The average of these two results is 0.9190, or about one per cent. less than the average density of the two solid metals composing it. Thus

$$0.399 \times 0.862 = 0.344$$
$$0.601 \times 0.971 = 0.584$$
$$\overline{0.928}$$

This expansion upon forming the liquid alloy is noticeably less than that which occurs upon melting the metals separately, sodium expanding 2.5 per cent. and potassium 2.4 per cent.[1] Hence it is to be inferred that the formation of the alloy from the liquefied metals would cause a slight contraction instead of an expansion.

Summary.—The densities and atomic volumes of the five alkali metals at 20° were found as follows, many preparations being used, and great care being exercised in all cases except that of caesium.

	Densities.	Atomic weights (Ag=107.93).	Atomic volumes
Lithium	0.534	7.0	13.1
Sodium	0.9712	23.008	23.70
Potassium	0.8621	39.114	45.38
Rubidium	1.532	85.48	55.8
Caesium	1.87	133.8	71.0

The density of an alloy of 39.9 per cent. of potassium and 60.1 per cent. of sodium was found to be 0.919.

THE VAPOR PRESSURE OF IODINE.

By Gregory Paul Baxter, Charles Hendee Hickey and Walter Chapin Holmes.

The vapor pressure of solid iodine was first accurately determined by Ramsay and Young[2], who obtained the following values by coating with iodine the bulb of a thermometer covered with asbestos, and measuring manometrically the tension of this iodine at different temperatures.

Temperature. Degrees.	Pressure. mm.	Temperature. Degrees.	Pressure. mm.
58.1	4.9	91.8	28.95
64.5	6.05	91.9	29.6
66.3	6.25	96.8	37.8
75.2	11.5	102.7	50.65
80.4	15.15	105.7	59.85
86.0	21.25	113.8	87.0

For the vapor pressure below 58° we are dependent partly upon ex-

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[1] Vincentini and Omodei (1888).
[2] J. Chem. Soc., 49, 453 (1886).

periments by Arctowski[1], who measured the rate with which powdered iodine volatilized from a crystallizing dish in a current of air of constant velocity. By combining the observed loss in weight of the crystallizing dish with the values of the vapor pressure observed by Ramsay and Young he obtained the results:

Temperature. Degrees.	Pressure. mm.
72	8.6
56	3.7
41	1.4
13	0.1

Very recently Wiedermann, Stelzner and Niedershulte[2] passed measured quantities of air over iodine contained in a tube and determined the loss in weight. The results are as follows:

Temperature. Degrees.	Pressure. mm.	Temperature. Degrees.	Pressure. mm.
10	0.06	70	8.35
20	0.25	90	27.
30	0.60	100	47.5
50	2.35		

Our method of experimentation was to pass a measured volume of pure dry air, first over the pure iodine, and then into a solution of sodium sulphite to absorb the volatilized iodine. From this sulphite solution the iodine was precipitated as silver iodide, which was collected and weighed.

The iodine was carefully freed from chlorine, bromine and cyanogen in the fashion already used and described by one of us.[3] After reduction to hydriodic acid by means of hydrogen sulphide and water, the solution was boiled for some hours to eliminate hydrocyanic acid. Next the hydriodic acid was heated with a slight excess of recrystallized potassium permanganate. This process set free five-eighths of the iodine, which was then distilled from the solution of potassium and manganous iodides from the retort into a flask cooled with running water. Then the processes of reduction with hydrogen sulphide, and oxidation of the hydriodic acid with permanganate were repeated, and the final product was again distilled from pure water. In order to dry the iodine, it was drained as completely as possible by suction, and exposed over sulphuric acid in a dessicator until all superficial moisture was eliminated. Finally the dried iodine was twice sublimed in a current of dry air into a retort.

The sodium sulphite and silver nitrate were carefully recrystallized until they were free from chlorides.

The air was purified and dried by conducting it over solid potassium

[1] Z. anorg. Chem., 12, 427 (1896).

[2] Verh. phys. Ges., 3, 159.

