1400 mm.—greater than the range covered by Stein. Also, there is no apparent trend in ϕ over a fourteen-fold increase in light flux. The value $\phi = 1.15$ reported by Bradshaw agrees well with the average of the final series, but we can offer no convincing explanation of the disagreement between our results and those of Stein. Liberal use of greased stopcocks, and the very small amount of hydrogen produced (always less than 10^{-7} mole) were possible disadvantages of his method.

Mechanisms.—There are two mechanisms that can be used to explain our quantum yield of unity over a considerable pressure range.

$$\begin{aligned} H_2S + h\nu &= H + HS && (1) \\ H + H_2S &= H_2 + HS && \\ HS + HS &= H_2S + S \text{ or } H_2S_2 && \\ H_2S + h\nu &= H_2 + S && (2) \end{aligned}$$

The first mechanism, recommended by Herzberg,[4] seems to be much the more probable. The work of Avery and Forbes,[6] as noted above, supports the same conclusion. The secondary reaction $HS + HS = H_2 + S_2$ must be infrequent at least, otherwise ϕ could become as great as two.

In Pairs in Hydrogen.—Mund and van Tiggelen,[7] as stated above, found that 2.1 molecules of hydrogen sulfide disappeared for each ion pair formed from hydrogen through action of α particles. If mechanism (1) is correct, *two* hydrogen atoms are required per molecule of hydrogen sulfide decomposed, unless stable H_2S_2 is formed in appreciable quantities. Then 4.2 hydrogen atoms must have been produced per ion pair, in better agreement with six, the number calculated by Eyring, Hirschfelder and Taylor.[8]

Summary

Highly purified hydrogen sulfide and hydrogen bromide were photolyzed successively, under identical conditions, in a rotating quartz cell of special design. Sulfur formed in any photolysis was distributed over a cylindrical surface 120 sq. cm. in area, and was proved to have negligible influence upon light transmission.

Stopcocks were avoided altogether by free use of breakable inner capillary seals, mercury valves and liquid air. High vacuum technique was employed consistently. Corrections for permanent gases obtained in blank experiments were less than 0.5%.

Assuming that one quantum produces exactly one molecule of hydrogen from hydrogen bromide at 400 mm., the quantum yield of hydrogen sulfide, referred to that of hydrogen bromide, is 1.02 ± 0.05 molecules of hydrogen per quantum. All systematic errors are canceled by means of this comparison.

This outcome agrees, within 13%, with that of preliminary experiments conducted in a rather similar apparatus in 1934.

Within experimental error, this quantum yield is independent of pressure, 8 to 1400 mm., and also of light flux ($\lambda = 208\ m\mu$) over a fourteen-fold range.

Correlation of our results with Herzberg's reaction mechanism, and with Mund and van Tiggelen's work, indicates that when α particles act upon hydrogen gas, 4.2 hydrogen atoms are produced per ion pair.

CAMBRIDGE, MASS. RECEIVED MARCH 18, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Specific Heats and Heat of Fusion of Iodine

BY K. J. FREDERICK AND J. H. HILDEBRAND

A careful search of the literature reveals the rather astounding fact that no direct determination of the heat of fusion of iodine has ever been reported, although varied indeed are the indirect determinations that appear in the works of reference. It is obviously desirable to have a direct determination of this important constant, and this we have carried out, employing the method of mixtures. This method also afforded us an opportunity to ascertain the heat capacities of both solid and liquid iodine.

According to Regnault[1] the mean specific heat of solid iodine between 9 and 98° is 0.05412 cal. per gram. This gives a mean molal heat capacity of 13.74 cal. per mole. Nernst and coworkers[2] give a value of 13.30 cal. per mole for the temperature 20°. Recently Carpenter and Harle[3] have measured the heat capacity of solid

(1) Regnault, *Ann. chim. phys.*, [2] **73**, 3 (1840), and [3] **26**, 268 (1849).

(2) (a) Nernst, *Berlin Sitzber.*, 247 (1910); (b) Nernst, *Ann. Physik*, [4] **36**, 395 (1911).

(3) Carpenter and Harle, *Phil. Mag.*, **23**, 193 (1937).

iodine by a differential method and report a value of 13.48 cal. per mole for 25° and a mean value of 14.04 cal. per mole for the interval 0–113°. These investigators also measured the heat capacity by the method of mixtures and found a lower mean value for this interval, 13.60 cal. per mole.

The heat capacity of liquid iodine has received much less attention. Favre and Silbermann[4] reported a value of 27.47 cal. per mole for the heat capacity of liquid iodine. This value was later discredited by Abegg and Halla,[5] who claimed a value of 16.0 cal. per mole. On the other hand the "International Critical Tables" contains the highly improbable value of 3.82 cal. per mole. All of these values are supposedly valid over the entire liquid range, 114–184°. In the work of Carpenter and Harle[3] differential measurements on liquid iodine indicate a value of 20.0 cal. per mole for the heat capacity at the melting point, followed by a rapid decrease with increasing temperature.

