yet, as already mentioned, adsorption of water vapor in their case exceeded that of hydrogen. The specific surface of alumina must therefore be markedly greater than that obtaining with good hydrogenating catalysts. The lower susceptibility of the dehydration catalysts to poisoning is in accord with this observation.

The lower heat of adsorption of water vapor combined with the lower temperature at which activated adsorption occurs, when contrasted with the corresponding data for hydrogen, provides a sufficient explanation of the exclusive hydration–dehydration characteristics of alumina.

Summary

The activated adsorption of water vapor by alumina has been studied.

It has been shown that the data obtained, when compared with similar data for hydrogen adsorption, account for the hydration–dehydration characteristics of alumina catalysts.

PRINCETON, N. J. RECEIVED MAY 22, 1934

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

The Vapor Pressure of Solid and Liquid Deuterium and the Heats of Sublimation, of Fusion and of Vaporization

BY GILBERT N. LEWIS AND W. T. HANSON, JR.

Setting out, seven months ago, to determine approximate values of the vapor pressure of solid and liquid deuterium, so many experimental difficulties had to be overcome that eventually it became possible, without much additional labor, to make these determinations with a high degree of accuracy. From these determinations we have been able to calculate the heat of vaporization from the solid and liquid states as well as the heat of fusion.[1]

In order to avoid the necessity of employing a thermometer, the vapor pressures of deuterium and of hydrogen were always measured simultaneously, the vapor pressure of the latter thus serving as our thermometric scale. To avoid any doubt as to the state of the hydrogen used for comparison it was always converted into the para form by the use of a small amount of active charcoal.

The essential parts of the apparatus are shown in Fig. 1. The gaseous deuterium was prepared from heavy water by dropping the latter into the tube J, which was then sealed off at the top, and after J was immersed in liquid air the tubes J and I were exhausted. The stopcock leading to the vacuum being then closed and the tube I being placed in liquid air, the water from J was distilled into the tube I, which contained sodium in an aluminum crucible. When the tube I was then heated for some hours at 350°, all of the hydrogen of the water was set free and was then transferred to the bulb L by means of the mercury pump at K.

The hydrogen was purified by standing with charcoal in the tube B at the temperature of liquid air. It was then drawn off slowly into the reservoir C, the tube B being kept in liquid air.

As a low temperature bath a large Dewar tube 75 cm. in height and of about five liters capacity was filled with liquid hydrogen. Constant temperatures below the boiling point of hydrogen were obtained satisfactorily by reducing the pressure on the boiling hydrogen through a needle valve, which was regulated by hand. The constancy of temperature throughout the thermostat was surprisingly good. Identical results were obtained whether the bath was full of boiling hydrogen or nearly empty. On several occasions the liquid was violently agitated by a stream of hydrogen from an outside source, without any noticeable effect.

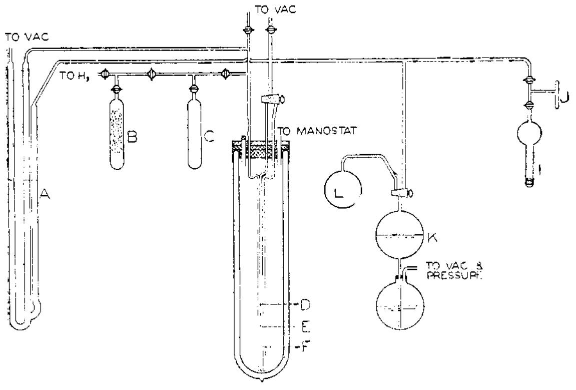

Fig. 1.

In this thermostat were three tubes D, E and F. They were made of Pyrex glass with very thin walls, approximately 0.1 mm., in order to ensure rapid heat transfer from the liquid hydrogen of the bath to the contents of the tube. The three tubes were wound together with several feet of fine copper wire to ensure constancy of temperature.

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[1] From some preliminary measurements similar calculations have been made by Brickwedde, Scott, Urey and Wahl, *Bulletin Am. Phys. Soc.*, **9**, 16 (1934). Our own measurements have been briefly reported in THIS JOURNAL, **56**, 1001 (1934).

The S-curves near the tops of these tubes were wound with adhesive tape to cut down radiation from above. Two of these tubes were connected to the deuterium system by means of a three-way stopcock, and the other one was connected to the hydrogen system. One of the deuterium tubes and the hydrogen tube contained several milligrams of charcoal.

