the bath. In order to avoid disturbances from evaporation at the surface of the bath, in experiments above 70° the water was covered with a layer of paraffine, which also reduced greatly the heat necessary to operate the bath and prevented unpleasant humidity in the laboratory even at 95°.

The corrections of the thermometers were found to hundredths of a degree by comparison with one standardized by the Physikalisch-Technische Reichsanstalt, due allowance being made for the exposed thread.

The procedure of an experiment was the usual one. After the apparatus had been connected, and the iodine tube with the first absorbing tube containing nearly saturated sodium carbonate solution had been allowed to come to the temperature of the thermostat, the aspirator was started. No water was collected from the aspirator bottle, however, until air began to bubble through the sodium carbonate solution in the first absorbing bulb. At this point the reading of the manometer in the aspirator bottle was taken and at the end of the experiment the pressure in the aspirator bottle was brought to exactly the same point. The temperature of the water in the aspirator also was noted. When the receiving bottle was full of water, its temperature was taken and if this temperature was different from the initial temperature of the aspirator, a correction was applied to the volume of the water. The difference was never more than 2°. At the end of the experiment the temperature of the air in the aspirator bottle was read and also the barometric pressure upon a Green barometer.

As soon as the absorbing tubes had been disconnected from the iodine tube at the close of an experiment, a small amount of hydrazine was added to the absorbing tube nearest the iodine tube. This served to collect any iodine vapor still unabsorbed and to decolorize the absorbing solution, which in experiments at higher temperatures was usually somewhat brown.

As the temperature rose the amount of carbon dioxide freed by the action of the iodine upon the sodium carbonate became appreciable. Some of this undoubtedly was held by the cold sodium carbonate solution in the second absorbing bulb, and some was dissolved in the water of the aspirator bottle. In order to remove this carbon dioxide a bulb containing a solution of potassium hydroxide was inserted in the aspirating system between the second absorbing bulb and the aspirator bottle in many of the experiments at 80° and above. Even at 85° it was doubtful whether any real benefit was produced by the potassium hydroxide bulb, so that it is certain that its omission at the lower temperatures introduced no error. At 90° the experiments in which the above precaution was taken yielded somewhat higher results, as would be expected.

The carbonate solution from both absorbing bulbs was rinsed into a large glass stoppered Erlenmeyer flask and an excess of hydrazine was added. Dilute nitric acid in slight excess was next slowly introduced through a funnel extending to the bottom of the solution. As soon as the brown color indicating an excess of acid appeared the flask was tightly stoppered and left till colorless. Then more nitric acid was added, and if any further quantity of iodine separated, the flask was again closed and left till colorless. Care was taken to prevent free iodine from reaching the surface of the solution until the flask was stoppered.

A very dilute solution of a slight excess of pure silver nitrate was used to precipitate the iodine. A large excess was avoided because of the danger of the occlusion of the silver nitrate by the iodine.[1] After long standing

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[1] Köthner and Aeuer, *Lieb. Ann.*, **337**, 123 (1905); Baxter, THIS JOURNAL, **27**, 880 (1905).

the precipitate was washed with water and collected upon a platinum-sponge Gooch crucible. It was dried at 180° in an electric oven before being weighed.

Calculation of the results was carried out as follows:

From the weight of silver iodide the weight of volatilized iodine was determined. The volume of this iodine as vapor was then calculated upon the assumption that 253.9 g. of iodine at 0° and 760 mm. would occupy 22.40 liters. The volume of air into which this iodine vaporized was reduced to the same conditions by means of the following formula:

$$V = v\frac{(B - h - m)}{760}\;\frac{273}{t + 273}$$

in which

$v$ = corrected volume of water run out.
B = barometric reading corrected to 0°.
$h$ = vapor pressure of water at the final temperature of the aspirator.
$m$ = diminution in pressure indicated by the manometer.
$t$ = final temperature of the aspirator.

