were read simultaneously on the two manometers. The readings were reduced to 0°.

The apparatus was constructed entirely of copper and Monel metal with the exception of the diaphragm, which was of hard German silver. All joints were silver soldered.

Results

The data are represented by the equation

$$\log_{10} P \text{ (cm.)} = -462.66/T + 8.7202 - 0.01656\ T$$

This equation was calculated by the "method of averages" from the one-hundred and forty points observed with three different samples of fluorine. No point deviates more than 0.15°, while three-fourths of them lie within 0.10° of the equation. Differentiation of this equation with respect to T and then equating to $\Delta H/RT^2$ of the Clausius–Clapeyron equation gives 1560 calories as the heat of vaporization at 85.21°K. the calculated boiling point. The entropy of vaporization is therefore approximately 18.3 entropy units. We believe the error in the boiling point is 0.1° or less.

The results of the earlier work on the vapor pressure of fluorine give 84.93°K. as the boiling point and 1600 calories as the heat of vaporization.[1] Moissan and Dewar[4] gave 85.1°K. as the boiling point of fluorine when recalculated, in close agreement with our figure.

If log P is plotted against log T for our data a curve is obtained that has exactly the same slope at equal volumes of vapor, as a similar plot for oxygen. This shows that fluorine obeys Hildebrand's rule[5] regarding the entropy of vaporization. From this criterion, fluorine is a normal liquid.

The author wishes to express his appreciation to Professor Hildebrand, who suggested this research, and under whose guidance it was carried out, and to Professor Giauque, who suggested the experimental technique at the low temperatures.

Summary

1. The vapor pressure of liquid fluorine has been measured from 6.3 to 75.2 cm. The vapor pressure is given by the equation

$$\log_{10} P \text{ (cm.)} = -462.66/T + 8.7202 - 0.01656\ T$$

2. The boiling point is calculated to be 85.21°K., a value correct within 0.1°.

3. The heat of vaporization is calculated to be 1560 calories per mole from the Clausius–Clapeyron equation and $\Delta S = 18.3$.

4. Fluorine obeys Hildebrand's rule regarding the entropy of vaporization.

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[4] Moissan and Dewar, *Compt. rend.*, **125**, 505 (1897).

[5] Hildebrand, THIS JOURNAL, **37**, 970 (1915).

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Atomic Weights of Iodine, Carbon and Sodium. The Ratio of Iodine Pentoxide to Sodium Carbonate

BY GREGORY PAUL BAXTER AND ARTHUR HAYS HALE

In three investigations in this Laboratory iodine pentoxide has been compared with silver,[1] with iodine by thermal decomposition[2] and with arsenic trichloride.[3] Since the results of these three comparisons are not wholly consistent, we have carried out a fourth comparison, with sodium carbonate by neutralization.

The Preparation of Iodine Pentoxide

Iodic acid remaining from the investigation of Baxter and Butler[2] was further purified by continuing the fractional crystallization to which it had already been subjected. This iodic acid had been prepared from iodine, which had already been freed from other halogens and organic matter, through potassium and barium iodates by treatment of the latter with sulfuric acid. Crystallization was carried out in platinum dishes except that some of the less pure fractions were temporarily stored in quartz. For the present work the material was handled wholly in platinum. The chief evidence of purity was obtained by carefully dehydrating and decomposing at as low a temperature as possible 25 g. of pentoxide, slightly less pure than the poorest used in the actual analyses, in a current of pure air while contained in a weighed platinum boat inside a quartz tube. The weight of the residue was 0.07 mg. and this was not altered by further heating to dull redness. Another 5-g. portion gave no weighable residue. The apparent percentage of impurity, 0.0003%, is too small to be of significance.

To prepare iodine pentoxide from iodic acid the procedure used by Baxter and Tilley[1] was employed. Iodic acid crystals were pulverized in an agate mortar and were

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[1] Baxter and Tilley, THIS JOURNAL, **31**, 203 (1909).

[2] Baxter and Butler, *ibid.*, **53**, 970 (1931).