The three manometer tubes at A were 15 mm. in diameter and the heights of mercury could be read easily with a cathetometer to 0.2 mm. Of these the one at the left was usually evacuated, although it was sometimes convenient to open it to the atmosphere, the barometric height being then determined. The intermediate manometer tube was connected with the hydrogen, and the right-hand tube to the deuterium system.

In making the vapor pressure measurements about 250 cc. of each gas was employed and since a part of this went into the manometer and connecting tubes only about one centigram of liquid was condensed in the tubes D and E (or F). We have no reason to believe that any higher accuracy can be obtained by using larger amounts.

Owing to the fact that hydrogen has a much greater vapor pressure than deuterium the observed vapor pressure of deuterium is extremely sensitive to small impurities of hydrogen. In our first series of experiments, in which nearly pure heavy water was used, a very surprising vapor pressure curve was obtained which could be interpreted only upon the assumption that our deuterium contained over 10% of hydrogen. This must have come from the sodium which was used to set free the deuterium, and was either dissolved in the metal or was present in some small amount of sodium hydroxide which remained after the tube containing the sodium had been heated and exhausted. Using the same sodium and a second sample of heavy water we next prepared another lot of deuterium which proved to contain less than 1% of hydrogen. Finally the preparation was once more repeated, using the same sodium and a sample of D_2O in which every effort was made to exclude contamination by ordinary water. Thus we obtained deuterium which later proved to contain less than 0.2% of hydrogen. This sample was now fractionated in the apparatus itself by slowly distilling away 60% of the liquid deuterium. The remaining 40% was used for the measurements of vapor pressure which are given below. Later this sample was further fractionated without, however, producing any change in vapor pressure as great as 0.1%. The vapor pressure measurements themselves afford a very exact determination of small amounts of hydrogen in deuterium; 0.03% of hydrogen changes the vapor pressure by 0.1% and therefore our sample contained less than 0.03% of hydrogen.

Our results are given in Table I. The first two columns, which give the measured vapor pressure of H_2 and D_2, and the third column, which gives their ratio, are the direct results of observation. The last column gives the absolute temperature calculated from p_1 by the equation which Keesom, Bilj and van der Horst[2] give for the vapor pressure of para hydrogen. A revision of their experiments might lead to slightly different values for T. The fourth column, which gives the fugacity of the deuterium, depends on certain assumptions which we shall presently discuss.

TABLE I

p_1 (cm.)	p_2 (cm.)	p_2/p_1	f_2	T
77.00	25.63	0.3328	24.95	20.30
61.17	19.08	.3119	18.66	19.56
51.21	15.13[b]	.2954	14.84	19.01
47.27	13.63	.2883	...	18.77
46.27	13.24	.2861	13.01	18.71
Triple point		...	12.71	18.66
45.26	12.87	.2844	...	18.64
44.94	12.69[c]	.2824	12.47	18.62
44.38	12.47	.2810	12.26	18.59
44.05	12.31[a]	.2795	...	18.56
43.71	12.16[c]	.2782	11.96	18.54
42.89	11.84[c]	.2761	...	18.49
42.14	11.51[c]	.2731	11.33	18.44
41.01	11.05[b]	.2694	...	18.36
38.06	9.85	.2588	9.71	18.15
29.22	6.61	.2262	6.55	17.44
21.56	4.13	.1915	4.10	16.65
11.85	1.69	.1426	1.68	15.30

[a] Pressure taken with D_2 in the tube containing charcoal.

[b] Average of one point with charcoal and one point without.

[c] Pressure taken while bath was warming. All others were taken with descending temperature.

The third tube (F) which entered our thermostat contained a few milligrams of charcoal. After making the vapor pressure measurements in the clean tube the deuterium was transferred to tube F with a view to establishing the low temperature equilibrium between the ortho and para forms of deuterium. In spite of the fact that the change of composition between the equilibrium states of deuterium at high temperature and low temperature is calculated to be considerably smaller than it is for hydrogen, we should expect an appreciable change of vapor pressure when the deuterium is transferred to the charcoal tube. Yet, as we have mentioned in our earlier communication, the measurements fell exactly upon the curve previously obtained and are in fact incorporated in Table I. We must assume that the equilibrium was not established by the charcoal, or that it had already been established without the charcoal, or that the difference in vapor pressures of ortho and para deuterium is smaller than in the case of hydrogen.