[3] Baxter, Pr. Am. Acad., 40, 421 (1904).

hydroxide in the column A, then over beads moistened with concentrated sulphuric acid containing a small quantity of potassium dichromate in the columns B and C. The U-tube D, which contained the iodine, was of about one centimeter internal diameter, and the column of iodine was over twenty centimeters long. The first absorbing tube E, containing sulphite, was connected by a ground joint with the iodine
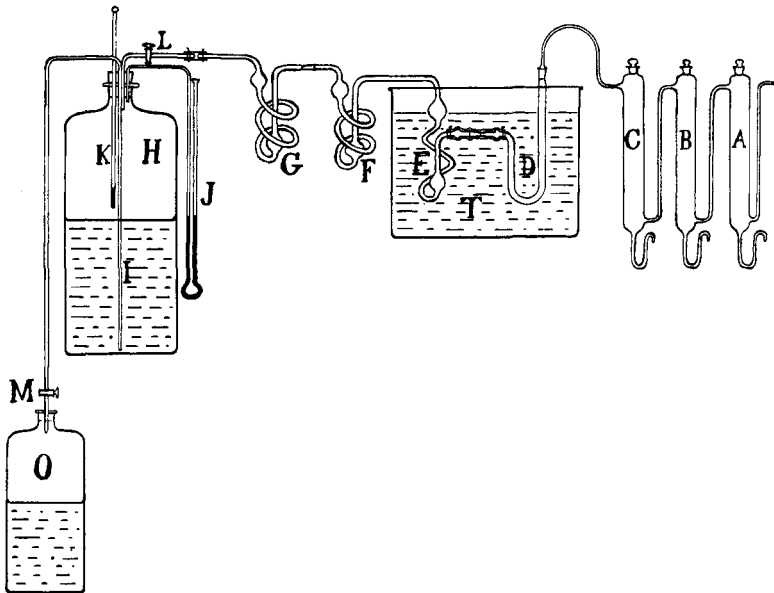
tube. During an experiment this joint was covered with a piece of rubber tubing, securely wired on, and was completely immersed in the water of the thermostat T, so as to prevent condensation of the iodine before reaching the absorbing tube. F and G are auxiliary absorbing tubes containing sulphite. The ground joint between the absorbers G and F was made absolutely tight with grease. G in turn was connected with the aspirator bottle H by a wired rubber connection. Through the rubber stopper of the aspirator bottle passed also a siphon tube I, a mercury manometer J, and a thermometer K. The velocity of the current of gas could be regulated by means of the stopcocks L and M. The volume of water run out of the aspirator bottle was measured in the bottle of known volume O.

The thermostat was thoroughly stirred by a mechanical stirrer. An electric regulator connected with an electric light bulb completed the final adjustment of the temperature, although at the higher temperatures an auxiliary burner was placed below the thermostat, while the lower temperatures were secured at 15° by a coil of lead pipe though which

flowed a current of cold water, and at 0° by filling the thermostat with ice and water.

In each experiment between seven and eight liters of air were passed through the apparatus. Then the tubes D, E and F, and G were disconnected and the iodine tube was placed in a desiccator, containing sulphuric acid, in which it was always preserved between determinations. Next the solution in the absorbing tubes E and F was rinsed into a glass-stoppered precipitating flask, where it was acidified with nitric acid and treated with as slight an excess as possible of silver nitrate. Silver iodide has been found to occlude silver nitrate, if the latter substance is present in excess[1]. After thorough shaking and several hours' standing the precipitated silver iodide was collected upon a Gooch crucible, dried at 150°, and weighed. The auxiliary absorbing tube G was also emptied and the solution tested for iodide, but invariably with negative results.

The barometer was read at the time of the experiment, and was corrected to 0°. The temperature of the aspirator bottle was read at the end of each experiment, and the small diminution in pressure within the bottle was measured by means of the mercurial manometer.

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 254.0 grams 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:

$$V_0 = V \frac{(B - h - m)}{760} \frac{273}{t + 273}$$

in which

$V =$ volume of water run out

$B =$ corrected barometric reading

$h =$ 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, 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.

[1] Köthner and Aeuer, Lieb. Ann., **337**, 123 (1905). Baxter, This Journal, **27**, 880 (1905).

Recent results with chlorine[1] and with bromine[2] have shown that at ordinary temperatures and pressures molecular quantities of these elements occupy considerably less than the theoretical volumes. Furthermore V. Meyer[3] 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, in our experiments the pressure of the iodine vapor was so very low that the above assumption seems safe.

Craffts and Meier[4], have found experimentally that iodine vapor is essentially undissociated at the boiling point of sulphur. Hence it is improbable that, even at the great dilution of the iodine vapor in our experiments, any measurable dissociation could have taken place.