We have the following listed values for the heat of fusion of iodine. Favre and Silbermann[4] found a value of 3000 cal. per mole for the heat of fusion. In Mellor[6] we find the calculated heat of fusion is 3290 cal. per mole. A number of authors have calculated that the heat of fusion from the difference between the heat of vaporization of the liquid from the vapor pressures of Ramsey and Young[7] and the heat of sublimation of the solid from the sublimation pressures.[8] The following values for this difference have been published: Dewar,[9] 3780 cal.; Baxter, Hickey and Holmes,[8] 1700 cal.; Lewis and Randall,[10] "Internat. Crit. Tables,"[11] Bichowsky and Rossini,[12] 4000 cal.; Kelley,[13] 3650 cal.; Hildebrand,[14] 3725 cal. Kelley[13] gives, also, certain values of the heat of fusion obtained from the solubility of iodine in solutions which are approximately ideal.[15] These are, 3720 cal. for solutions in SnI_4, 3880 cal. in S_8 and 3700 cal. from Beckmann's freezing point constant.

Preparation and Purification of Sample.—The iodine used in this work was Merck reagent, purified according to the method employed by Baxter[16] in his work on the determination of the atomic weight of iodine. This method consists chiefly in first distilling the iodine from a strong solution of potassium iodide, followed by its subsequent reduction with hydrogen sulfide and its later oxidation with permanganate. The iodine thus purified had a melting point of 113.6°, as observed by an immersion method.

The iodine used in the determinations was enclosed in small Pyrex glass capsules evacuated before sealing. The capsules had an external diameter of 12 mm., an internal diameter of 10 mm. and varied in length, averaging around 8 cm. The ratio of weight of iodine to weight of glass was about 3.5. Four different capsules were prepared and each one was used in a considerable number of the runs. The average air space in the capsules was 1.3 cc. Calculations indicate that the iodine vapor and air in the capsules is a negligible factor, even when the temperature of the run is as high as 160°.

Apparatus.—The furnace was made of a heat-insulated copper block 11 cm. in diameter and 32 cm. in length. A 1.5-cm. hole was drilled in the center of the block, extending two-thirds of the way up from the bottom. The central bore was extended 3 cm. beyond the bottom with a monel tube of the same bore closed with a brass cap. The glass capsule was supported in the furnace by a wire inserted at the side of the block. A hole was drilled down from the top as closely as possible to the central bore. A No. 30 chromel-alumel thermocouple cased in a thin 3-mm. Pyrex tube was inserted in this in order to measure the temperature of the furnace. The block was heated electrically and the amount of heat given to the block was suitably regulated by adjusting the current by rheostats. This method of controlling the furnace temperature was found to be quite satisfactory, for the temperature could be maintained within ±0.05° for any desired length of time.

The calorimeter was made of a pint Dewar flask (500-cc.) with a tightly fitting copper cover. A "basket" of copper gauze was suspended from the cover near the bottom of the flask to catch the capsule of iodine as it dropped in from the furnace above. Through the cover there extended a glass stirrer, electrically driven, and a 6-junction (No. 32 copper–No. 26 advance) thermocouple whose junctions were cased in thin 6-mm. Pyrex tubes filled with pure solid naphthalene. The calorimeter was placed in a water thermostat regulated at approximately 25 ± 0.1°. The furnace was supported directly above the calorimeter at such a height that the calorimeter could be swung directly underneath the furnace and the capsule dropped.

The amount of water in the calorimeter, approximately 325 cc., was weighed to ±0.05 g. The heat capacity of the calorimeter was determined by means of a copper rod weighing 60.261 g. The chromel–alumel thermocouple

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[4] Favre and Silbermann, *Ann. chim. phys.*, [3] **37**, 469 (1853).

[5] Abegg and Halla, "Handbuch der anorganische Chemie," Leipzig, 4, ii, 1913, p. 356.

[6] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, Vol. II, 1922, p. 54.

[7] Ramsey and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[8] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907); W. F. Giauque, *ibid.*, **53**, 507 (1931); L. J. Gillespie and L. H. D. Fraser, *ibid.*, **58**, 2260 (1936).

[9] Dewar, *Chem. News*, **91**, 216 (1905).

[10] Lewis and Randall, THIS JOURNAL, **36**, 2259 (1914).

[11] "Int. Crit. Tables," I, 103.

[12] Bichowsky and Rossini, "The Thermochemistry of Chemical Substances," Reinhold Pub. Corp., New York, N. Y., 1936, p. 25.

