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ON THE ADSORPTION OF DEUTERIUM ON REDUCED NICKEL.

Studies at Low Temperatures.

By Shun-ichiro Iijima.

Pace and Taylor[1] studied the rates of adsorption of both hydrogen and deuterium on chromium oxide, on supported nickel, and on a mixture of chromium oxide and zinc oxide at 110°—184°C., and reported that their rates of adsorption were equal. Klar,[2] on the other hand, studied their rates of adsorption on nickel at 0°—100°C., and Beebe[3] on copper at −78°C., and Maxted[4] and Moon on platinum at −79°—50°C. and they all found that the rate of adsorption of hydrogen was larger than that of deuterium. Besides, Klar[5] and Fajans[6] obtained, though indirectly, the similar results.

These studies, however, were made at different temperatures, or on different adsorbents, and some of them at extremely low pressures. In addition, all of them but Maxted's were merely qualitative. As regards the study of Maxted, the physico-chemical meaning of the formula from which the velocity constant of adsorption was calculated, is not clear.

The present author investigated the rates of adsorption of two kinds of hydrogen on nickel under about 15.5 cm. pressure and at the temperatures −45°, −78° and −112°C., and obtained the velocity constants of adsorption of both kinds of hydrogen from the equation formerly proposed by him.[7]

Experimental.

Materials.

(a) Reduced nickel and hydrogen. Reduced nickel and hydrogen were prepared in the same way as described in his preceding paper.[7]

(b) Deuterium. Deuterium was prepared by the action of metallic calcium ("Calcium metallicum raspatum," Kahlbaum) on heavy water ($d_4^{20}=1.1049$, 99.55%, Norsk Hydro-Elektrisk Kvaelstofaktieselskab), and it was passed through a glass tube cooled in liquid air, and finally filtered by a palladium plate heated in an electric furnace.

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1) Pace and Taylor, *J. Chem. Phys.*, **2**, 578, (1934).
2) Klar, *Naturwiss.*, **22**. 822, (1934).
3) Beebe, *J. Am. Chem. Soc.*, **57**, 2527, (1935).
4) Maxted and Moon, *J. Chem. Soc.*, 1542, (1936).
5) Klar, *Z. physik. Chem.*, [B], **27**, 319, (1934).
6) Fajans, *Z. Physik. Chem.*, [B], **28**, 239, (1935).

Apparatus and Procedure.

The apparatus used and the procedure were the same as described in the preceding paper.[7]

Results and their Considerations.

Pressure-Time Curve.

Reduced nickel was desorbed and kept at a constant temperature (−45°, −78° or −112°C.) and over it a known quantity of hydrogen or deuterium was introduced. The pressure in the vessel was observed 1 minute after the start of the introduction and then at suitable intervals. The pressure, which was about 15.5 cm. 1 minute after the start, was gradually decreased by the adsorption and this is shown in Fig. 1. The reduced nickel used was prepared from 11.0352 g. of nickel oxide.

Adsorbed Amount-Time Curve.

The number n, of mols of the gas in the vessel, is related to the pressure p in it by the equation:[7]

$$n = k'p + k''p^2, \quad \ldots\ldots\ldots\ldots\ldots(1)$$

where k' and k'' are known constants dependent on the temperature and the volume of the vessel. The number of mols of the gas introduced in the vessel at the start is known. Accordingly, if we know the pressure in the vessel at any time, the total quantity of the gas adsorbed from the start to that time can be calculated. The total quantities adsorbed from the start to each time when

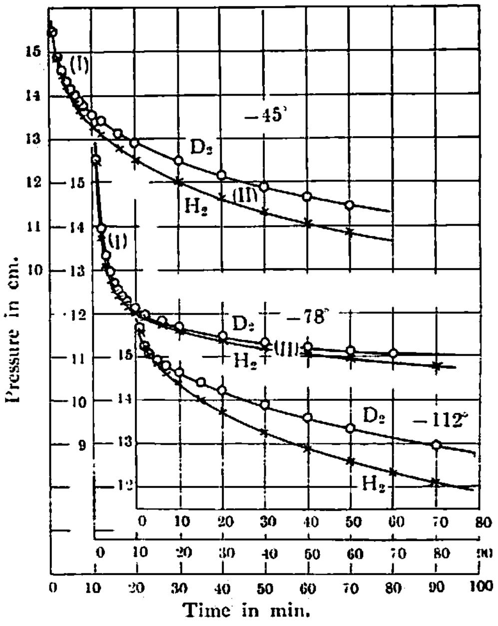

Fig. 1.