Since the pressure within the iodine tube was that of the room,[1] the vapor pressure of iodine is then equal to

$$\frac{\text{volume of iodine vapor}}{\text{volume of iodine} + \text{volume of air}} \times \text{barometric pressure.}$$

This method of calculation involves the following assumptions:

1. That no solvent effect is exerted by air upon iodine.
2. That one mole of iodine has a volume of 22.40 liters.

It is well known that in the cases of chlorine and bromine at ordinary temperatures and pressures molecular quantities of these elements occupy considerably less than the theoretical volumes. Furthermore V. Meyer[2] found that at 253° the density of iodine vapor compared with air is 8.86, whence the volume of a mole is 22.2 liters. However, since in our experiments the pressure of the iodine vapor was low even at the higher temperatures, the above assumption seems safe.

Craffts and Meier,[3] have found experimentally that iodine vapor is essentially undissociated at the boiling point of sulfur. Hence, it is improbable that, even at the great dilution of the iodine vapor in our experiments, any measurable dissociation could have taken place.

The bottles in which the water was measured were standardized by filling them from a standardized liter flask, after they had been wet with water and allowed to drain. Previous to use they were allowed to drain the same length of time. The cubical coefficient of expansion of glass is

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[1] This was shown by a manometer located immediately before the iodine tube.

[2] *Ber.*, **13**, 397 (1880).

[3] *Ibid.*, **13**, 861 (1880).

so small, 0.0025%, that no correction is necessary for the slight differences between the temperature of standardization and that of experiment.

In order to make sure that complete saturation of the air with iodine was attained, the rate at which the air was passed through the tube was varied in different experiments within wide limits, the time required for a volume of a liter being in some cases as small as one-half hour and sometimes as much as an hour. The velocity of the air current shows no apparent influence.

Weights were standardized to tenths of a milligram, and a vacuum correction of +0.00007 g. was applied to the larger weights of silver iodide.

TABLE I.—THE VAPOR PRESSURE OF IODINE.

| Temperature centigrade. Degrees. | Rate per hour. L. | Volume of air corr. to 0° and 760 mm. Cc. | Barometric pressure corr. to 0°. Mm. | Weight of AgI. G. | Vapor pressure of iodine. Mm. |
|---|---|---|---|---|---|
| 50 | 1.6 | 7152 | 765.3 | 0.4222 | 2.149 |
| 50 | 1.6 | 7025 | 753.3 | 0.4218 | 2.151 |
| 50 | 1.6 | 7183 | 763.2 | 0.4279 | 2.163 |
| | | | | Mean, | 2.154 |
| 55 | 2.0 | 6917 | 746.1 | 0.5973 | 3.061 |
| 55 | 1.1 | 7034 | 759.0 | 0.5984 | 3.067 |
| 55 | 1.2 | 7019 | 761.7 | 0.5973 | 3.079 |
| 55 | 1.5 | 7238 | 758.9 | 0.6173 | 3.075 |
| 55 | 1.3 | 7059 | 751.9 | 0.6049 | 3.061 |
| | | | | Mean, | 3.069 |
| 60 | 1.6 | 7123 | 751.3 | 0.8517 | 4.261 |
| 60 | 1.7 | 6635 | 744.0 | 0.8064 | 4.288 |
| 60 | 1.5 | 7175 | 749.7 | 0.8710 | 4.316 |
| 60 | 1.5 | 7124 | 758.8 | 0.8453 | 4.271 |
| 60 | 2.0 | 6161 | 749.2 | 0.7457 | 4.300 |
| 60 | 1.0 | 7116 | 754.6 | 0.8497 | 4.273 |
| 60 | 1.2 | 7057 | 745.6 | 0.8551 | 4.284 |
| | | | | Mean, | 4.285 |
| 65 | 1.5 | 7169 | 762.7 | 1.1819 | 5.951 |
| 65 | 1.8 | 6979 | 751.2 | 1.1660 | 5.939 |
| 65 | 1.3 | 7087 | 767.8 | 1.1655 | 5.976 |
| 65 | 1.0 | 7211 | 762.8 | 1.1919 | 5.967 |
| 65 | 2.0 | 7267 | 770.2 | 1.1916 | 5.977 |
| | | | | Mean, | 5.962 |
| 70 | 1.2 | 7227 | 768.6 | 1.6422 | 8.242 |
| 70 | 1.6 | 7243 | 765.3 | 1.6531 | 8.241 |
| 70 | 1.2 | 7183 | 763.5 | 1.6310 | 8.180 |
| 70 | 1.8 | 7167 | 765.3 | 1.6400 | 8.263 |
| 70 | 1.3 | 7230 | 770.2 | 1.6245 | 8.167 |
| 70 | 1.5 | 7048 | 746.6 | 1.6274 | 8.133 |
| 70 | 1.0 | 6267 | 757.6 | 1.4299 | 8.156 |
| 70 | 1.8 | 7136 | 761.0 | 1.6276 | 8.190 |
| 70 | 1.1 | 7135 | 760.4 | 1.6299 | 8.196 |
| 70 | 1.6 | 7097 | 757.5 | 1.6262 | 8.189[1] |
| | | | | Mean, | 8.196 |

