from carbon dioxide and other weaker acids.

Acknowledgment.—The authors wish to acknowledge the interest taken in the work by Mr. W. F. Davidson, Director of Research and Test, Consolidated Edison Company of New York, Inc.

Summary

Experimental results on the potentiometric titration of acids illustrate the variation of the relative strength of acids as the character of the solvent is changed.

BROOKLYN, N. Y. RECEIVED JULY 9, 1937

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

A Comparison of the Data of State of Normal and Para Hydrogen from the Boiling Point to 55°K.

BY EARL A. LONG[1] AND OLIVER L. I. BROWN

In the course of some low-temperature investigations on gaseous deuterium, it became of interest to us to determine a possible influence of ortho and para states on the equation of state of a gas. Although the effect of molecular rotation and the force fields set up by different spin couplings should be small, one might predict measurable differences in the *PVT* relationships of ortho and para forms of a gas at low temperatures. Lewis and Hanson[2] suggested the possibility of such behavior for the case of normal and para hydrogen, which should exhibit a greater difference than the two forms of deuterium. At the suggestion of Professor Gilbert N. Lewis, we have compared the two forms of hydrogen.

The apparatus and method, involving the use of a "double" constant-volume gas thermometer, have been described previously.[3]

Normal Hydrogen.—Electrolytic hydrogen from the laboratory generator was passed through a charcoal trap immersed in liquid air to remove about 0.01% oxygen impurity known to be present. The hydrogen was then passed over a white-hot platinum wire in order to restore the "normal" equilibrium between ortho and para states.

Para Hydrogen.—The para hydrogen was prepared by adsorption of hydrogen on activated charcoal at the boiling point of hydrogen for approximately five hours. A carefully purified sample of "Carbo-Norit" charcoal was used, and the apparatus was thoroughly evacuated and flushed with hydrogen before cooling to 20°K. Analysis with a Bonhoeffer thermal conductivity gage[4] showed a complete conversion at 20°K., corresponding to a para hydrogen content of 99.8% in the sample. The two thermometer bulbs were evacuated to 10^{-5} mm. of mercury pressure, then flushed repeatedly with normal and para hydrogen, respectively, before being filled, to ensure the absence of any traces of oxygen.

Pressure Readings.—The pressures were read in two identical glass manometers, of 16-mm. internal diameter, by comparison with a steel meter bar calibrated by the United States Bureau of Standards. The comparison instrument was a Société Génévoise cathetometer, reading to 0.02 mm. The corrections for thermal expansion of the thermometer bulbs, and the "dead-space" corrections for the small amount of gas in the connecting capillaries and fixed points of the manometers, were applied in the usual manner.[5] All pressures are expressed in international atmospheres.

In calculating temperatures, the data of Cath and Onnes[6] were used for the corrections to the normal hydrogen thermometer.

Results

Our results are expressed in terms of the empirical equation of state of Kamerlingh Onnes[7]

$$pV_A = A_A + (B_A/V_A) \qquad (1)$$

where p is given in international atmospheres, V_A (in Amagat units) is the volume expressed in terms of the normal volume as unity, and B_A is the "second virial coefficient." A_A is given by

$$A_{A_T} = \left(\frac{A_{A_0}}{273.10}\right) T \qquad (2)$$

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[1] National Research Fellow, 1934–36.

[2] Lewis and Hanson, THIS JOURNAL, **56**, 1687 (1934).

[3] Long and Gulbransen, *ibid.*, **58**, 203 (1936).

[4] *Cf.* Farkas and Farkas, "Light and Heavy Hydrogen," Cambridge University Press, 1935, pp. 20–24.

[5] *Cf.* Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929); Cornish and Eastman, *ibid.*, **50**, 643 (1928).

[6] Cath and Onnes, *Comm. Phys. Lab. Univ. of Leiden*, No. 156, 26 (1922).

[7] Kamerlingh Onnes, *ibid.*, No. 71 (1901).

using 273.10°K. as the absolute temperature of the ice-point, and

$$A_{A_0} = (1 - B_{A_0}),\ \text{at } 0°\text{C.} = 273.10°\text{K.}$$
$$= (1 - 0.000605) = 0.999395$$

as given by Nijhoff and Keesom.[8] V_A is calculated from our measured ice-point pressures by the relation[9]

$$V_A = \frac{A_{A0}}{p_0} + \frac{B_{A0}}{A_{A0}} \qquad (3)$$

V_A is a constant in each set of measurements, since our measured pressures were always calculated to those corresponding to the ice-point volume of the system. We used the accepted value of A_{A_0} for para as well as normal hydrogen as it may be assumed that any differences in the compressibilities at this high temperature are negligible.

