

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

**Dissociative Adsorption of Hydrogen by Copper and its Kinetic Consequences<sup>1,2</sup>**BY LOYAL CLARKE<sup>3</sup>**Types of Sorption of Hydrogen by Copper**

A number of investigators<sup>4-13</sup> have made measurements recently on the sorption of hydrogen by copper.

Benton<sup>5</sup> cited evidence that the sorption of hydrogen is complex; that even at 0° and above, that is, in the range where van der Waals adsorption is relatively unimportant, two types of processes were involved. The more rapid of these he attributed to activated adsorption and the slower to solution. Ward<sup>7</sup> made similar observations and has found, for the early portion of his runs, that a straight line is obtained when the total sorption is plotted against the square root of the time. These lines intersect the axis at finite sorptions and the intercepts have been interpreted as activated adsorption. The remaining slow sorption he attributed to solution in crystal irregularities out of contact with the gas phase. Melville and Rideal<sup>13</sup> have confirmed Ward's findings. Regardless of any controversy regarding the physical nature of the slow process, the experimental evidence for a separation of the two processes is ample and the two types will be referred to herein as primary activated adsorption and secondary sorption. Beebe, Low, Wildner and Goldwasser<sup>11</sup> in their recent paper did not discuss this separation explicitly but did note the persistence of a slow sorption after the initial rapid process, and they further adopted a procedure for determining their isotherms, which probably allowed sufficient time for approach to equilibrium for the primary activated adsorption but insufficient time for appreciable amounts of secondary sorption. Their isotherms have been assumed, for the purpose of

this paper, to represent a close approach to the equilibrium isotherm for primary activated adsorption alone.

**Kinetics of Primary Activated Adsorption**

Davisson and Germer<sup>14</sup> noted the appearance of extra electron diffraction lines from incompletely outgassed nickel crystals and showed that these lines could be accounted for best by a definite arrangement of adsorbed atoms. The exact structure was not determined but was shown to be closely related to that of the underlying nickel and a possible arrangement on {111} planes was suggested. I shall assume that a similar condition exists when hydrogen is adsorbed on copper.

Consider a surface containing N identical points where hydrogen atoms may be adsorbed, a fraction  $\sigma$  of which are already occupied. Since two hydrogen atoms result from the adsorption of a molecule of hydrogen, the additional assumption that the rate of adsorption is proportional to the number of collisions of the gas molecules with two adjacent vacant points is made. Further assuming that a random arrangement of hydrogen atoms is maintained, the rate of adsorption would then be

$$k_1 N p (1 - \sigma)^2$$

the rate of desorption

$$k_2 N \sigma^2$$

and the net rate

$$d(N\sigma)/dt = k_1 N p (1 - \sigma)^2 - k_2 N \sigma^2 \quad (1)$$

At equilibrium

$$\frac{d(N\sigma)}{dt} = 0 \text{ and } N\sigma = \frac{N \sqrt{\frac{k_1}{k_2}} p}{1 + \sqrt{\frac{k_1}{k_2}} p} \quad (2)$$

$N\sigma$  is the amount of adsorption expressed as the number of atoms and may be replaced by the single letter  $S$ . Similarly,  $N$  is the number of atoms adsorbed at saturation (complete coverage), which is approached at high pressures. We may indicate this in the nomenclature itself by replacing  $N$  by  $S_\infty \cdot S$  and  $S_\infty$  may be expressed in any convenient units and need not be limited to those of  $N$ . Equation (2) becomes

(14) Davisson and Germer, *Phys. Rev.*, **30**, 706 (1927).

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(2) This is the second of a series of papers on kinetics of adsorption. The first appeared in *THIS JOURNAL*, **59**, 736 (1937).

(3) Assistant chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

(4) Benton and White, *THIS JOURNAL*, **53**, 3301 (1931).

(5) Benton, *Trans. Faraday Soc.*, **28**, 202 (1932).

(6) Ward, *Proc. Roy. Soc. (London)*, **A133**, 506 (1931).

(7) Ward, *ibid.*, **A133**, 522 (1931).

(8) Durau and Franssen, *Z. Physik*, **89**, 767 (1931).

(9) Griffin, *THIS JOURNAL*, **56**, 845 (1934).

(10) Griffin, *ibid.*, **57**, 1206 (1935).

(11) Beebe, Low, Wildner and Goldwasser, *ibid.*, **57**, 2527 (1935).

(12) Soller, Goldwasser and Beebe, *ibid.*, **58**, 1703 (1936).

(13) Melville and Rideal, *Proc. Roy. Soc. (London)*, **A153**, 77 (1936).

$$S = S_{\infty} \sigma = \frac{S_{\infty} b \sqrt{p}}{1 + b \sqrt{p}} \quad (3)$$

where  $b = \sqrt{k_1/k_2}$

The close relation in both the form and the significance of the constants to the Langmuir isotherm may be noted.