[3] Baxter and Shaefer, *ibid.*, **55**, 1957 (1933).

mixed with a small proportion of the first product formed in the dehydration, $I_2O_5 \cdot HIO_3$. The mixture was then placed in a platinum boat which had been weighed while enclosed in a weighing bottle, and the boat was heated to about 100° in a quartz tube which formed part of a Richards bottling apparatus. At the same time a current of pure dry air was passed through the tube. As soon as the first stage in the dehydration was completed the temperature was raised to about 200° and maintained at this point until the second stage in the dehydration was over. After a short heating at 240° the boat was cooled and the weight of its contents adjusted by removal so that a few milligrams excess remained over that required by the sodium carbonate, the weight of which had previously been obtained as described below. The boat and contents were then heated for four hours at 240° in a current of pure, dry air and finally were transferred to the weighing bottle by means of the bottling apparatus. Material prepared in this way has been found to retain uniformly 0.0023% of water.[1] Mr. A. C. Titus has found in this Laboratory that similar iodine pentoxide adsorbs 0.001% of air. The final weight of iodine pentoxide has therefore been corrected by subtracting 0.0033%. Ordinarily the pentoxide remained pure white during the dehydration, although occasionally a slight brownish tint appeared which, however, seemed to be without effect on the results of the analyses.

The Preparation of Sodium Carbonate

The purification of sodium carbonate was effected by the method used by Richards and Hoover.[4] Commercial sodium carbonate was dissolved, filtered and recrystallized three times in porcelain dishes with centrifugal drainage in a porcelain centrifuge. After solution and a second filtration through platinum sponge, six more crystallizations wholly in platinum were carried out, with centrifugal drainage in platinum in each case. A third filtration through platinum sponge was followed by still another crystallization. Finally the water of crystallization was removed by efflorescence under a bell jar containing freshly fused sodium hydroxide. A second sample was prepared in an identical fashion except that the number of crystallizations in platinum was one fewer, and the preliminary dehydration was conducted more rapidly over an electric hot-plate.

Richards and Hoover[4] came to the conclusion that only sodium carbonate which had been fused in an atmosphere of carbon dioxide is really normal in composition. Our experience leads to the same conclusion. Sodium carbonate which had been thus treated remains essentially constant in weight on successive fusions. In an attempt to discover whether the solidified salt retains carbon dioxide, in several cases salt which had been fused in pure carbon dioxide and weighed was again fused in atmospheres containing various proportions of carbon dioxide and nitrogen. Usually this resulted in violet discoloration and a small gain in weight although sometimes a slight loss occurred. When fused again in pure carbon dioxide the weight again approached the original. Since the evidence certainly did not point to retention of carbon dioxide we adopted the method of fusion in this gas.

The fusion was carried out in a bottling apparatus connected with a carbon dioxide generator and purifying train and a train for supplying pure air. The dried salt was placed in a weighed platinum boat which was entirely surrounded with a sleeve of platinum foil and placed in the quartz tube of the bottling apparatus. The tube was gradually heated to the bare fusion of the salt, and then the carbon dioxide was displaced by pure air while the tube was cooling. In the earlier experiments because of the voluminous nature of the effloresced carbonate several charges of salt were necessary to provide the desired quantity. The carbonate which had been dried rapidly was more compact and only one filling was required.

The weighing bottle and boat used in the preparation of the sodium carbonate usually showed a gain in weight, amounting on an average to 0.06 mg. per experiment. This gain was traced to the slight sticking of the boat to the platinum cylinder in which it was enclosed during the fusion. On this account the weight of the system *after* the experiment was used in finding the weight of the carbonate. The effect of this gain in weight on the ratio of sodium carbonate to iodine pentoxide is however less than 0.001%.

The Method of Analysis

The procedure of neutralization was conducted in such a way that effervescence did not occur until both reactants had been dissolved. After this slight losses by spattering were of little importance. The two boats containing iodine pentoxide and sodium carbonate were placed in a Pyrex flask containing about 800 ml. of water and the flask was rotated in a whirling machine constructed to operate intermittently at intervals of fifteen seconds. About an hour was required for complete solution. The resulting solution was about tenth normal in carbonic acid and therefore about saturated, so that the evaporation of the carbon dioxide took place quietly with no spattering. The solution of sodium iodate was next evaporated over an electric stove in a clean atmosphere in a large platinum still to a volume of about 350 ml. Since the excess of iodic acid was only a few milligrams, minor losses in this evaporation were of little importance.

Brom thymol blue was eventually found to be a suitable indicator for this neutralization. Since the end-point is very nearly neutral the effect of dissolved carbon dioxide is of considerable importance. It was found necessary therefore to conduct the final setting of the end-point in an atmosphere free from this gas.