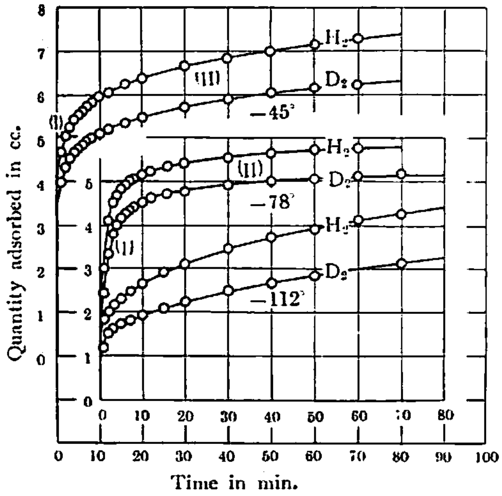

Fig. 2.

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[7] Iijima, *Rev. Phys. Chem. Japan*, 12, 1, (1938).

pressure was observed were calculated and are shown in Fig. 2.

The Rate of Adsorption.

It has been already reported by the author[7] that in the case of the adsorption of hydrogen on reduced nickel the following relation holds:

$$\log\frac{p}{p-p_e}=Kt+C, \qquad \text{(2)}$$

where t is the time elapsing from the start, p the pressure at time t, and K and C are constants, being

$$K=\frac{k_1 p_e}{2.303}\times\frac{1}{[k'+k''(p_0+p_e)](p_0-p_e)}, \qquad \text{(3)}$$

and

$$C=\log\frac{p_0}{p_0-p_e}, \qquad \text{(4)}$$

where p_e is the equilibrium pressure, p_0 the pressure when $t=0$, and k_1 the velocity constant of adsorption. In the case of the adsorption of deuterium on reduced nickel, the question whether the relation represented by equation (2) held or not was examined. The values of $\log\frac{p}{p-p_e}$ (ordinate) and t (abscissa) were plotted, and the linear relation was obtained as shown in Figs. 3, 4 and 5. This justifies the applicability of equation (2) to the present case.

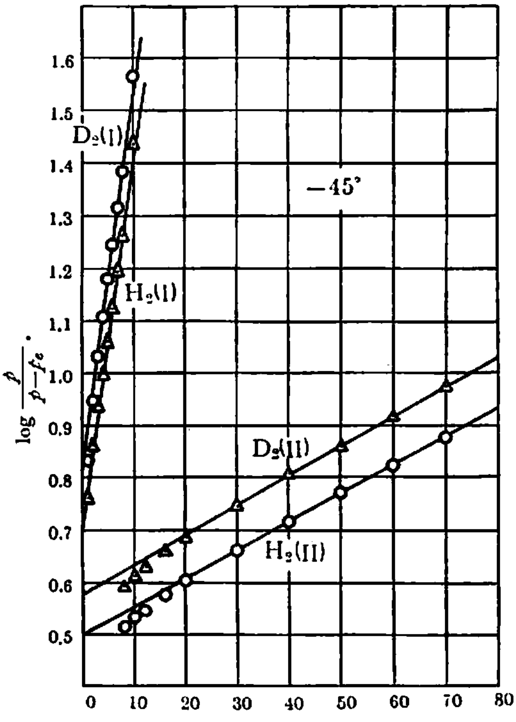

Fig. 3.