Equation (3) may be conveniently applied to the data by plotting  $\sqrt{p}/S$  against  $\sqrt{p}$  and fitting the best straight line to the points. This has been done for the available data and the results are given in Table I.

TABLE I  
BEST VALUES OF CONSTANTS  $S_{\infty}$  AND  $b$  FOR HYDROGEN ON  
VARIOUS PREPARATIONS OF COPPER

System	Temp., °C.	Authority	$S_{\infty}$ millimoles per g. of Cu.	$b$ atm. <sup>-1/2</sup>
H <sub>2</sub> -Cu	0	Beebe <i>et al.</i> <sup>11</sup>	$1.69 \times 10^{-4}$	29.6
D <sub>2</sub> -Cu	0	Beebe <i>et al.</i> <sup>11</sup>	$1.72 \times 10^{-4}$	21.8
H <sub>2</sub> -Cu	0	Benton <sup>5</sup>	$6.58 \times 10^{-4}$	7.2
H <sub>2</sub> -Cu I	25	Ward <sup>6</sup>	$0.93 \times 10^{-4}$	7.2
Cu II	25	Ward <sup>6</sup>	$.97 \times 10^{-4}$	3.7
Cu III	25	Ward <sup>6</sup>	$.52 \times 10^{-4}$	5.0

In every case equation (2) represents the data with fair accuracy. The points from the isotherms of Beebe, Soller, Wildner and Goldwasser are reproduced in Fig. 1. The points were obtained

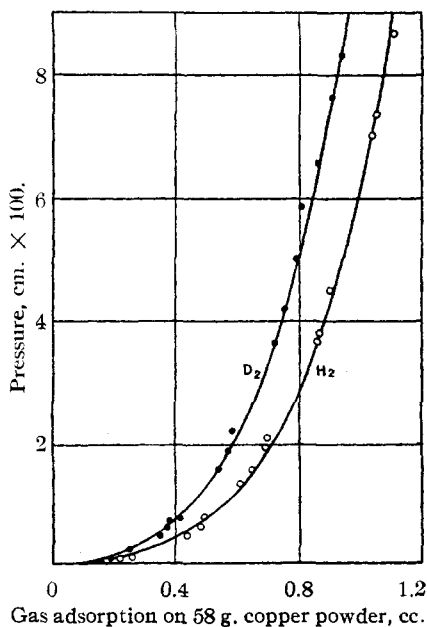


Fig. 1.—Adsorption isotherms of hydrogen and deuterium on copper at 0°. Data of Beebe, Low, Wildner and Goldwasser.<sup>11</sup>

by tracing an enlarged photograph of their Fig. 2. The solid lines were computed from equation (3), using the values of  $S_{\infty}$  and  $b$  corresponding to

those given in Table I, but in different units. Returning to the definition of  $S_{\infty}$ , it is evident that its value is proportional only to the number of points on the surface available for adsorption, and should be the same for hydrogen as for deuterium. Actually, the values given in Table I for deuterium and hydrogen (on the same preparation) are very nearly the same.

The spread in the values of  $b$  for the different preparations indicates that the surface characteristics differ according to the method of preparation: the agreement with equation (3) indicates that the surface of any given preparation is moderately uniform. Ward<sup>6</sup> arrived at a similar conclusion from a consideration of heats of adsorption. He found that for any given preparation the heat of adsorption is constant and independent of the amount adsorbed, but changes according to the past history of the preparation, dropping to a constant value of about 9 kcal. per mole after repeated outgassing at 200°. The material so treated has subsequent constant behavior, but the total adsorption is so low as to hamper the accuracy of his isotherms (a situation that is doubly unfortunate, since on this material alone did he make adsorption measurements at several temperatures).

The temperature dependence of the adsorption may be derived directly from kinetics used in equation (1). The temperature dependence of the fundamental rate constants would be

$$k_1 = A_1 e^{-E_1/RT} / \sqrt{T} \quad (4)$$

$$k_2 = A_2 e^{-E_2/RT} \quad (5)$$

$b$  would be then given by

$$b = \sqrt{\frac{k_1}{k_2}} = \sqrt{\frac{A_1}{A_2}} \cdot T^{-1/4} \cdot e^{-(E_1 - E_2)/2RT} \quad (6)$$

$E_1 - E_2$  will be recognized as the decrease in energy content per mole on adsorption and is related to the heat of adsorption by the relation

$$E_1 - E_2 = -\Delta E = q + \Delta(PV) = q - RT \quad (7)$$

If the mechanism from which this isotherm has been derived is correct, then equation (1) should give the rate of adsorption prior to the establishment of equilibrium. Integration of this equation at constant pressure and temperature yields a result that may be expressed in the form

$$t = B \ln \left\{ \frac{C - S}{D - S} \times \frac{D}{C} \right\} \quad (8)$$

where

$$B = \frac{b}{2k_1 \sqrt{p}}, \quad C = \frac{S_{\infty} b \sqrt{p}}{b \sqrt{p} - 1}, \quad D = \frac{S_{\infty} b \sqrt{p}}{1 + b \sqrt{p}}$$

It may be noted that  $D$  is the equilibrium adsorption.