[1] KOH bulb used.

TABLE I.—THE VAPOR PRESSURE OF IODINE (*continued*).

| Temperature centigrade. Degrees. | Rate per hour. L. | Volume of air corr. to 0° and 760 mm. Cc. | Barometric pressure corr. to 0°. Mm. | Weight of AgI. G. | Vapor pressure of iodine. Mm. |
|---|---|---|---|---|---|
| 75 | 1.2 | 7064 | 762.2 | 2.2046 | 11.18 |
| 75 | 1.2 | 7151 | 760.0 | 2.2409 | 11.19 |
| 75 | 1.2 | 6885 | 739.2 | 2.2327 | 11.26 |
| 75 | 1.2 | 7082 | 753.5 | 2.2385 | 11.19 |
| 75 | 1.0 | 7154 | 763.7 | 2.2414 | 11.24 |
| | | | | Mean, | 11.21 |
| 80 | 1.4 | 4620 | 761.3 | 1.9568 | 15.08 |
| 80 | 1.3 | 4641 | 769.4 | 1.9438 | 15.07 |
| 80 | 1.1 | 7170 | 759.7 | 3.0461 | 15.09 |
| 80 | 1.4 | 4674 | 774.0 | 1.9473 | 15.08 |
| 80 | 2.0 | 7188 | 760.9 | 3.0486 | 15.09 |
| 80 | 1.4 | 4564 | 755.3 | 1.9559 | 15.13[1] |
| 80 | 1.5 | 4582 | 760.5 | 1.9442 | 15.09[1] |
| 80 | 1.7 | 4545 | 770.6 | 1.9024 | 15.08[1] |
| | | | | Mean, | 15.09[1] |
| 85 | 1.0 | 4606 | 762.0 | 2.6079 | 20.04 |
| 85 | 1.9 | 4563 | 757.1 | 2.6205 | 20.19 |
| 85 | 1.9 | 4585 | 764.6 | 2.6057 | 20.18 |
| 85 | 1.7 | 4573 | 755.3 | 2.6421 | 20.26 |
| 85 | 1.9 | 4608 | 761.7 | 2.6390 | 20.25 |
| 85 | 1.3 | 4499 | 755.5 | 2.6066 | 20.32[1] |
| 85 | 1.2 | 4595 | 767.2 | 2.6011 | 20.17[1] |
| 85 | 1.5 | 4379 | 758.7 | 2.5067 | 20.16[1] |
| | | | Mean, rejecting the first, | | 20.21 |
| 90 | 1.3 | 4645 | 765.2 | 3.5377 | 26.82[1] |
| 90 | 1.1 | 4614 | 762.1 | 3.5371 | 26.88[1] |
| 90 | 1.3 | 4542 | 762.3 | 3.4489 | 26.65[1] |
| | | | | Mean, | 26.78 |
| 95 | 1.4 | 4583 | 764.7 | 4.6367 | 35.20[1] |
| 95 | 1.5 | 4605 | 771.3 | 4.6310 | 35.31[1] |
| 95 | 1.5 | 4551 | 762.0 | 4.6215 | 35.21[1] |
| | | | | Mean, | 35.24 |