The measured ice-point pressures were, for normal hydrogen, 0.950353 atmosphere, and, for para hydrogen, 0.949502 atmosphere, each value being a mean of two determinations, taken before and after the low-temperature measurements. The maximum deviation in both ice-point pressures was 0.05 mm.

The data are shown in Table I, in which column I gives the absolute temperature, column II the measured values of pV_A, column III gives A_{A_T}, and column IV gives the values of B_A, the second virial coefficient.

The values of B_A in column V were calculated from the equation

$$B_A \times 10^3 = 7.041 \times 10^{-3}T - 0.6063 \qquad (4)$$

which was fitted to the assembled data on normal and para hydrogen by the method of least squares. This equation reproduces the B-values for both forms of the gas, as may be seen from column V, and from Fig. 1. The agreement is shown graphically in Fig. 1, in which we have also plotted the measurements on normal hydrogen made in the Leiden Laboratory.[10] The solid curve in Fig. 1 represents equation (4), and the experimental data are shown by circles.

TABLE I

PVT DATA FOR NORMAL AND PARA HYDROGEN

T, °K.	A_{A_T}	pV_A	$-B_A \times 10^3$	$-B_A \times 10^3$ from Eq. 4	ΔB_A (Exp. - Eq. 3) $\times 10^3$
Normal Hydrogen, $V_A = 1.052209$					
20.87	0.076373	0.075931	0.465	0.459	+0.006
24.11	.088229	.087817	.434	.437	− .003
27.65	.101184	.100797	.407	.412	− .005
32.43	.118676	.118323	.371	.378	− .007
37.08	.135692	.135370	.339	.345	− .006
41.64	.152379	.152084	.310	.313	− .003
46.45	.169981	.169713	.282	.279	+ .003
Para Hydrogen, $V_A = 1.053152$					
20.87	0.076373	0.075924	0.473	0.459	+0.014
24.11	.088229	.087816	.435	.437	− .002
27.65	.101184	.100798	.407	.412	− .005
32.43	.118676	.118318	.377	.378	− .001
37.08	.135692	.135366	.343	.345	− .002
41.49	.151830	.151530	.316	.314	+ .002
41.64	.152379	.152080	.315	.313	+ .002
43.95	.160833	.160547	.301	.297	+ .004
48.45	.177300	.177048	.265	.265	.000
52.51	.192158	.191935	.235	.237	− .002
56.21	.205698	.205493	.216	.211	+ .005

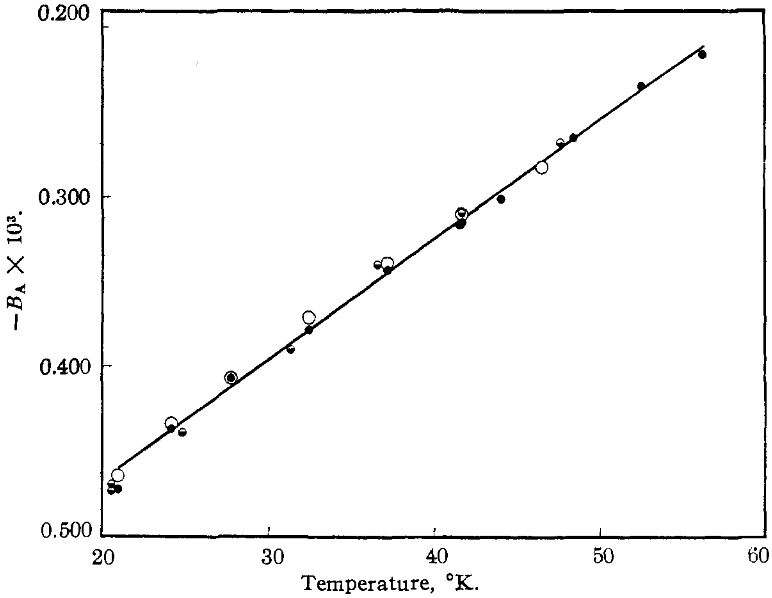

Fig. 1.—Equation 4; ○, "normal" hydrogen; ●, para hydrogen; ⊖, van Agt and Onnes; Nijhoff and Keesom.

It is apparent from Fig. 1 and Table I that normal and para hydrogen show no essential difference in their deviations from perfect gas behavior, within the experimental error of the low pressures used in this investigation. It may be that deviations would be found at higher pressures, but probably to only a slight extent.

We may predict that deuterium should ex-

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(8) Nijhoff and Keesom, *Comm. Phys. Lab. Univ. of Leiden*, No. 188-d.

(9) We are much indebted to Professor W. H. Keesom for pointing out to us the correct method of calculating V_A and its related quantities.

(10) Van Agt and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. of Leiden*, No. 176-b; Nijhoff and Keesom, *ibid.*, No. 188-e.

hibit the same agreement in the *PVT* behavior of the ortho and para forms of the gas.

