

The heat of fusion is 1351.6 cal./mole. The heat of vaporization at the boiling point is 5581 cal./mole.

The vapor pressure of solid and liquid ammonia has been measured and the data have been represented by the equations: solid ammonia 176.92 to 195.36°K . $\log_{10} P$ (int. cm. Hg) = $1630.700/T + 9.00593$; liquid ammonia 199.26 to 241.59°K . $\log_{10} P$ (int. cm. Hg) = $-1612.500/T - 0.012311T + 0.000012521T^2 + 10.83997$.

The molal entropy of the gas at the boiling point has been calculated by means of the third

law of thermodynamics and the experimental data. The value found, 44.13 ± 10 e. u., is in excellent agreement with the value 44.10 e. u. calculated from spectroscopic data.

From band spectrum data the entropy of ammonia at 298.1°K . and 1 atmosphere was calculated to be 45.91 cal./deg. per mole.

The above entropy value, which should be used in ordinary thermodynamic calculations, does not include the nuclear spin entropy. The absolute entropy is 52.22 cal./deg. per mole.

BERKELEY, CALIF.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Relative Atomic Weight of Oxygen from Air and Water Determined by an Interchange Reaction

BY THOMAS O. JONES AND NORRIS F. HALL

An important difference in the composition of oxygen from the air and from water has been brought to light recently both in America and in Japan,¹ and this has been confirmed subsequently² by others. Various somewhat questionable assumptions and methods incident to the earlier papers have been discussed by Smith and Matheson,² but there seems little doubt of the reality of the difference, which readily accounts for certain otherwise unexplained results of workers other than the discoverers.³ All of the results referred to above were obtained by burning elementary hydrogen with different sorts of oxygen, and electrolytic methods were generally employed to produce one or both of the gases.

We have now demonstrated this important effect by a method which involves neither electrolysis nor combustion, and which may prove practical for the preparation of large quantities of water abnormal as to its O^{18} content. The equilibrium between water and oxygen



if established at low temperatures would, according to Dole,^{1a} account for the observed difference. On the other hand, it is found, using the methods

(1) (a) Dole, *THIS JOURNAL*, **57**, 2731 (1935); *J. Chem. Phys.*, **4**, 268, 1936 (6 γ); (b) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 36, 414 (1936) (7 γ).

(2) (a) Greene and Voskuyl, *THIS JOURNAL*, **58**, 693 (1936) (6 γ); (b) Hall and Johnston, *ibid.*, **58**, 1920 (1936) (6.6 γ); (c) Smith and Matheson, *Bur. Standards J. Research*, **17**, 625 (1936) (8.6 γ).

(3) (a) Hall and Jones, *THIS JOURNAL*, **58**, 1915 (1936) and the present paper; (b) Dole¹ and *THIS JOURNAL*, **58**, 580 (1936); (c) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 419 (1936).

outlined by Urey and Greiff,⁴ that at *high* temperatures the constant of this reaction closely approaches unity (at 1000°A ., K is 1.0038, at 1500°A ., K is 1.0002, at 2500°A ., K is 1.0004), and that the departure of oxygen from a perfectly random atomic distribution in the three molecular forms is negligible in this temperature range.

Consequently, at 1500°A ., for example, the $\text{O}^{18}/\text{O}^{16}$ ratio of a sample of water in equilibrium with a large excess of air should be *the same* as in the air within 0.1 γ (water density at 25°) and within 0.09 γ at 2000°A . These differences are less than the probable error of the density determination. If then a sample of ordinary water were vaporized, heated with excess air and recondensed, its density should measurably increase, provided (a) air oxygen is really heavier and (b) there is an approach to equilibrium. The D/H ratio should remain unaffected.

Assuming that 7 γ is the correct value of the Dole effect for surface water, the equilibrium density increases to be expected are roughly

T , $^\circ\text{A}$.	γ	Ref.
223	1.2	1a
273	4.8	1a
293	5.7	1a
373	6	2b
575	6.7	2b
1500	6.9	This
2000	6.91	paper

(4) Urey and Greiff, *THIS JOURNAL*, **57**, 321 (1935).

Experimental

In a first series of runs a large excess of cleaned air was passed through samples of ordinary water at room temperature with entirely negative results. (Average change of density in five runs lasting three to six days each $+0.3 \gamma \pm 0.5 \gamma$.)