At 50° the vapor pressure of iodine, 2.154 mm., agrees exactly with that previously found by Baxter, Hickey and Holmes. At 55° the value found here is slightly lower, but that is not surprising, because in the earlier work difficulty was experienced above 50° from separation of iodine at the ground joint between the iodine tube and the first absorbing tube. Our results are uniformly lower than those of Wiedermann, Stelzner and Niedershulte.[2] The curve plotted with our values against the temperature (Curve 1) makes a very satisfactory extension of the one obtained by Baxter, Hickey and Holmes, and is not very different from that plotted

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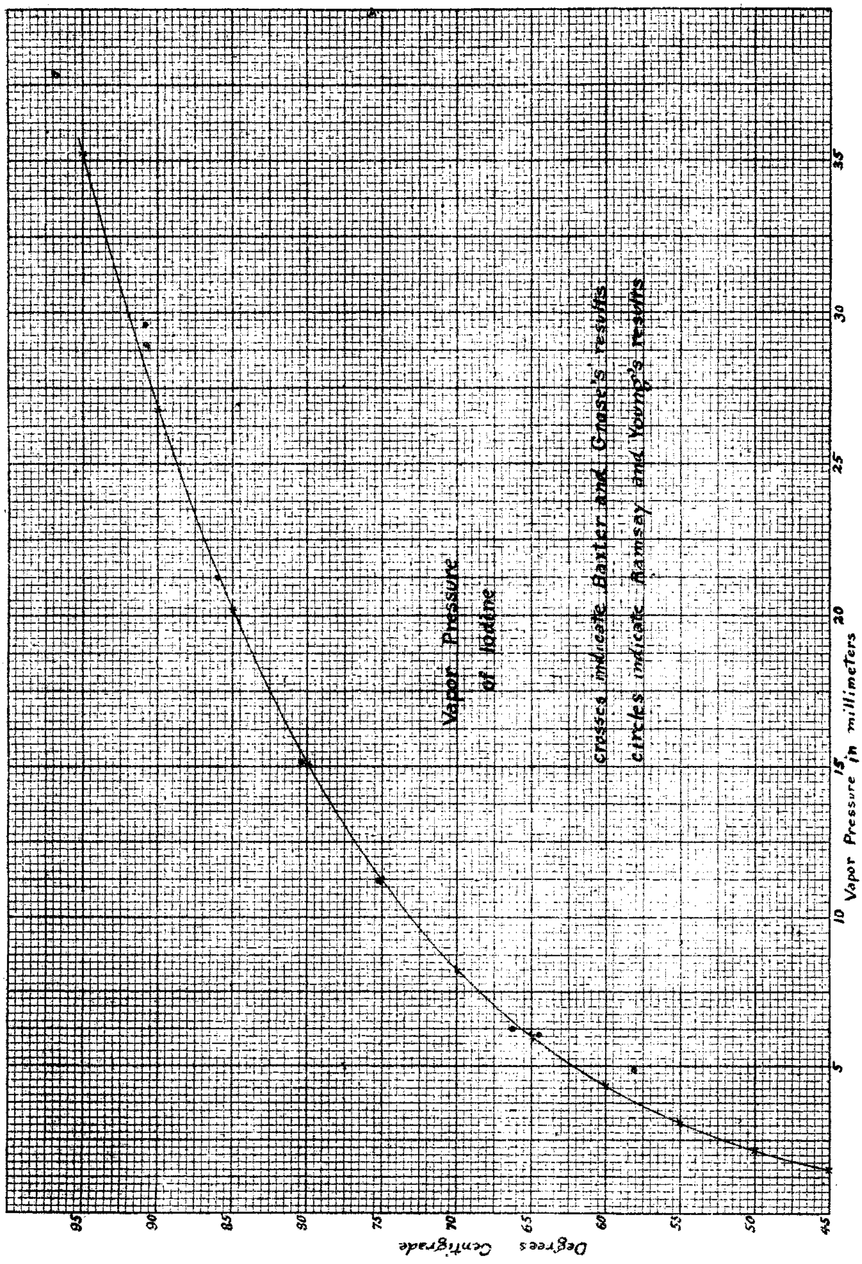
[1] KOH bulb used.