The selection of brom thymol blue as indicator was due to the fact that a solution of recrystallized sodium iodate, obtained from the analytical operation, is yellow when in contact with ordinary air but becomes pale green when boiled in vacuum and cooled. We could find no evidence of the separation of a complex iodate from aqueous solutions of the salt since the mother liquor from which sodium iodate separated gave the same

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(4) Richards and Hoover, THIS JOURNAL, **37**, 96 (1915).

reaction with brom thymol blue as the crystals.[5]

The method of finding the exact end-point was to boil in a vacuum the evaporated solution obtained in the analysis and then after admitting air which had been freed from carbon dioxide to finish the neutralization in the cold with 0.006 normal iodic acid and sodium hydroxide which had been freed from carbonate by means of barium hydroxide. The iodic acid solution was prepared from a weighed quantity of iodine pentoxide and the sodium-barium hydroxide solution was compared with the iodic acid in the fashion described above. Under the conditions of the experiment the volume of standard solution required for the complete color change of brom thymol blue from yellow to green was less than 0.2 ml., corresponding to less than 0.001% in the weights of substance used in the main comparison. Since the end-point used lay between these points the uncertainty is appreciably less than this.

The results of all the analyses completed after the technique had been perfected are given in the table. All weighings were made by substitution with counterpoises. The weights were standardized to hundredths of a milligram. Vacuum corrections were computed from the air density observed at the time of weighing with the use of the densities

Weights, 8.3 I_2O_5, 4.799[1] Na_2CO_3, 2.53[4]

THE RATIO OF IODINE PENTOXIDE TO SODIUM CARBONATE

Analysis	Na_2CO_3 in vacuum, g.	I_2O_5 in vacuum, g.	I_2O_5 in excess, g.	Corr. wt. of I_2O_5 in vacuum, g.	Ratio I_2O_5: Na_2CO_3
1	8.98436	28.30358	0.00741	28.29617	3.14949
2	9.56078	30.12165	.00851	30.11314	3.14965
3	7.55451	23.79800	.00544	23.79256	3.14945
4	9.33412	29.40671	.00838	29.39833	3.14956
5	8.46160	26.66002	.00977	26.65025	3.14955
6	9.29771	29.28914	.00602	29.28312	3.14950
7	9.70811	30.57842	.00309	30.57533	3.14946
8	8.42645	26.54277	.00385	26.53892	3.14948
9	8.81736	27.77203	.00288	27.76915	3.14937
				Average	3.14950
				Extreme deviation	0.00028
				Probable error	± .000018

Although the small "probable error" of the average ratio, 0.0006%, undoubtedly gives a false impression of the reliability of the result, it is not unreasonable to suppose that the uncertainty is considerably less than the extreme deviation, 0.009%, which happens to be determined by two more discrepant determinations. The extreme deviation of the remaining seven is only 0.00011 or 0.003%. It therefore seems worth while to examine the bearing of the final ratio on the atomic weights of the elements involved. Obviously by assuming two of the atomic weights involved the third may be computed. This has been done for several possible values of each element. The discovery of the existence of the isotope C^{13} together with the evidence of recent determinations of the density of various gaseous compounds of carbon points to an atomic weight of carbon somewhat higher than the present International value, 12.00. The International value for sodium is 22.997 but Johnson[6] has recently found a slightly lower value, 22.994. Hönigschmid and Striebel[7] have recently found the atomic weight of iodine to be 126.917, a value appreciably lower than that in current use previously, 126.932.

The following three tables indicate the various possibilities.

THE ATOMIC WEIGHT OF IODINE

	C = 12.000	C = 12.005	C = 12.010
Na = 22.997	126.914	126.922	126.930
Na = 22.994	126.905	126.913	126.922

THE ATOMIC WEIGHT OF CARBON

	I = 126.915	I = 126.917	I = 126.920	I = 126.925
Na = 22.997	12.001	12.002	12.004	12.007
Na = 22.994	12.007	12.008	12.010	12.013

THE ATOMIC WEIGHT OF SODIUM

	I = 126.915	I = 126.917	I = 126.920	I = 126.925
C = 12.000	22.998	22.998	22.999	23.001
C = 12.005	22.995	22.996	22.997	22.998
C = 12.010	22.993	22.993	22.994	22.996

It is evidently unsafe to go beyond the conclusion that the atomic weight of iodine is probably not higher than 126.92 and that of carbon probably higher than 12.00. Further evidence on the atomic weights of carbon, sodium and iodine is necessary before it will be possible to determine how closely the ratio found in our work fits the rather involved situation.

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[5] Meerburg, *Z. anorg. Chem.*, **45**, 333 (1905).

[6] Johnson, *J. Phys. Chem.*, **37**, 923 (1933).

[7] Hönigschmid and Striebel, *Z. physik. Chem.*, Bodenstein Festband, 282 (1931); *Z. anorg. allgem. Chem.*, **208**, 53 (1932).