[13] K. K. Kelley, *Bull. U. S. Bur. Mines*, **383** (1935); **393** (1936).

[14] J. H. Hildebrand, THIS JOURNAL, **59**, 2083 (1937).

[15] M. E. Dorfman and J. H. Hildebrand, *ibid.*, **49**, 729 (1927).

[16] Baxter, *Proc. Am. Acad. Arts Sci.*, **40**, 421 (1904).

used in the furnace was calibrated against the melting point of ice, the transition point of sodium sulfate decahydrate and the boiling point of freshly distilled water. The 6-junction thermocouple used in the calorimeter was calibrated merely against the first two of these standards, for this couple was used only in the neighborhood of 25°. The heat content of the glass tubing used in the capsules was determined at several temperatures. The thermocouples were used in conjunction with a Leeds and Northrup type K_2 potentiometer which was graduated to 0.5 microvolt. The potentiometer was connected to a sensitive galvanometer. With this set-up temperature changes of 0.001° in the calorimeter and 0.01° in the furnace could be detected.

Measurements.—The tube containing the iodine was heated in the furnace at a given temperature (within ±0.05°) for over an hour before it was dropped into the calorimeter. At the beginning of a run the temperature of the water in the calorimeter was a little below that of the thermostat temperature, 25°. With the stirrer and thermocouple inserted, readings were taken on the calorimeter, simultaneously with those on the furnace, until the rate of change of the temperature in the calorimeter was uniform. The stirrer was then disconnected, the calorimeter swung into place and the capsule dropped. Approximately twenty seconds elapsed between the time the stirrer was stopped and started again. The temperature change of the calorimeter was read every minute until a uniform cooling rate was obtained. A satisfactory constant temperature was obtained in most cases very shortly after the capsule was dropped, for the rate of cooling was just about offset by the rate of heating due to stirring. The total change in temperature of the calorimeter varied from 0.13 up to 1.8°.

The large amount of heat required to melt the iodine necessitated a different procedure for the runs just above the melting point. The capsules for these runs were first heated for over an hour 10–15° above the melting point and then cooled down to just above the melting point and held there for about two hours.

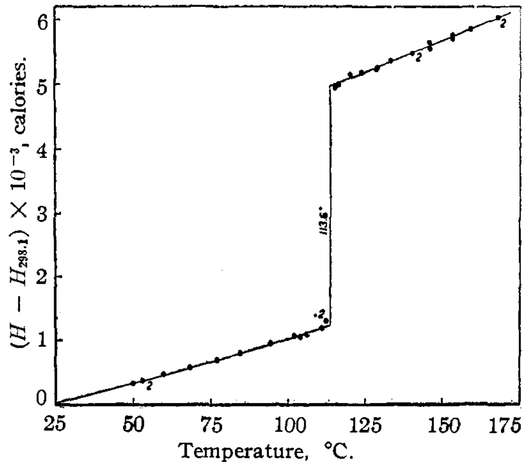

Fig. 1.

Results and Discussion

The total heat of the copper rod used in determining the heat capacity of the calorimeter was found from its specific heat equation

$$c_p = 0.09076 + 0.0000415T$$

determined empirically by Bronson, Chisholm and Dockerty.[17] It was found from the runs on the Pyrex glass used in making the capsules that its specific heat could be expressed within ±0.2% by the equation $c_p = 0.1141 + 0.0002532T$. The value of the heat capacity of the calorimeter used was 11.4 ± 0.4 cal. per degree.

The results of the runs made on solid iodine are given in Table I, while the runs on liquid iodine are listed in Table II. The second column in each table represents the amount of heat required to raise one mole of iodine from 25° up to the final temperature of the run. We shall refer to this quantity as $H-H_{298}$.

TABLE I

Temp., °C.	$H-H_{298}$, cal./mole
49.87	321.1
52.92	371.4
53.05	370.1
59.97	473.7
68.50	579.0
77.25	696.8
84.21	798.1
94.27	953.4
102.05	1074.5
103.91	1064.6
105.98	1102.4
110.87	1191.5
112.48	1312.9
112.53	1302.2

TABLE II

Temp., °C.	$H-H_{298}$, cal./mole
115.18	4950.0
116.45	5004.6
120.08	5146.6
123.77	5184.7
128.62	5238.4
128.84	5256.5
133.12	5370.2
140.25	5475.1
140.11	5478.9
146.02	5559.0
145.89	5642.4
153.33	5713.9
153.28	5760.1
158.87	5854.1
168.49	6031.0
168.10	6049.3

The data given in the tables are plotted in Fig. 1. A subscript 2 adjacent to a point signifies that two of the results listed in the tables become coincident within the limits of plotting.