[2] *Verh. phys. Ges.*, **3**, 159 (1905).


Vapor Pressure
of Iodine
crosses indicate Baxter and Grose's results
circles indicate Ramsay and Young's results
Vapor Pressure in millimeters
5
10
15
20
25
30
35
Degrees Centigrade
95
90
85
80
75
70
65
60
55
50
45

Curve I.

with Ramsay and Young's[1] results over the same temperature range, thus giving a very satisfactory comparison of a static and a dynamic method.

Many attempts were made to find a mathematical relationship between vapor pressure and temperature, and two of these were successful enough to warrant drawing attention to them. If the logarithm of the vapor pressure is plotted against the logarithm of the absolute temperature, the result is not far from a straight line. This curve can be represented very closely by the equation

$$\log p = -106.3930 + 46.611 \log \mathrm{T} - 0.031677\,\mathrm{T}$$

which differs from the thermodynamic equation developed by Clausius only in that the absolute temperature appears in the numerator instead of the denominator of the last term. The results obtained with this equation over the range 0–95° are given in Table II.

TABLE II.

| Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. | Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. |
|---|---|---|---|---|---|---|---|
| 0 | 0.032 | 0.030 | +0.002 | 60 | 4.285 | 4.285 | 0.000 |
| 15 | 0.131 | 0.131 | 0.000 | 65 | 5.962 | 5.962 | 0.000 |
| 25 | 0.311 | 0.305 | +0.006 | 70 | 8.210 | 8.196 | +0.014 |
| 30 | 0.469 | 0.469 | 0.000 | 75 | 11.19 | 11.21 | —0.02 |
| 35 | 0.699 | 0.699 | 0.000 | 80 | 15.11 | 15.09 | +0.02 |
| 40 | 1.027 | 1.025 | +0.002 | 85 | 20.21 | 20.21 | 0.00 |
| 45 | 1.494 | 1.498 | —0.004 | 90 | 26.78 | 26.78 | 0.00 |
| 50 | 2.146 | 2.154 | —0.008 | 95 | 35.20 | 35.24 | —0.04 |
| 55 | 3.050 | 3.069 | —0.019 | | | | |

The most satisfactory results were obtained by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Through the range under consideration the points fall almost upon a straight line (see Curve 2), and by using the function $1/(\mathrm{T}-19)$ instead of $1/\mathrm{T}$ the plot becomes exactly a straight line within the limit of error of the experimental results. This means of course that the vapor pressure can be calculated from an equation of the form $\log p = \mathrm{A} - \mathrm{B}/(\mathrm{T} - 19)$. This equation has already been proposed by Antoine.[2] It is essentially the thermodynamic equation without the term involving the logarithm of the absolute temperature. With the values 9.7522 and 2863.54 for A and B, respectively, Table III was computed.