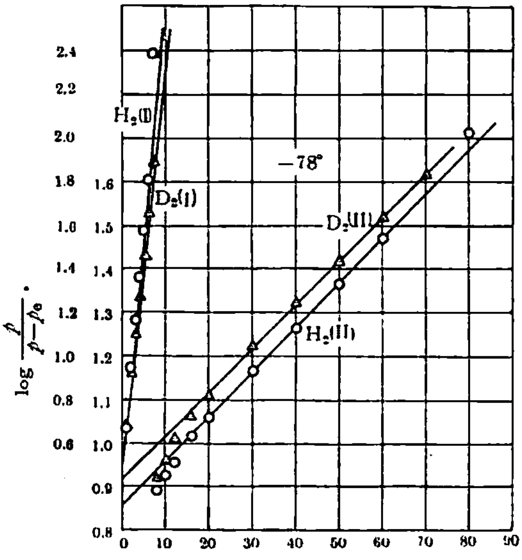

Fig. 4.

The Velocity Constant of Adsorption.

From the diagrams, which show the linear relation between $\log \frac{p}{p-p_e}$ and t, the values of K and C were obtained, and from equations (3) and (4) the velocity constant of adsorption k_1 calculated. The results are given in Table I.

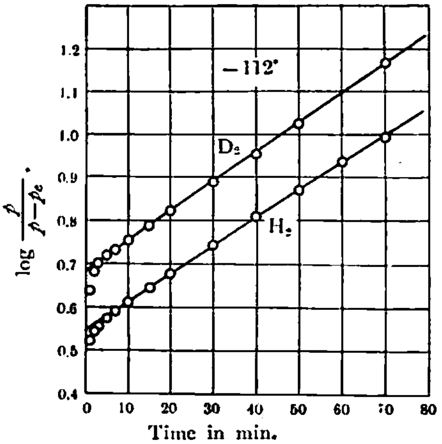

Fig. 5.

Table I.

Adsorption		Velocity const. of adsorption × 10^6		
		k_{1H_2}	k_{1D_2}	k_{1H_2}/k_{1D_2}
−45°C.	(I)	0.850	0.711	1.195
	(II)	0.133	0.113	1.177
−78°C.	(I)	6.19	4.39	1.410
	(II)	0.102	0.083	1.229
−112°C.		0.179	0.128	1.398

As is seen in Table I, the ratio of the velocity constants, k_{1H_2}/k_{1D_2}, is greater than unity, that is to say, the velocity constant of adsorption of hydrogen on reduced nickel is greater than that of deuterium at the experimental temperatures.

The Heat of Activation of the Adsorption.

The decrease in the number of mols of hydrogen in the vessel at unit time, that is, the rate of adsorption $-\frac{dn}{dt}$ may be expressed by

$$-\frac{dn}{dt}=k_1 p(1-\theta)-k_2\theta, \quad \text{......................................}(5)$$

where p is the pressure of hydrogen, k_1 and k_2 the velocity constants of adsorption and desorption respectively, and θ the fraction of the active surface of the nickel participating in adsorption. In this case if the adsorption is activated, k_2 may be very small as compared with k_1. Therefore, $k_2\theta$ may be neglected in comparison with $k_1 p(1-\theta)$ provided that θ does dot approach 1 and p is within the experimental range. Then equation (5) becomes

$$-\frac{dn}{dt}=k_1 p(1-\theta). \quad \text{..}(6)$$

To make clear the meaning of k_1, the mechanism of the adsorption should be considered from the standpoint of the kinetic theory of gas.

The mass m of gas striking a unit of surface at unit time is given, from the simple kinetic theory, as follows:

$$m=p\sqrt{\frac{M}{2\pi RT}}\,, \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where p is the pressure of the gas, M the molecular weight of it, T the temperature, R the gas constant.

From equation (7) the number n_1 of mols of gas striking a unit of surface at unit time is given by the following equation:

$$n_1=\frac{m}{M}=\frac{p}{\sqrt{2\pi RMT}}\,, \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

and from this equation the number n_2 of mols of gas striking the total active surface uncovered with hydrogen at unit time is given as follows:

$$n_2=n_1\,\alpha\beta(1-\theta)=\frac{\alpha\beta(1-\theta)p}{\sqrt{2\pi RMT}}\,, \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

where α is the total surface of the nickel, β the fraction of the surface which is active, and θ the fraction of the active surface participating in adsorption.

