explosion, which occurs under suitable pressure conditions. Thus 50 mm. of ozone requires 80 mm. of hydrogen, while 40 mm. of ozone requires 100 mm. of hydrogen to cause the mixture to explode at 85°. The amount of hydrogen converted to water in the non-explosive reaction is only a fraction of the ozone decomposed.

An ordinary glass vessel becomes activated during the course of a reaction. In each succeeding reaction the vessel exhibits increased activity. The criterion for activity is the rate of reaction. Thus, an explosive limit mixture will not explode until several runs are carried out in the vessel first, while with a non-explosive mixture the reaction rate increases in each succeeding experiment until a constant value is reached. The activity lasts for several hours. Experiments were performed which indicate that the activity is due to the formation, during the reaction, of hydrogen atoms which are adsorbed on the walls. A mechanism of the process is suggested by which hydrogen atoms take part in a chain of reactions accounting for the bulk of the enhanced decomposition of ozone, *i. e.*, $H + O_3 = OH^* + O_2^*$ and $OH^* + O_3 = 2O_2 + H$, where * represents a molecule rich in energy.

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A Note on the Heat of Sorption of Water Vapor by Massive Gold

BY ELLIOTT PIERCE BARRETT

A paper by Barry and Barrett[1] describes the methods used and the results obtained in a study of the heat of sorption of water vapor by massive gold in a saturated atmosphere. It is the purpose of this communication to point out that the relationship between heat of sorption and weight of vapor sorbed obtained from that investigation is similar to that found by other investigators working with quite different systems.

In the joint paper to which reference has been made, it was shown that for water vapor and gold, the integral heat of sorption, H, at any time, t, measured from the beginning of sorption, is given by the relation

$$\log H = a - b/t^c \qquad (1)$$

where a, b and c are empirical constants. An analogous equation

$$\log W = a' - b'/t^{c'} \qquad (2)$$

was shown to describe the increment in weight, W, of the gold which accompanied the liberation of heat and which was assumed to measure the quantity of water vapor sorbed by the gold.

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(1) Barry and Barrett, THIS JOURNAL, **55**, 3088 (1933).

Since it was also found that c and c' were identical to well within the limits of experimental error, equations 1 and 2 can be combined and the quantity t eliminated from them so that H is expressed directly as a function of W by the relationship

$$H = mW^n \tag{3}$$

which is identical in form with the equation $q = ax^b$ found by Lamb and Coolidge[2] to describe the relationship between heat of sorption and weight sorbed in the case of eleven organic vapors sorbed by steam-activated coconut charcoal.

The constants m and n of equation 3 have been evaluated from the experimental data and a comparison between the integral heat of sorption as measured and as calculated from equation 3 is made in Table I.

TABLE I

COMPARISON OF OBSERVED VALUES OF INTEGRAL HEAT OF SORPTION WITH THOSE CALCULATED FROM THE EQUATION $H = 13.3W^{0.340}$

Time, hours	Wt. sorbed per sq. cm. in grams $\times 10^6$	Obs. heat per sq. cm. in milli-calories	Calcd. heat per sq. cm. in milli-calories
0.5	1.08	13.7	13.7
1.0	2.34	17.8	17.8
1.5	3.32	20.1	20.0
2.0	4.21	21.7[a]	..
2.5	4.86	22.9	22.8
3.0	5.51	23.5	23.8
3.5	6.03	24.6	24.5
4.0	6.54	25.2[a]	..
4.5	6.92	25.7	25.7
5.0	7.25	26.2	26.1
5.5	7.57	26.6	26.4
6.0	7.95	27.0	26.9
Infinity	24.85[b]	39.7[c]	39.7

[a] Used to evaluate m and n. [b] Calculated from equation 2. [c] Calculated from equation 1.

It is interesting to compare these results with the data of Lamb and Coolidge, to which reference has been made above. Their values of n for the several vapors vary from 0.900 to 0.959, indicating that the change in the differential heat of sorption with increasing sorption is small. The relatively small value of n which appears in Table I shows clearly that, for water vapor and gold, the differential heat of sorption changes rapidly with increasing sorption for small values of W and that, as the weight sorbed increases, the value of the differential heat changes more slowly.

Since the actual measurements of the heat of sorption of water vapor by gold only covered a period of six hours, measured from the beginning of sorption, and since it is impractical to make calorimetric measurements over a sufficient length of time to determine even three-quarters of the integral sorption heat at equilibrium, it becomes important to form some estimate of the reliability of equation 3 when it is used to calculate values of H beyond the experimental time limit. Such an estimate can be made

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(2) Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

readily since the experimental conditions were such that it was thermodynamically necessary for the differential heat of sorption to approach the heat of evaporation of water as the system approached equilibrium.

