type $k = Ae^{-Q/RT}$ must yield to others more complex in form, in which the term independent of T may have a value different from that of A by many powers of ten. For this reason no correlation of these A's can be founded securely until it has been proved that Q is in fact independent of T—that the simple Arrhenius equation is valid. Such proof is usually difficult, if not impossible, of attainment, and as a result Arrhenius constants furnish less reliable material for theoretical treatment than do heats of activation. What has just been said obviously applies to any attempted interpretation of A in terms of a collision number, whether the reaction being considered takes place in the gas phase or in solution.

Summary

1. Experimental evidence has been presented for the first time to show that hydrogen peroxide is reduced by bromide or by chloride according to the rate law

$$-d(H_2O_2)/dt = k_1^0(H_2O_2)(X^-) + k_1(H_2O_2)(X^-)(H^+) \quad (2)$$

which is formally identical with that long known to govern its rate of reduction by iodide.

2. The simplest kinetic interpretation of this rate law assumes that the two rate-determining steps

$$H_2O_2 + X^- \xrightarrow{k_1^0} H_2O + XO^- \quad (3)$$

$$H_2O_2 + X^- + H^+ \xrightarrow{k_1} H_2O + HXO \quad (4)$$

proceed simultaneously and independently.

3. The effects of k_1^0 and k_1 on temperature variation have been determined; equations of the type $k = Ae^{-R/RT}$ adequately summarize the experimental results. Reasonably accurate values of the parameters A and Q for six closely related reactions (one pair for each halide studied) are now available (Table IV).

4. A partial interpretation of certain regularities which these parameters show has been attempted. The stand has been taken that heats of activation (the Q's) are probably of greater fundamental significance than Arrhenius constants (the A's).

5. Certain difficulties attending the "stray loss" correction have been briefly touched upon.

BERKELEY, CALIF. RECEIVED MAY 10, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activated Adsorption of Water Vapor by Alumina

BY HUGH S. TAYLOR AND AUSTIN J. GOULD

In an earlier communication[1] on the relation between activated adsorption and specific reactions at surfaces it was emphasized that the relative dehydration and dehydrogenation efficiencies of oxide surfaces would be dependent upon the velocities of desorption of water vapor and hydrogen, respectively, from the surface in question. These velocities will in their turn be dependent upon the activation energies of adsorption of the two gases and their respective heats of adsorption. Taylor and Sickman[2] demonstrated by measurements of adsorption of water vapor and hydrogen on zinc oxide, a predominantly dehydrogenation catalyst, that the velocity of desorption of hydrogen from the surface was pronouncedly more rapid than that of water vapor under similar conditions, even though the amount of adsorption of water vapor was greater than that of hydrogen. We have now demonstrated the reverse behavior in the case of a typical dehydration catalyst, precipitated alumina. With such material it has already been shown[1] that hydrogen is only markedly adsorbed in the activated form above 400° with an activation energy of adsorption as great as 27,500 calories, and, as is obvious from the temperature of binding, with a heat of adsorption which must be at least 30,000 calories. We have shown that activated adsorption of water vapor occurs in a much lower temperature range and with much lower heats of adsorption. The experiments also reveal an astonishingly large adsorptive capacity of alumina for water vapor at high temperatures.

Experimental

The apparatus employed was similar to that used by Taylor and Sickman.[2] A small bulb containing water, distilled *in vacuo*, and immersed in an ice-bath, furnished the water vapor. This bulb was connected through a three-way stopcock to a mercury reservoir and to a bulb of 523 cc. capacity which in turn was connected through a

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[1] Taylor, *Z. physik. Chem.*, Bodenstein Festband, 475 (1931).

[2] Taylor and Sickman, THIS JOURNAL, **54**, 602 (1932).

stopcock to the catalyst chamber. When the two bulbs were connected, the vapor pressure of water in the large bulb rapidly reached the equilibrium pressure, 4.57 mm. The stopcock connecting the two bulbs was then closed and the known amount of water vapor contained in the large bulb was displaced by mercury into the absorption vessel. Since some parts of the apparatus were at room temperature it was necessary to work in the pressure range below 23 mm. The pressure measurements were made by reading the differences in the heights of two mercury columns by means of a cathetometer. Tubing 22 mm. in diameter was used for this manometer to facilitate accuracy of reading and to avoid errors due to capillary effects. One arm of the manometer was continuously evacuated to provide the zero pressure reading, the other was connected to the adsorption system.