Above 95° both equations yield values increasingly higher than those observed by Ramsay and Young, possibly because the vapor pressure is becoming irregular as the melting point 114° is approached. Below

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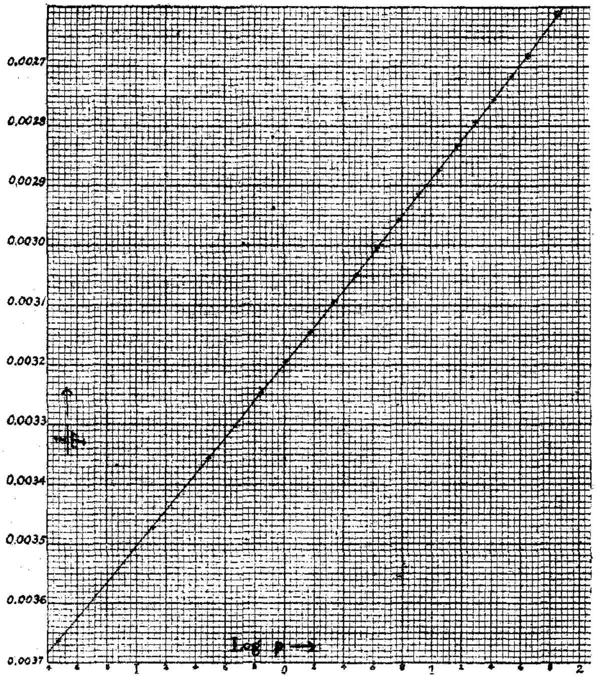
[1] *J. Chem. Soc.*, **49**, 453 (1886). Obtained by coating a thermometer bulb with iodine and measuring the pressure manometrically.

[2] *Compt. rend.*, **110**, 632 (1890); **112**, 284 (1891); **113**, 328 (1892); **116**, 170 (1893).

0° the calculated values are not widely different from those of Haber and Kerschbaum.[1]



Curve 2.

TABLE III.

| Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. | Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. |
|---|---|---|---|---|---|---|---|
| 0 | 0.030 | 0.030 | 0.000 | 60 | 4.291 | 4.285 | +0.006 |
| 15 | 0.128 | 0.131 | —0.003 | 65 | 5.965 | 5.962 | +0.003 |
| 25 | 0.308 | 0.305 | +0.003 | 70 | 8.205 | 8.196 | +0.009 |
| 30 | 0.467 | 0.469 | —0.002 | 75 | 11.18 | 11.21 | —0.03 |
| 35 | 0.698 | 0.699 | —0.001 | 80 | 15.09 | 15.09 | 0.00 |
| 40 | 1.029 | 1.025 | +0.004 | 85 | 20.19 | 20.21 | —0.02 |
| 45 | 1.497 | 1.498 | —0.001 | 90 | 26.79 | 26.78 | +0.01 |
| 50 | 2.151 | 2.154 | —0.003 | 95 | 35.26 | 35.24 | +0.02 |
| 55 | 3.056 | 3.069 | —0.013 | | | | |

It is also interesting to calculate from the experimental results the molecular heat of sublimation of solid iodine by means of the Clausius equation

$$L = T\,dp/dT\,(V - V_1)$$

where L = heat of sublimation.

T = absolute temperature.

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[1] *Z. Electrochem.*, **20**, 296 (1914).

$dp/dT$ = change of vapor pressure per degree of temperature, expressed in atmospheres.

$V$ = volume of one mol of iodine vapor at T° and at vapor pressure, expressed in liters.

$V_1$ = volume of one mol of solid iodine at T° in liters.

The change in vapor pressure with the temperature was calculated by dividing the difference in vapor pressure in each five degree interval by five. The absolute temperature was taken as the mean of the five degree interval. The vapor pressure at this temperature was estimated from a large scale curve. $V_1$ is so small, compared with V, that it is neglected in the calculations. The final result is multiplied by 0.02425 to convert it from liter atmospheres to kilogram calories. The values in kilogram calories multiplied by 4.183 give the results in kilojoules.