The heat of activation E of the adsorption for a molecule may be given by

$$E=E_1+E_2\,, \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

where E_1 represents energy possessed by an active point, and E_2 energy possessed by a gas molecule striking the active point. Let the fraction of the gas molecules which have energy greater than E_2 be represented by $e^{-\frac{E_2}{kT}}$ (k being the Boltzmann constant) for simplicity, then the number of mols n_0 of gas which may be adsorbed at unit time is given by

$$n_0=n_2 e^{-\frac{E_2}{kT}}=\frac{\alpha\beta(1-\theta)p}{\sqrt{2\pi RMT}}\,e^{-\frac{E_2}{kT}}. \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

This becomes

$$n_0=\frac{A}{\sqrt{M}}\,p(1-\theta)e^{-\frac{E_2}{kT}}, \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

provided that

$$\frac{\alpha\beta}{\sqrt{2\pi RT}}=A.$$

It is clear from the above discussion that n_0 in equation (12) is the same with the $k_1p(1-\theta)$ in equation (6). Hence, equation (13) is obtained:

$$n_0=\frac{A}{\sqrt{M}}p(1-\theta)e^{-\frac{E_1}{kT}}=k_1p(1-\theta), \qquad\text{(13)}$$

or

$$k_1=\frac{A}{\sqrt{M}}e^{-\frac{E_1}{kT}}. \qquad\text{(14)}$$

From equations (10) and (14) equation (15) is obtained:

$$k_1=\frac{A}{\sqrt{M}}e^{-\frac{E-E_1}{kT}}. \qquad\text{(15)}$$

Let k_{1H_2} and E_{H_2} represent the velocity constant of adsorption and heat of activation of hydrogen and k_{1D_2} and E_{D_2} those of deuterium respectively, and let the real molecular weight be substituted in M, then from equation (15) equation (16) is obtained for hydrogen and equation (17) for deuterium:

$$k_{1H_2}=\frac{A}{\sqrt{2}}e^{-\frac{E_{H_2}-E_1}{kT}}, \qquad\text{(16)}$$

and

$$k_{1D_2}=\frac{A}{\sqrt{4}}e^{-\frac{E_{D_2}-E_1}{kT}}, \qquad\text{(17)}$$

Hence,

$$\log\frac{k_{1H_2}}{k_{1D_2}}=\log\sqrt{2}+\frac{E_{D_2}-E_{H_2}}{2{\cdot}303kT}. \qquad\text{(18)}$$

If we have the velocity constants of adsorption for both kinds of hydrogen, k_{1H_2} and k_{1D_2}, at the same temperature, we can know the difference between the heats of activation of the adsorption of both hydrogen molecules, $E_{D_2}-E_{H_2}$. The difference of the heat for each per mol calculated from the data in Table I is given in Table II.

Table II.

Adsorption		k_{1H_2}/k_{1D_2}	$(E_{H_2}-E_{D_2})\times N$
−45°C.	(I)	1.195	76 (cal.)
	(II)	1.177	83
−78°C.	(I)	1.410	1
	(II)	1.229	54
−112°C.		1.398	4

(N is Avogadro's number.)

As is seen in Table II the heat of activation of deuterium is smaller than that of hydrogen, but the difference between these two values is small. Maxted and Moon[4] have calculated the heat of activation of adsorption of both kinds of hydrogen on platinum according to Arrhenius' equation and obtained 2400 cal. for deuterium and 2500 cal. for hydrogen.

Summary.

(1) The rates of adsorption of deuterium and hydrogen on reduced nickel at −45°, −78° and −112°C. have been observed.

(2) It has been found that the equation for the adsorption velocity of hydrogen on reduced nickel which the author has proposed in his preceding paper is also applicable to the adsorption velocity of deuterium on the same adsorbent.

(3) The velocity constant of adsorption of deuterium is smaller than that of hydrogen.

(4) The difference between the heats of activation of the adsorption of both kinds of hydrogen has been measured from an equation derived from the kinetic theory. The heat of activation of deuterium is smaller than that of hydrogen, though the difference between the two is very small.

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