In series 2 (4 runs at 100°) the results were also negative. Here air was bubbled through boiling water which was condensed and frozen out of the air stream and continuously returned to the flask. The average density change was $+0.15 \gamma \pm 0.35 \gamma$.

Since it seemed possible that the exchange might be promoted by catalysts of the type on which the reaction of oxygen and hydrogen is known to occur, steam and air were passed in series 3 over finely divided palladium, platinum, and platinum and silver oxide mixtures on asbestos. The results were again entirely negative. No significant changes in density were observed in nine days of treatment at temperatures up to 300° .

After this work was finished, we learned that W. Heinlen Hall and Johnston^{2b} (p. 1922) had already reached the conclusion that "an exchange reaction between steam and molecular oxygen does not appear to be significantly catalyzed by platinum at 300° ."

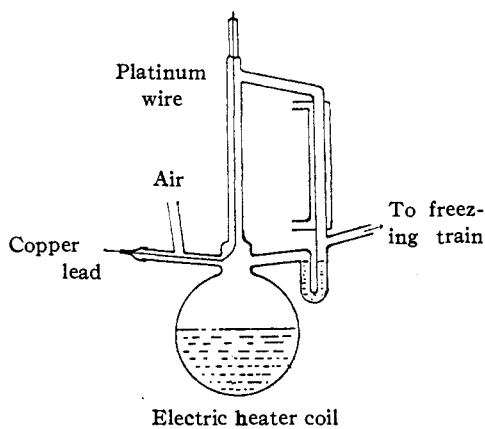


Fig. 1.—Equilibrator.

It now seemed quite likely that a much higher temperature would be required for activation. An apparatus was accordingly constructed which facilitated passing clean (dried) air together with steam over a platinum wire heated by an electric current to temperatures ranging from 1500°A. to 1800°A. (Fig. 1). A single strand of no. 30 wire about 25 cm. long was hung vertically under slight tension between bare copper leads in the center of an 8-mm. glass tube connected to a flask of water heated to $90\text{--}95^\circ$. The volume of the water samples was 100–110 cc. Air was admitted through a side-arm above the water surface. After passing the hot wire the bulk of the water vapor was condensed immediately from the air stream and returned to the original sample. That water which remained in the air stream was caught by means of a freezing train and also returned to the flask. The air flow was constant and limited to a rate such that nearly all the vapor could be removed in the freezing train. The loss of water in six days of treatment was less than 1%, a loss so small that it could not account for the changes in density ob-

served. The quantity of air which passed over the wire with the water and the rate of reaction at 1800°A. were such that equilibrium was apparently established within three days. In each determination the time allotted was from two to three times this period. The rate of air flow was approximately 15 liters per hour. The temperature of the wire was determined by means of an optical pyrometer. In this series four samples of ordinary water were run under the regular conditions as described above with the wire heated to approximately 1800°A. Two other samples were run under exactly the same conditions as the first four except that the temperature of the wire was set at 1500 and 1600°A. , respectively. Each sample was purified carefully and its density determined by means of a magnetic swimmer as described in a previous paper.^{3a} The results are given in Table II.

TABLE II

Sample	T, °A.	Time, days	Density increase, $\Delta\gamma$
1a	1800	2.5	6.3
1b	1800	5	6.6
2	1800	4.5	6.9
3	1800	8	7.1
4a ^a	1800	7	7.1
4b	1800	3	7.3
Average of first four			7.0
5	1600	6	3.2
6	1500	6	3.3

^a Sample 4a was replaced in the apparatus and equilibrated again for three days (becoming sample 4b). The slight increase in density was within the experimental error in the determination, indicating that equilibrium had been reached in the previous trial.

The results at lower temperatures (samples 5 and 6) were obtained with all other conditions unchanged and indicated that at 1600°A. about twenty-five days instead of three would be required for complete equilibrium and about sixty days at 1500°A. These data do not permit the calculation of the activation energy, because the limiting factor in attaining equilibrium at 1800°A. was that at any one instant the quantity of air in contact with the steam was limited. The great increase in the time required indicated, however, that the velocity of the reaction is greatly reduced by this reduction in temperature. From the fact that high temperature appears to be the necessary condition for the reaction, it may be presumed to depend on thermal dissociation rather than on activated adsorption.