The alumina was prepared by precipitation of the hydroxide from dilute solutions of the nitrate by addition of dilute ammonium hydroxide. This was followed by prolonged washing of the precipitate with water and subsequent ignition in a muffle furnace. It was found that evacuation of the oxide for twelve hours at 480° with a mercury vapor-oil pump system sufficed to reduce the concentration of adsorbed vapor to such a point that no appreciable pressure developed if the pumps were turned off and the catalyst kept at 480°. The alumina employed weighed 9.6 g.

Experimental Results

The existence of activated adsorption and the slowness of attainment of equilibrium is illustrated by the following data: 116 cc. of water vapor measured at N. T. P. showed in successive observations at various time intervals the following pressures at 218°: 1.33, 1.24, 1.20, 0.85, 0.80 mm. The temperature of the system was then raised to 302°. A pressure of 16.65 mm. developed, which then diminished in the following manner.

Time in hours	1	2	9	17	39	66	104	122
P, mm.	15.60	14.92	7.65	6.77	5.67	5.15	4.82	4.62

The evaporation followed by readsorption which thus occurs on raising the temperature constitutes, as was already emphasized in another case,[3] positive evidence of activated adsorption. It is also clear that the slowness with which equilibrium is attained makes a precise determination of isotherms a practically impossible task.

Since the residual pressures are so low that the amount on the surface varies but little, an approximate calculation of the heat of adsorption may be obtained by recording the pressures developed at various temperatures when a given amount of water vapor, 28 cc. at N. T. P., was introduced into the adsorption system. The pressure at each temperature was recorded after the adsorbent had been held at the given temperature for several hours and the rate of decrease of pressure had become quite small. Similar experiments were made also with 306 cc. of water vapor at N. T. P. in the system. The data follow.

TABLE I

PRESSURE-TEMPERATURE RELATIONS OF ADSORBED WATER VAPOR

Volume in system, cc. N. T. P.			
28		306	
Temp., °C.	*P*, mm.	Temp., °C.	*P*, mm.
218	Inappreciable	0	Inappreciable
302	0.18	80	0.90
444	4.22	110	4.50
		132	12.95
		184	>23

Calculations using the Clapeyron-Clausius equation give for the 28 cc. data a value of $\lambda = 18.3$ k. cal.; for the 306 cc. data, two values are $\lambda = 14.4$ and 14.8 k. cal. Dohse and Kälberer[4] report a calorimetric value of 13 k. cal. for the adsorption of water vapor on bauxite.

One outstanding point of interest in this work was the magnitude of the quantity of water vapor held by alumina at elevated temperatures and low pressures. The following table gives some of the values.

TABLE II

ADSORPTION OF WATER VAPOR PER GRAM OF ALUMINA

Cc. N. T. P./g. Al_2O_3	Temp., °C.	*P*, mm.
32	132	12.9
32	110	4.5
12	302	4.6
2.9	444	4.2

The pressures recorded are all somewhat higher than equilibrium values because they were taken when the pressure was still decreasing slowly. Pearce and Alvarado[5] record a pressure of 80 mm. for an adsorption of 31.2 cc. per gram at 99.4°, approximately 18 times greater than our value at 110°. We attribute this to the fact that they evacuated their system only at the temperature of boiling water. Their surface was thus largely contaminated with water vapor before the start of their adsorption experiment. The astonishing capacity of clean alumina surfaces to adsorb water vapor is evident from a comparison with the data of Taylor and Sickman[2] on zinc oxide. They found a pressure of 4 mm. at 300° when only 1.25 cc. per gram was adsorbed, and

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(3) Taylor, THIS JOURNAL, **53**, 589 (1931).

(4) Dohse and Kälberer, *Z. physik. Chem.*, **5B**, 131 (1929).

(5) Pearce and Alvarado, *J. Phys. Chem.*, **29**, 256 (1925).

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.

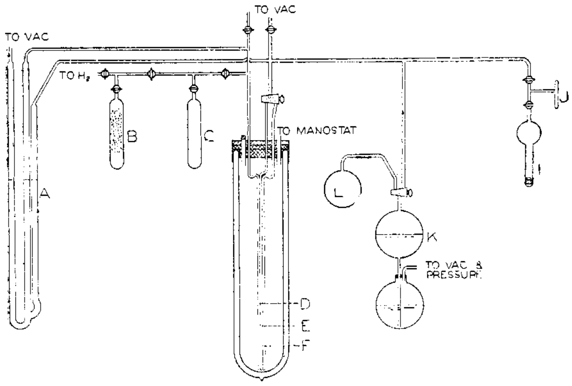

Fig. 1.

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).