Employing arbitrary values of  $k_1$ ,  $b$ , and  $S_\infty$  it has been found possible to approximately fit the data of Soller, Goldwasser and Beebe<sup>12</sup> on the adsorption time relation of hydrogen and deuterium on copper at 0°. This agreement is sufficiently close to indicate that the kinetics might be applicable; however, the agreement might well be fortuitous because of flexibility introduced by the adjustable constants. Therefore it does not seem possible to decide whether the kinetics are applicable for the calculation of adsorption rates on the basis of available data. Similar data at other pressures and temperatures would permit a decision. Dr. Beebe informs me that such work is in progress in his laboratory.

#### Application of Kinetics to Other Systems

It has been found that equation (2) may be applied successfully to the adsorption isotherms of hydrogen or iron at 300 and at 400° by Morosov.<sup>15</sup> These isotherms do not include a secondary slow sorption, which was excluded by the method of Ward.<sup>7</sup> The ratio of the value of  $b$  at 300° to that at 400° is 1.2. From equations (6) and (7) this corresponds to  $E_1 - E_2 = +3.4$  kcal. or  $q = 4.6$  kcal.

The adsorption isotherm of oxygen on silver<sup>16</sup> is compatible with equation (3) but affords no adequate test of its validity, as most of the measurements are in the range approaching saturation.

(15) Morosov, *Trans. Faraday Soc.*, **31**, 659 (1935).

(16) Benton and Drake, *THIS JOURNAL*, **56**, 255 (1934).

The same authors also give data on the rates of desorption, which could perhaps be treated by equation (1) except for the irreproducible nature of the surface.

The kinetics of the catalysis of water formation from hydrogen and oxygen by silver<sup>17</sup> suggest that the adsorbed oxygen is atomic.

Equation (3) is not applicable to the data of Emmett and Brunauer<sup>18</sup> on the sorption of nitrogen on a promoted iron catalyst. In view of the heterogeneous nature of the catalyst and the probability that some of the adsorbed hydrogen is in the interior, this disagreement is not surprising. No other applications have been attempted.

I wish to express my thanks to Dr. H. H. Storch, under whose direction this work has been done, for his helpful suggestions and to Prof. R. A. Beebe, of Amherst College, who has been kind enough to discuss with me freely some of the experimental aspects of hydrogen adsorption on copper.

#### Summary

It has been shown that the assumptions of dissociative adsorption on a uniform surface lead to kinetics which account for the observed equilibria in the primary activated adsorption of hydrogen on copper. The possibility of extension of these kinetics to rates and to other systems is discussed.

(17) Benton and Elgin, *ibid.*, **51**, 7 (1929); **48**, 3027 (1926).

(18) Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

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## A Gas Density Balance for Determination of the Absolute Density of Protium-Deuterium Mixtures and Other Gases

BY NELSON R. TRENNER<sup>1</sup>

Small abnormalities in the results of an investigation of the velocity of sound in the best deuterium gas<sup>2</sup> and in an investigation of the photochemical reaction between bromine and deuterium<sup>3</sup> prompted the necessity of examining the absolute density of our best deuterium gas. This was undertaken by use of the suspended gas density balance, similar in principle to those designed

by Whytlaw-Gray,<sup>4</sup> Aston<sup>5</sup> and T. S. Taylor,<sup>6</sup> but modified so as to permit reasonable ease of construction, adjustment and operation. Such a balance is described below together with some of the results obtained with it. It has proved of especial value as a primary concentration standard in our work with the hydrogen isotopes.

(1) National Research Fellow in Chemistry, 1933-1935.

(2) W. T. Richards, *J. Chem. Phys.*, **4**, 563 (1936).

(3) N. R. Trenner, *ibid.*, forthcoming publication.

(4) Whytlaw-Gray, Patterson and Cawood, *Proc. Roy. Soc. (London)*, **134A**, 10 (1931).

(5) F. W. Aston, *ibid.*, **89A**, 439 (1914).

(6) T. S. Taylor, *Phys. Rev.*, **10**, 653 (1917).