This technique appears to make possible the easy preparation in a few days of considerable quantities of water whose slightly high density is due to oxygen alone. This aspect of the problem is now being studied further. An unknown sample of water may be normalized by this method

(with respect to air oxygen rather than to a standard water) as an alternative to treatment with equilibrated carbon dioxide, sulfur dioxide, etc.⁵

We are indebted to the Research Committee of

(5) Dr. Charles H. Greene kindly writes as follows (December 22, 1936): "There is a small error in your result. The hot platinum in your apparatus brings the water vapor to the same isotopic composition as atmospheric oxygen. Water vapor, however, is slightly richer in O¹⁸ than the liquid water with which it is in equilibrium. Thus the liquid water in your apparatus, after equilibrium is attained, will be somewhat richer in O¹⁸ than atmospheric oxygen. From the results of Wahl and Urey, *J. Chem. Phys.* **3**, 411 (1935), I estimate the effect as 0.9 = 0.3 p. p. m. This correction would bring your results into very good accord with our own."

If Dr. Greene's correction is accepted, our value of the Dole effect for liquid fresh water becomes 6.1 γ, assuming that complete equilibrium was reached.

the University and to the Wisconsin Alumni Research Foundation for grants in aid of this work.

Summary

It has been found that the exchange equilibrium between water vapor and oxygen is rapidly established on a hot wire at 1800°A. and above, but much more slowly at lower temperatures. Water thus equilibrated with excess air increases in density by about 7 p. p. m., and the Dole effect is confirmed. Oxygen-abnormal water may be prepared conveniently by this method, and the oxygen isotope ratio of an unknown sample may be studied with its aid.

MADISON, WIS.

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The Oxybromides of Silicon

BY WALTER C. SCHUMB AND CAROLYN H. KLEIN

Although considerable information has been gathered concerning the oxychlorides of silicon,¹ little was known of the oxybromides of that element at the outset of this research. An investigation of the oxybromides of silicon was begun in 1934, with the object of isolating an homologous series of these compounds.

Of the various methods previously employed in the preparation of the oxychlorides, the ones which appeared most promising for adaptation to oxybromide preparation were the oxidation of the silicon tetrahalide, and the reaction of a mixture of oxygen and the halogen on silicon. In addition to these two successful methods, we have made studies of the oxidation of hexabromodisilane Si₂Br₆, silicobromoform SiHBr₃, and of Si₂OBr₆, as well as the effect of ozone and of silver oxide on silicon tetrabromide.

I. The Reaction of a Mixture of Oxygen and Bromine with Silicon and with Calcium Silicide.—The apparatus used in a study of the simultaneous effect of oxygen and bromine on silicon was similar to that used by Gattermann² for the preparation of silicon tetrabromide. A stream of oxygen, dried with calcium chloride, was bubbled through a trap of bromine (at 55°) at a rate of about 3 liters per hour (a velocity such that some oxygen bubbled through at the exit of the apparatus). The mixture of oxygen and bromine resulting was then passed over commercial silicon

(averaging 97.5% Si) heated by a gas furnace to the desired temperature, about 700°. The product of the reaction was collected in a trap cooled in ice water.

The crude product was distilled fractionally, the excess bromine and silicon tetrabromide passing off first, followed by higher boiling material, which was collected up to 225° under a high vacuum. After repeated fractionation with an efficient column a separation of the compounds present in the mixture was effected. The combined results of two experiments, together with the formulas of the compounds isolated and identified by methods described below, are collected in Table I.

These substances all hydrolyze in the presence of moisture of the air, the speed being directly proportional to the volatility of the compound. They are miscible in all proportions with carbon tetrachloride, carbon disulfide, chloroform, and silicon tetrabromide. With the exception of the first and third, they have not been reported previously in the literature, and the two which were reported were prepared independently and by a different process.³

In order to determine the effect of a lower reaction temperature on the products formed, calcium silicide was used in another experiment in place of silicon, it being known that certain silicides react more readily with halogens at a lower temperature than does silicon itself. The reaction was carried out at a temperature of 180 to 200°, but in this case the product consisted almost wholly of hexabromodisilane, oxybromides being formed only in minute amounts. Evidently, in spite of an excess of oxygen, a Si-Si bond formed in preference to a Si-O-Si linkage.

Incidentally, the procedure just mentioned constitutes a far more satisfactory method of preparation of Si₂Br₆ than any hitherto described, as the yield is almost quantitative.

(1) L. Troost and P. Hautefeuille, *Bull. soc. chim.*, [2] **16**, 243 (1891).

(2) L. Gattermann, *Ber.*, **22**, 186 (1889).

(3) H. Rheinboldt and W. Wisfeld, *Ann.*, **517**, 197 (1935).