With regard to the experimental accuracy of the work the following points may be emphasized : The bottle O in the figure was standardized by weighing it after it had been wet with water and allowed to drain three minutes, and then weighing it again filled with water. The weight of water was converted to true volume. In use, after each filling, it was allowed to drain the same length of time. The cubical coefficient of expansion of glass is so small, 1/400 per cent., that no correction is necessary for the slight differences between the temperature of standardization and that of experiment.

The aspirator bottle H was completely filled with water at the temperature of the room before the experiment, so that no error in measuring the air could result from the change in temperature of the water remaining in the aspirator. In order to produce a change in volume of one-tenth of one per cent. in the case of water, a change in temperature of five degrees is necessary.

The vapor pressure of water at 20° is only 17.4 mm., hence a liter of water vapor under these conditions weighs less than 0.02 gram. Although evaporation to this extent takes place in the collecting bottle, the total water lost in this way amounts to only two thousandths of a per cent. Undue evaporation was prevented by loosely plugging the mouth of the collecting bottle with cotton.

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 seven and one half liters being in some cases as small as three and one half hours and sometimes as much as seven hours. In no case did the velocity of the air current show any influence, except in one

[1] Friedel and Craffts, C. R., 107, 301 (1888). Leduc, C, R., 116, 968 (1893). Moissan and Binet du Jassoneix, C. R., 137, 1198 (1903). Treadwell and Christie, Z. anorg. Chem., 47, 446 (1905).

[2] Jahn, Ber., 15, 1242 (1882).

[3] Ber., 13, 397 (1880).

[4] Ber., 13, 861 (1880).

experiment at 50°, subsequently discarded, where only two hours were required for five liters. Even in this experiment, the error produced was only 0.02 mm., i. e. less than one per cent. This shows conclusively that saturation of the air with iodine vapor must have been complete in all the experiments.

Attention may be called to the fact that an error in the weight of the silver iodide of nearly 2 mg. is required to affect the observed vapor pressure in the hundredths place.

The thermometer was found to be correct to five hundredths of a degree by comparison with a thermometer calibrated by the Physikalisch-Technische Reichsanstalt.

In some experiments at 50° and in most of those at 55° a minute quantity of iodine crystals was found between the saturating and the first absorbing tube, in spite of the fact that the joint was kept well covered with the water of the thermostat during the experiment, so that the value at 55° is a little uncertain. At 60° this effect was so marked that the experiments were given up. Furthermore at 60° saturation of the air with iodine proved hard to attain.

Temperature of thermostat. Degrees.	Duration of experiment. Hours.	Volume of air. cc.	Barometer corrected. mm.	Temperature of aspirator. Degrees.	Difference in manometer. mm.	Weight of silver iodide. Gram.	Vapor pressure of iodine. mm.
0	5	7499	763.5	20.2	16	0.0053	0.029
0	5	7479	773.1	18.6	18	0.0056	0.030
0	4.5	7479	752.4	17.8	16	0.0058	0.031
						Average	0.030
15.0	5	7479	762.5	20.3	16	0.0241	0.131
15.0	4	7482	741.6	18.9	19	0.0242	0.132
15.0	5	7479	753.8	19.0	17	0.0241	0.131
						Average	0.131
25.0	7.5	7566	753.9	20.7	24	0.0571	0.311
25.0	3	7566	769.0	17.7	20	0.0582	0.311
25.0	3.5	7566	761.4	17.7	17	0.0586	0.312
25.0	6	7566	771.1	19.8	17	0.0580	0.312
25.0[1]	7	8018	758.2	20.8	12.0	0.0596	0.301
25.0[1]	6	8000	753.4	21.1	15.6	0.0577	0.295
25.0[1]	7.5	8000	757.9	24.0	17.5	0.0569	0.296
25.0[1]	5	8000	757.9	22.7	14.8	0.0593	0.305
						Average	0.305
30.0	3.5	7566	768.5	19.8	18	0.0883	0.475
30.0	3.5	7566	766.0	23.7	20	0.0851	0.468
30.0	5.5	7566	765.1	21.2	21	0.0852	0.463
						Average	0.469

[1] Experiment by Mr. Hickey. The remainder were performed by Mr. Holmes.