A recently published paper by Schäfer [*Z. physik. Chem.*, **36**, 85 (1937)] describes a similar investigation of the data of state of normal and para hydrogen, his results agreeing very well with ours, although calculated differently.

Summary

The data of state of normal and 99.8% para hydrogen have been compared at low pressures, from the boiling point to 55°K.

The measurements show no essential differences in the *PVT* behavior of the two forms of gaseous hydrogen. The data also agree well with the accurate measurements of the Leiden Laboratory.

BERKELEY, CALIF. RECEIVED JULY 6, 1937

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

The Formation of Water and Hydrogen Peroxide at Low Pressures

BY W. H. RODEBUSH, C. W. J. WENDE AND R. W. CAMPBELL

The reactions between hydrogen and oxygen and their various dissociation products have been studied over a wide range of experimental conditions and the literature is much too voluminous to be cited here. This work concerns itself with reactions of active species produced by the electrodeless discharge at low pressures. The reactions occurring under these conditions should be similar to those occurring in the photochemical reaction[1] at higher pressures, but they are not necessarily important in the explosive reaction at higher temperatures.

The formation of hydrogen peroxide in dissociated water vapor was studied extensively by Rodebush and Wahl.[2] Campbell and Rodebush[3] showed that hydrogen peroxide is only formed in appreciable quantities on a liquid air cooled surface. Oldenberg has studied the rate of disappearance of hydroxyl in dissociated water vapor by spectrographic methods.[4] The reaction between atomic hydrogen and molecular oxygen has been studied by Geib,[5] who found that peroxide is only formed at temperatures well below −80°. He concluded that the peroxide was formed by the direct combination of hydrogen atoms with oxygen on the walls of the trap.

A preliminary survey of this work was presented by one of the authors at the Princeton Symposium on Molecular Structure.[6] At that time the authors had not yet realized the importance of pressure as a variable. The results presented here were obtained in experiments in which the pressure was controlled carefully.

Experimental

The gas or vapor was dissociated by pumping it rapidly through an electrodeless discharge of high frequency.[7] From the discharge it was pumped rapidly to the reaction chamber and the products were frozen out in traps with various refrigerants. The apparatus was made of Pyrex glass. No stopcocks were used and the apparatus was cleaned with chromic acid and washed with water. The pressures were measured by a manometer filled with dibutyl phthalate and the percentage dissociation was determined by a Wrede[8] gage.

The Reactions of Dissociated Water Vapor.—Water vapor was drawn from a calibrated reservoir and passed through a length of capillary tubing into the discharge. The reservoir was kept in a thermostated bath, so that the rate of flow could be varied by changing the bath temperature over the range 10–45°.

The reaction may take three possible courses: water passed into the system may reappear in the trap as such; it may be converted into peroxide; or it may be lost as permanent gases. The results are given in terms of "per cent. conversions," that is, the percentage of the admitted water which undergoes each of the above reactions. It should be noted that on this basis two molecules of water are required to furnish one molecule of peroxide.

1. **The Reaction in the Trap at −180°.**—Dissociated water vapor was led directly into a liquid air trap. Per cent. conversions are plotted against pressure (in millimeters of mercury) in Fig. 1. Below 0.8 mm. pressure, the composition of the products was quite uniform, and the conversions were roughly: water, 40%; peroxide, 50%; and permanent gases, 10%. From 0.8 to 1.1 mm. the "loss" increased. This was probably due to a reaction on the walls of the connecting tube or on the walls of the trap near the surface of the liquid air. The sharp rise in the "water" curve above 1.1 mm. may be ascribed to a decrease in the efficiency of the discharge at higher pressures.

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(1) For references and discussion of the photochemical reactions between hydrogen and oxygen see J. R. Bates, *J. Chem. Phys.*, **1**, 457 (1933); M. G. Evans, *ibid.*, **2**, 726 (1934); H. A. Smith and G. B. Kistiakowsky, THIS JOURNAL, **57**, 835 (1935).

(2) W. H. Rodebush and M. H. Wahl, *J. Chem. Phys.*, **1**, 396 (1933).

(3) R. W. Campbell and W. H. Rodebush, *ibid.*, **4**, 298 (1936).

(4) O. Oldenberg, *ibid.*, **3**, 266 (1935).

(5) K. H. Geib, *Z. physik. Chem.*, **A170**, 1 (1934).

(6) W. H. Rodebush, *J. Phys. Chem.*, **41**, 283 (1937).

(7) W. H. Rodebush and W. C. Klingelhoefer, THIS JOURNAL, **55**, 130 (1933).

(8) E. Wrede, *Z. Physik*, **54**, 53 (1929).