The following empirical equation was found to fit the data for solid iodine within ±0.5% : $H-H_{298} = 13.07\ (t - 25) + 1.07 \times 10^{-4}\ (t - 25)^3$. The first derivative of this relationship, a measure of the molal heat capacity of iodine in the limited interval 25–113.6°, is

$$c_p = 13.07 + 3.21 \times 10^{-4}\ (t - 25)^2$$

where c_p is the heat capacity in cal. per mole and t is the temperature in degrees centigrade. The very nature of this equation indicates that it is valid only over the limited interval for which it was derived. It does represent, however, the

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[17] Bronson, Chisholm and Dockerty, *Can. J. Research*, **8**, 282 (1933).

rise in heat capacity of the solid form as the melting point is approached. We obtain from this empirical equation a value of 13.07 cal. per mole for 25°, and a mean value of 13.97 cal. per mole for the interval 25–100° in good agreement with the work already mentioned.

A straight line was found to fit the data for liquid iodine within experimental error. This gives then a constant molal heat capacity for liquid iodine of 19.5 ± 0.3 cal. per mole for the interval 113.6–160°. It will be recalled that Carpenter and Harle[3] found an initial value of 20.0 cal. per mole at the melting point, followed by a rapid decrease with increasing temperature. In this connection it should be mentioned that their work embraces only five runs on liquid iodine with individual deviations of over 3%. The method employed in this work is not suitable for investigating this trend of heat capacity. However, it would now appear certain that the values given by Favre and Silbermann,[4] Abegg and Halla,[5] and the "International Critical Tables" are quite erroneous.

The heat of fusion of iodine at the melting point is calculated to be 3740 ± 20 cal. per mole.

Acknowledgment.—The authors wish to express their appreciation of the assistance given them by Mr. Austin L. Wahrhaftig in the calibration of the apparatus and in the preparation of the iodine capsules.

Summary

Employing the method of mixtures, the heat of fusion of iodine at the melting point was found to be 3740 ± 20 cal. per mole. The molal heat capacity of solid iodine in the limited temperature interval 25–113.6° can be expressed within ±0.5% of the measured values by the equation $c_p = 13.07 + 3.21 \times 10^{-4}(t-25)^2$. For liquid iodine from the melting point up to 160°, the molal heat capacity is 19.5 ± 0.3 cal.

BERKELEY, CALIFORNIA RECEIVED APRIL 8, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Solubility of Gold Hydroxide in Alkali and Equilibria in the Saturated Solutions[1]

BY HERRICK L. JOHNSTON AND HOLLIS L. LELAND[2]

The extent of acid character associated with the hydroxides of the silver sub-group elements, as measured by solubility of the oxide or hydroxide in alkali, forms an interesting study because of the regular increase in air-stable valence from silver to gold. Quantitative data on the equilibria present in alkaline solutions of silver and of di-valent copper have been presented in earlier papers.[3] This paper presents similar data for trivalent gold. The results show the expected dependence on the valence of the metal, and establish quantitatively the correctness of the explanation we have assigned previously to solutions of this character.

Experimental

Apparatus and procedure were similar to those employed in the earlier work from this Laboratory except for such changes as were necessary to adapt the procedure to gold.

Auric hydroxide was prepared out of contact with air, by the method of Roseveare and Buehrer,[4] in the preparation train described by Johnston, Cuta and Garrett.[3] Gold was precipitated from a boiling aqua regia solution of gold by the dropwise addition of three normal potassium hydroxide; the mother liquor was siphoned off and the precipitate dissolved in the minimum amount of boiling three normal potassium hydroxide; and, finally, the gold was again precipitated by dropwise addition of sulfuric acid until the solution was just acid to litmus. This product was boiled for an hour;[4] washed twice with conductivity water; and transferred under nitrogen to a special wash flask[3] where it received fifteen additional washings with conductivity water. Qualitative tests for sulfate and chloride ions, made after the tenth washing, were invariably negative. The product was then stored under conductivity water and nitrogen until ready for use. Six separate lots of auric hydroxide were prepared in this manner to furnish the samples needed in this investigation. The data from the six lots are indistinguishable.

The product prepared in the above manner was reddish-brown in color and was composed of agglomerates of small biaxial crystals.[5] The crystalline character was estab-

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(1) Presented before the Division of Physical and Inorganic Chemistry of The American Chemical Society, at its Rochester meeting, September, 1937.

(2) Present address: Esso Laboratories, Standard Oil Development Company, Elizabeth, N. J.

(3) (a) H. L. Johnston, F. Cuta and A. B. Garrett, THIS JOURNAL, **55**, 2311 (1933); (b) L. A. McDowell and H. L. Johnston, *ibid.*, **58**, 2009 (1936).

(4) Roseveare and Buehrer, *ibid.*, **49**, 1989 (1927).

(5) Precipitation from *hot, strongly basic* solutions was found to yield a dense, black product whose properties differ markedly from