Temperature of thermostat. Degrees.	Duration of experiment. Hours.	Volume of air. cc.	Barometer corrected. mm.	Temperature of aspirator. Degrees.	Difference in manometer. mm.	Weight of silver iodide. Gram.	Vapor pressure of iodine, mm.
35.0	3.5	7566	759.6	19.4	19	0.1311	0.705
35.0	5	7566	772.7	21.1	19	0.1286	0.697
35.0	3.5	7479	772.8	21.6	17	0.1271	0.697
						Average	0.699
40.0	5.5	7479	767.0	20.3	19	0.1885	1.029
40.0	5	7479	772.8	21.7	21	0.1859	1.024
40.0	5	7479	749.9	21.1	20	0.1858	1.021
						Average	1.025
45.0	5	7456	767.0	21.4	25	0.2691	1.493
45.0	5.5	7479	758.6	20.5	16	0.2765	1.505
45.0	4.5	7479	769.1	20.1	15	0.2760	1.496
						Average	1.498
50.0	5	7479	762.3	20.1	17	0.3955	2.149
50.0	7.5	7479	767.7	20.1	16	0.3982	2.160
50.0	5.5	7479	765.7	20.6	22	0.3923	2.150
50.0[1]	5	8021	762.8	25.9	13	0.4085	2.122[2]
50.0[1]	6	8000	756.6	26.9	13.3	0.4118	2.158
						Average	2.154
55.0	4.5	7487	756.7	25.0	16	0.5571	3.092
55.0	5	7479	766.1	23.9	25	0.5504	3.077
55.0	7	7479	754.3	29.7	15	0.5413	3.084
						Average	3.084

These results disagree somewhat with those of previous experimenters, although the vapor pressure curve, when extended coincides fairly well with the curve obtained by Ramsay and Young.

It is interesting to calculate from these results the molecular heat of sublimation of solid iodine by means of the formula

$$\mathrm{I} = \mathrm{T}\,\frac{dp}{d\mathrm{T}}\,(\mathrm{V} - \mathrm{V_1})$$

where I = heat of sublimation.

T = absolute temperature.

$\frac{dp}{d\mathrm{T}}$ = change of vapor pressure per degree of temperature, expressed in atmospheres.

V = volume of one mole of iodine vapor at $\mathrm{T}°$ and at vapor pressure, expressed in liters.

$\mathrm{V_1}$ = volume of one mole of solid iodine at $\mathrm{T}°$ in liters.

[1] Experiment by Mr. Hickey. The remainder were performed by Mr. Holmes.
[2] Rejected in computing the average.

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
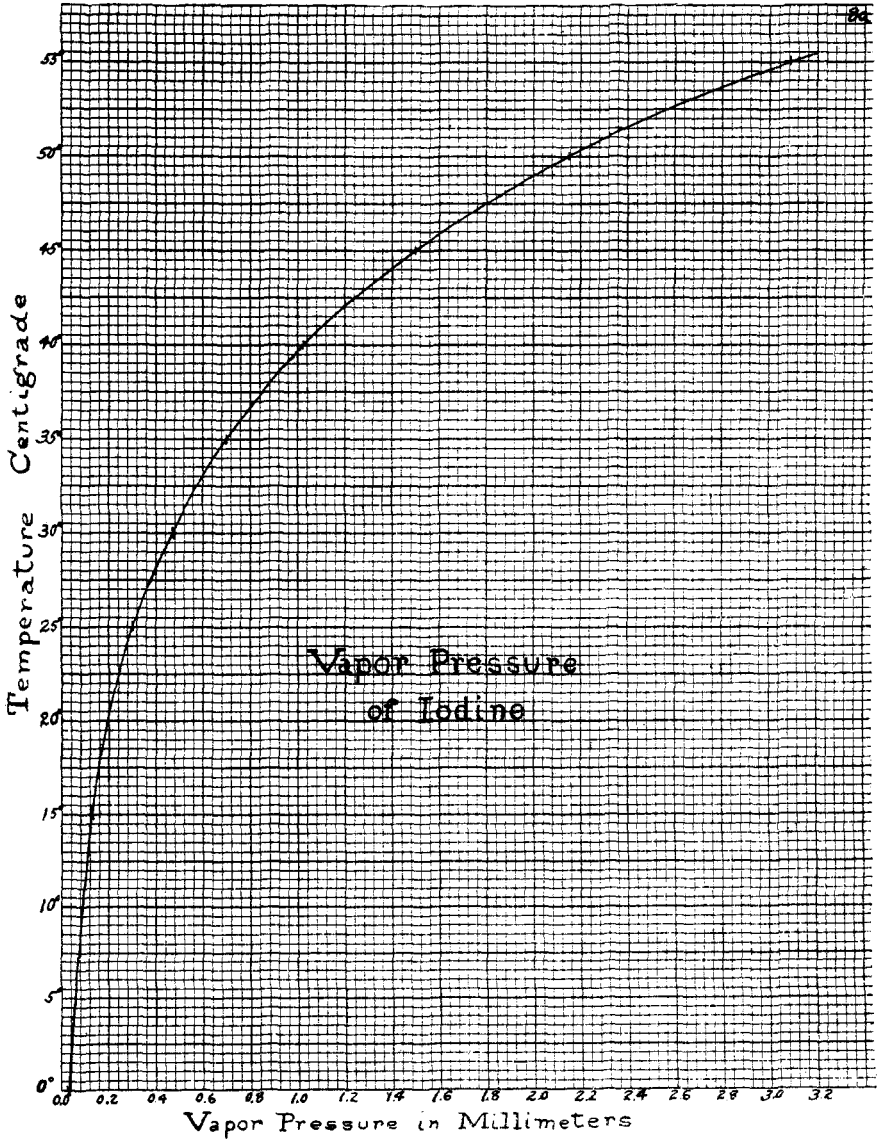
interval. The vapor pressure at this temperature was estimated from the curve here given. V_1 is so small, compared with V, that it is neglected in the calculations. The final result is multiplied by 0.02425 to convert