TABLE IV.

| Temperature. Degrees. | Vapor pressure estimated. Mm. | Molecular heat of sublimation. Kilogram calories. | Molecular heat of sublimation. Kilojoules. |
|---|---|---|---|
| 273 + 52.5 | 2.575 | 15.0 | 62.7 |
| 273 + 57.5 | 3.630 | 14.6 | 60.9 |
| 273 + 62.5 | 5.070 | 14.8 | 62.0 |
| 273 + 67.5 | 7.000 | 14.7 | 61.6 |
| 273 + 72.5 | 9.61 | 14.9 | 62.4 |
| 273 + 77.5 | 13.03 | 14.6 | 60.9 |
| 273 + 82.5 | 17.48 | 14.7 | 61.6 |
| 273 + 87.5 | 23.33 | 14.6 | 60.9 |
| 273 + 92.5 | 30.75 | 14.6 | 61.2 |
| | Mean, | 14.7 | 61.6 |

These values agree as well as could be expected, for at 75° an error in the determination of the vapor pressure of four-hundredths of a millimeter produces an error of 1% in *dp*, and of 0.3% in V. In fact, the agreement of the heats of sublimation is good confirmation of the accuracy of the experimental work.

The mean value of the molecular heat of sublimation between 50° and 95° is only slightly lower than the mean between 0° and 55° as found by Baxter, Hickey and Holmes, 15.1 kilogram calories or 63 kilojoules.[1]

There seems to be only a slight tendency in the heat of sublimation to diminish up to 95°, although Ramsay and Young's results between 95° and the melting point 114° do indicate a perceptible drop.[2]

## Summary.

1. The vapor pressure of solid iodine is found to have the following values:

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[1] *Loc. cit.*, 135.

[2] Baxter, Hickey and Holmes, *Ibid.*, 135.

| Temperature. Degrees. | Vapor pressure. Mm. | Temperature. Degrees. | Vapor pressure. Mm. |
|---|---|---|---|
| 50 | 2.154 | 75 | 11.21 |
| 55 | 3.069 | 80 | 15.09 |
| 60 | 4.285 | 85 | 20.21 |
| 65 | 5.962 | 90 | 26.78 |
| 70 | 8.196 | 95 | 35.24 |

2. These results together with those obtained by Baxter, Hickey and Holmes between 0° and 50° may be expressed very closely by either of the two formulas

$$\log p = -106.3930 + 46.611 \log T - 0.031677\,T$$
$$\log p = 9.7522 - 2863.54/(T - 19).$$

3. The average molecular heat of sublimation of iodine at these temperatures is calculated to be 14.7 kilogram calories or 61.6 kilojoules.

A portion of the apparatus and materials used were provided through the generous assistance of the Carnegie Institution of Washington.

CAMBRIDGE, MASS.

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# ON FRACTIONAL DISTILLATION WITH REGULATED STILLHEADS.

## [SECOND COMMUNICATION.]

## DISTILLATION OF TERNARY MIXTURES.

BY M. A. ROSANOFF, JOHN F. W. SCHULZE AND R. A. DUNPHY.

Received January 18, 1915.

On the basis of an interesting series of experiments, F. D. Brown[1] describes the distillation of mixtures through a regulated stillhead in terms of the following law, or rule: "In distillations with a stillhead maintained at a constant temperature, *the composition of the distillate is constant,* and is identical with that of the vapor evolved by a mixture whose boiling point equals the temperature of the stillhead." Sometime ago this rule was examined by Rosanoff and Bacon in connection with mixtures whose boiling-point curve passes through a maximum or a minimum,[2] and it was shown that in a case of this type two different distillates may be expected at certain temperatures, depending upon the composition of the liquid originally introduced into the still; but that, whichever of the two possible distillates is produced, the distillation proceeds in conformity with Brown's law, in as far as the composition of the distillate is constant, and is identical with that of the vapor evolved by a mixture whose boiling point equals the temperature of the stillhead.

But both Brown's experiments and those just mentioned dealt exclusively

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[1] Brown, *J. Chem. Soc.*, **37**, 59 (1880); *Ibid.*, **39**, 521 (1881).

[2] Rosanoff and Bacon, first communication of the present series, THIS JOURNAL, **37**, 301 (1915).