Both hydrogen and deuterium at these temperatures are so far from being perfect gases that the ordinary approximate method of determining the heat of vaporization from the slope of the curve

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(2) Keesom, Bilj and van der Horst, *Leiden Comm.* **217a**.

log p against $1/T$ could not be employed. If, however, the equation of state is known there are several ways of making exact thermodynamic calculations. Even for hydrogen the equation of state is not fully known. It has been shown by Simon and Lange[3] that the equation of state obtained from the critical data gives no agreement between the calculated and observed values of the heat of vaporization of hydrogen. They found, however, that they could obtain such agreement by means of the following equation of state

$$pv = RT\left[1 + \frac{0.107\,p}{T}\left(1 - \frac{6600}{T^2}\right)\right] \qquad (1)$$

where p is in atmospheres.

We shall assume for want of any better information that this is a true equation of state for hydrogen. We next must inquire whether the same equation of state will apply to both hydrogen and deuterium. It is hard to see how the two gases can differ much with respect to the intermolecular forces, unless the equation of state is affected by the rotation of the molecules, and it would be interesting to ascertain whether the equation of state is the same for ordinary and para hydrogen. We shall assume that Equation 1 is true not only for hydrogen but also for deuterium.

From the equation of state we may calculate the fugacity by the equation of Lewis and Randall[4]

$$RT \ln f = RT \ln p - \int_0^p \alpha \mathrm{d}p \qquad (2)$$

where α is the difference between the volume of a gas and the volume of a perfect gas under similar conditions. Hence from Equation 1

$$\alpha = -0.107R\left(1 - \frac{6600}{T^2}\right) \qquad (3)$$

and

$$\ln \frac{f}{p} = \frac{0.107\,p}{T}\left(1 - \frac{6600}{T^2}\right) \qquad (4)$$

Having obtained from this equation the values of the fugacity given in Table I, we have plotted log f against $1/T$. The slope of this curve multiplied by 4.579 gives the *ideal* heat of vaporization or, in other words, the heat of evaporation into a vacuum. The points for the liquid fall on a straight line. Those for the solid also lie nearly upon a straight line except for minor deviations at the very low temperatures, where the experimental error was largest. At the triple point, which we find to be 18.66°K., our plot gives for the heat of vaporization of the liquid 308.3 and of the solid 357.2 cal. per mole. If the equation of state and the temperature scale are correct, these values of the ideal heat of vaporization are accurate to less than 0.5 cal. We estimate also that these values are not more than a few tenths of a calorie higher than the actual heats of vaporization as they would ordinarily be measured. The difference between the two heats of vaporization, 48.9 calories per mole, is the heat of fusion of deuterium at its triple point. This value is more accurate than the two heats of vaporization in that it is practically unaffected by the choice of an equation of state.

By extrapolating from our plot of log f against $1/T$ and by using the equation of state we find 23.6°K. as the boiling point of deuterium.

During the course of the experiments that we have described it was necessary to obtain as much information as possible each time that the expensive and laborious process of filling the bath with liquid hydrogen was performed. Several observers were therefore required and we wish to express our great obligation to Dr. R. T. Macdonald and Dr. P. W. Schutz for their very generous aid.

Summary

We have measured between 20 and 15°K. the vapor pressure of deuterium containing less than 0.03% hydrogen. Small amounts of hydrogen produce large changes in the observed vapor pressure. The measurements for the liquid are accurate to 0.1% and for the solid to 0.1 or 0.2%, except at the three lowest temperatures.

The vapor pressures were compared to those of para hydrogen and temperatures were thus obtained from an equation of Keesom, Bilj and van der Horst. An equation of state used by Simon and Lange for hydrogen we have assumed to apply also to deuterium. Thence the fugacities were determined and from these values we find the ideal heat of vaporization of the liquid deuterium 308.3, and of solid deuterium 357.2 cal. per mole. The heat of fusion is therefore 48.9 cal. per mole, and this value is almost independent of the equation of state employed.

The vapor pressure of para hydrogen at its boiling point is three times that of deuterium and is seven times that of deuterium at our lowest temperature. The vapor pressure of liquid deuterium is not observably affected by the

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[3] Simon and Lange, *Z. Physik*, **15**, 307 (1923).