it from liter atmospheres to kilogram calories. The values in kilogram calories multiplied by 4.183 give the results in kilojoules.

Temperature. Degrees.	Vapor Pressure Estimated.	Molecular Heat of Sublimation. Kilogram calories.	Molecular Heat of Sublimaion. Kilojoules.
273 + 7.5	0.068 mm.	15.5	64.8
273 + 20.0	0.202 "	14.7	61.5
273 + 27.5	0.382 "	15.4	64.6
273 + 32.5	0.571 "	15.0	62.6
273 + 37.5	0.850 "	14.7	61.5
273 + 42.5	1.245 "	15.1	63.0
273 + 47.5	1.800 "	14.9	62.2
273 + 52.5	2.570 "	15.3	63.9
	Average......15.1		63.0

These values agree as well as could be expected, for at 30° an error in the determination of the vapor pressure of one hundredth of a millimeter produces an error of nearly five per cent. in dp, and of nearly two per cent. in V. In fact, the close agreement of the heats of sublimation is good confirmation of the accuracy of the experimental work.

From Ramsay and Young's observations similar calculations may be made. To obtain the following results, $\frac{dp}{dT}$ was found by dividing the difference between two observed pressures by the difference in the corresponding temperatures, while V was calculated from the observed vapor pressure at an intermediate temperature.

SOLID IODINE

Temperature.	Molecular Heat of Sublimation. Kilogram calories.	Molecular Heat of Sublimation. Kilojoules.
64.5	6.2	25.8
66.3	18.7	78.1
75.2	13.3	55.4
80.4	14.8	62.0
86.0	14.6	61.1
91.8	14.0	58.6
96.8	14.3	59.9
102.7	13.7	57.5
111.6	12.8	53.6

LIQUID IODINE

Temperature.	Molecular Heat of Sublimation. Kilogram calories.	Molecular Heat of Sublimation. Kilojoules.
117.8	11.1	46.2
130.1	10.8	45.3
147.7	10.6	44.6
171.9	10.2	42.7
180.8	10.1	42.1

The great fluctuations in the heat of sublimation at the lower temperatures are undoubtedly due to inaccuracy in the observed vapor pressures at these temperatures, while the results at higher temperatures indicate a

gradually diminishing heat of sublimation, with a sudden drop in this value at the melting point of iodine, as is to be expected. This drop, 1.7 kilogram calories or 7.4 kilojoules, must represent with fair accuracy the molecular latent heat of melting of iodine.

The only recorded determination of the heat of vaporization of iodine was made by Favre and Silbermann,[1] who obtained in one experiment the value 6.0 kilogram calories for one mole of iodine at about 147°. They also found the molecular latent heat of melting of iodine to be 3.0 kilogram calories.

Summary :—

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

Temperature. Degrees.	Vapor Pressure. mm.
0	0.030
15	0.131
25	0.305
30	0.469
35	0.699
40	1.025
45	1.498
50	2.154
55	3.084

2. The molecular heat of sublimation of iodine at these temperatures is calculated to be 15.1 kilogram calories or 63 kilojoules.

CAMBRIDGE, MASS.,
   OCT. 29, 1906.

[1] Ann. de Chim. et de Phys., (3) 37, 469 (1853).