Extrapolation, by means of equation 2, gives 24.85×10^{-6} g. as the weight of water vapor sorbed per square centimeter of gold at equilibrium. Differentiation of equation 3 gives

$$dH/dW = 4.52/W^{0.66} \tag{4}$$

Substitution of 24.85 in equation 4 gives 543 calories per gram as the heat of evaporation of water, which value is in error by 6%. Since the estimated error of measurement is 5%, it may be said that equation 3 describes the phenomenon with reasonable accuracy.

It is apparent from the form of equation 4 that, as W approaches zero, the differential heat of sorption approaches infinity. There are two possible interpretations of this observation. One is that the equation does not hold for very small values of W, although it does describe the phenomenon through the experimental range and, by deductive inference, out to infinite time. The other is that the equation does have significance even though W be an infinitesimal. The rational consequence of the second assumption is not that the first molecule of vapor sorbed liberates infinite heat but, simply, that it is impossible to remove the last molecule of water from a gold surface.

In the paper by Barry and Barrett[1] it was suggested that the exceedingly protracted nature of the phenomenon was probably due to diffusion of water vapor into the massive gold; so that, although sorption upon the exposed surface was extremely rapid, being, in all probability a true adsorption, the nature of the initial process was masked, since diffusion of adsorbed water into the gold would unsaturate the surface, thereby necessitating the adsorption of further water vapor in order to establish equilibrium between the gold surface and the saturated atmosphere.

Recently W. R. Ham, Professor of Physics at the Pennsylvania State College, has interested himself in this phase of the problem and has very kindly communicated to the writer the results of his preliminary measurements of the rate of diffusion of water vapor through gold. Ham has found that the diffusion at 400° and higher temperatures is readily measurable and although diffusion at these temperatures cannot be regarded as proof that the phenomenon occurs at room temperature, it does lend credibility to the original hypothesis.

It is possible to calculate from Ham's data the differential heat of sorption for very low relative humidities. His average value for measurements of about two hours' duration is 2500 calories per gram. The average heat of sorption found by Barry and Barrett during the first two hours of measurement was 5100 calories per gram. In view of the different working conditions the agreement in order of magnitude is gratifying.

Summary

It is shown that the integral heat of sorption of water vapor by massive gold is described by the equation $H = mW^n$, which is identical in form with the equation of Lamb and Coolidge for the sorption of organic vapors by charcoal.

The consequences of this observation are discussed and a possible mechanism by which the sorption occurs is considered.

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Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen

BY ANTON B. BURG AND H. I. SCHLESINGER

The development of a rapid and efficient method of preparing diborane (B_2H_6)[1] has made desirable the finding of efficient methods of preparing from it the less volatile hydrides of boron. Our experiments in this direction have led to the development of a satisfactory procedure for the preparation of the hydride B_5H_{11} and to a study of the properties of this hitherto little known substance. These investigations, in turn, have made possible improvements in the preparation of B_5H_9 from diborane, and have indicated a method by which useful quantities of the tetraborane (B_4H_{10}) may be prepared without recourse to the less efficient procedures involving the use of boron alloys.

When the pentaborane, B_5H_{11}, is heated at 100° without addition of excess of hydrogen, the first detectable effect is the production of small quantities of hydrogen, diborane, tetraborane and traces of a slightly volatile substance which seems to be an octaborane. Non-volatile solids appear soon afterward, but the formation of the latter seems to be inhibited to a certain extent by the accumulation of hydrogen. Within an hour the system, involving the substances named above, seems to reach a condition of equilibrium which is slowly shifted by the very gradual formation of B_5H_9,[2] traces of $B_{10}H_{14}$ and the non-volatile solids.

The indications that reversible changes are involved in these reactions led to the study of the effect of a high initial concentration of hydrogen. Under these conditions, the first reaction proceeds almost entirely according to the equation $2B_5H_{11} + 2H_2 \rightleftarrows 2B_4H_{10} + B_2H_6$. The tetraborane reacts further, but more slowly, mainly according to the equation $B_4H_{10} +$

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(1) Schlesinger and Burg, THIS JOURNAL, **53**, 4321 (1931).

(2) Because of the existence of the two substances B_5H_9 and B_5H_{11} which cannot be satisfactorily named till more is known about their structure, we shall refer to them only by formula. The term pentaborane will hereinafter be used only to refer to mixtures of the two.