[4] "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 195.

presence of charcoal. The triple point of deuterium is 18.66°K., and the boiling point is found by extrapolation to be 23.6°K.

BERKELEY, CALIFORNIA RECEIVED MAY 28, 1934

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

The Racemization of *l*-Bromosuccinic Acid by Bromide Ion in Non-Aqueous Solvents. The Mechanism of Organic Reactions

BY A. R. OLSON AND H. H. VOGE

The various attempts which have been made to explain mechanisms of organic reactions such as substitutions and molecular rearrangements, can be divided into two groups: (a) those in which primary dissociations into radicals or ions are assumed in the mechanism, and (b) those in which additions or simultaneous additions and dissociations occur. A detailed exposition of this latter view-point can be found in papers by Meer and Polanyi[1] and by Olson,[2] and an experimental proof of the mechanism for a particular case in an article by Olson and Long.[3] It is to be noted that not only has it been demonstrated that the latter theory is capable of explaining the experimental facts, but also that the former theory must meet objections of the following type.

The average strength of a carbon–bromine bond for a substance in the gaseous state is 65,400 calories per mole.[4] This presupposes a dissociation into neutral particles. Since the ionizing potential of carbon is very much greater than the electron affinity of bromine, a dissociation into ions would require much more energy than this. Even if we assume that it requires only 65,400 calories per mole to separate the molecule into a bromide ion and a positive residue, we can easily calculate by means of the Arrhenius equation, rate $= Se^{-E/RT}$, that, at room temperature, under the most favorable conditions, it would require millions of years to produce enough bromide ion to be detected by silver nitrate. Actually if bromosuccinic acid is dissolved in water a detectable amount of bromide ion will be formed in a few minutes. Furthermore Olson and Long[5] have shown that in aqueous solutions the heat of activation of the reaction *l*-bromosuccinic acid + Br^- = *d*-bromosuccinic acid + Br^- is 22,300 calories per mole. Obviously, either the mechanism does not involve such a simple bond rupture, or the physical properties of the solvent operate to reduce greatly the bond strength. This latter alternative appears, *a priori*, to be unreasonable when we remember that most of the work of separation is done at distances which are small compared to intermolecular distances.

The widespread use of simple dissociations in the explanation of reaction mechanisms caused us to investigate this possibility more fully by studying the reaction *l*-bromosuccinic acid + Br^- = *d*-bromosuccinic acid + Br^- in methyl alcohol, acetone and acetic acid, as well as in acetone containing various amounts of water.[6]

Experimental Method and Preparation of Materials

The reaction rates were studied polarimetrically using the equipment described by Olson and Long.[3]

Methyl Alcohol.—Commercial methyl alcohol was fractionally distilled in a 60-cm. bead-filled column. The center fraction which was retained had a constant boiling point. It was treated with magnesium after the method of Lund and Bjerrum[7] to ensure removal of all water, and was subsequently fractionated in a small column to yield the alcohol used as a solvent.

Acetone.—Acetone was purified in the manner recommended by Conant and Kirner.[8] The alkaline permanganate solution was fractionated in a 60-cm. bead-filled column. The central fraction had a constant boiling point of 56.2° (corr.). To this fraction was added sodium hydroxide, and it was again fractionated in the 60-cm. column to give the acetone used in the experiments.

Acetic Acid.—A high grade of glacial acetic acid was twice fractionated in a 25-cm. column with retention of

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(1) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932).

(2) Olson, *J. Chem. Phys.*, **1**, 418 (1933).

(3) Olson and Long, THIS JOURNAL, **56**, 1294 (1934).

(4) Pauling, *ibid.*, **54**, 3570 (1932).

(5) Olson and Long, unpublished work in this Laboratory.

(6) For references on investigations of the effect of solvent on reaction velocity see: Soper and Williams, *Proc. Roy. Soc.* (London), **A140**, 59 (1933); Thompson and Blandon, *J. Chem. Soc.*, 1237 (1933); Walden, "Electrochemie nichtwassriger Lösungen," Barth, Leipzig, 1924, pp. 370–426; Christiansen, Landolt-Börnstein, "Tabellen," Zweiter Erg. bd., Verlag Julius von Springer, Berlin, 1931, pp. 1621–1632.

(7) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

(8) Conant and Kirner, THIS JOURNAL, **46** 232 (1924).