

ON THE ADSORPTION OF HYDROGEN ON REDUCED NICKEL.

Studies at Low Temperatures.

By SHUN-ICHIRO IJIMA.

It may be considered that the surface of reduced nickel consists of several parts with different degrees of activity. When gaseous hydrogen is adsorbed on such a surface at constant temperature, the velocity of the adsorption may vary at each part. At low temperatures the velocity of the adsorption may become negligibly small on the parts possessing less activity, and only the adsorption on those parts of higher activity should be taken into account. Moreover, at low temperatures the diffusion of hydrogen into the lattice of reduced nickel may be extremely slow, so that at these temperatures the mechanism of adsorption may become fairly simple.

Few reports on the quantitative study of the velocity of adsorption in the solid and gas systems have hitherto been made.¹⁾ Velocity equations of adsorption have been proposed, but almost all of them are empirical. Quantitative studies at low temperatures have scarcely been made except those at certain temperatures.

The author studied quantitatively the velocity of adsorption of hydrogen by reduced nickel in a low temperature range between -23°C. and -130°C. , and obtained relatively simple relations.

Experimental.

Materials:

(a) Reduced nickel. Kahlbaum's pure nickel nitrate free from cobalt was dehydrated by careful heating in a pyrex vessel. The dehydrated salt was heated to about 300°C. for

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30 hours. The nickel oxide thus obtained was confirmed to be free from nitric acid radical using "nitron" and then reduced by heating in a current of hydrogen until no measurable amount of water came out in an hour.

(b) Hydrogen. Hydrogen was prepared by electrolysis from 30% solution of pure caustic soda, and purified by passing through heated platinized asbestos and finally dried with phosphorus pentoxide.

Apparatus :

The apparatus employed in the experiment is shown in Fig. 1 (a). In the figure, A is a pyrex vessel in which a known quantity of nickel oxide is to be reduced. The nickel thus reduced was used ; B is a hydrogen reservoir of about 85 c.c. placed in a thermostat ; C is a

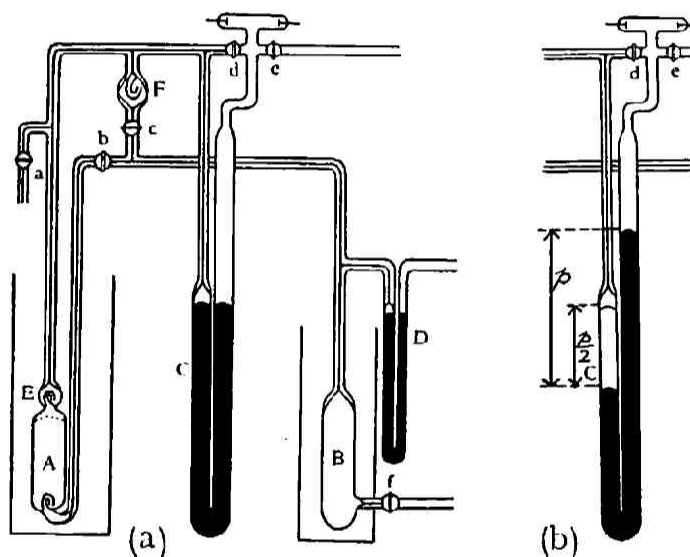


Fig. 1.

mercury manometer about 75 cm. high and 1.2 cm. in inner diameter and having two graduations, one indicating the capacity in c.c. and the other the height of mercury in cm.; D is a differential manometer containing mercury connected with another mercury manometer not shown in the figure ; and a, b, c, d, e, and f are stop-cocks.

The total capacity of A inclusive of the capillary tubes and others connected to A is 29.12 c.c. when the pressure is zero. The total capacity varies with the pressure as is seen in Fig. 1. (a) and (b) in Fig. 1 show the states when the pressures are zero and p cm. of mercury respectively.

The total number of mols, n , of gaseous hydrogen in the vessel when the pressure is p cm. will be expressed by the ideal gas law as follows :

$$n = \frac{pV_b}{RT_b} + \frac{pV_r}{RT_r} + \frac{pv}{RT_r}, \quad (1)$$

where T_b is the temperature of the bath, T_r the room temperature, R the gas constant, p the pressure of hydrogen, V_b the capacity of the part in the thermostat excluding the volume of

nickel in it (the volume of nickel may be calculated from its weight and the density of nickel), V_r the capacity of the part in the air (exclusive of the part of the manometer C), and v the capacity of the part above the meniscus of mercury in the manometer C (when the pressure is zero, the capacity of this part will be zero).

When the pressure is p cm., v is given by the equation $v = a \cdot \frac{p}{2}$, as is seen in Fig. 1(h), where a is the cross section of the mercury column. Therefore, equation (1) may be rewritten thus:

$$n = \frac{pV_b}{RT_b} + \frac{pV_r}{RT_r} + \frac{p}{RT_r} \cdot \frac{ap}{2} = p \left(\frac{V_b}{RT_b} + \frac{V_r}{RT_r} \right) + p^2 \frac{a}{2RT_r} \quad (2)$$

In equation (2), the terms $\left(\frac{V_b}{RT_b} + \frac{V_r}{RT_r} \right)$ and $\frac{a}{2RT_r}$ may be regarded as invariable in an experiment. Let them be k' and k'' respectively, then the total number of mols of gaseous hydrogen in the vessel is given by

$$n = k'p + k''p^2. \quad (3)$$

Procedure:

In order to make the reduced nickel free from hydrogen (desorption), the vessel A containing nickel together with hydrogen was heated to 280°C. and kept at that temperature while being evacuated by means of a Cenco-Hyvac and a mercury diffusion pump until the pressure was reduced to 10^{-1} – 10^{-5} cm. Evacuation was continued one hour more.

The desorption finished, the vessel A with its content was placed in a thermostat and kept at a constant temperature and then hydrogen was introduced for a moment into A from the reservoir B²⁾ by opening the stop-cock c; a stop-watch was started at this moment and the pressure in A was observed by means of the manometer C 1 minute after the start and then at suitable intervals. All the results obtained are reproducible.

The low temperature baths used were as follows:

- 23°C. An intimate mixture of liquid and solid carbon tetrachloride.
- 45.2°C. An intimate mixture of liquid and solid monochlorobenzene.
- 78°C. An intimate mixture of ethyl alcohol and solid carbon dioxide.
- 95°C. An intimate mixture of liquid and solid toluene.
- 112°C. An intimate mixture of liquid and solid carbon disulphide.
- 121°C. } The temperature was regulated by dropping liquid air appropriately into a
- 130°C. } Dewar flask with a tiny electric heater installed at its bottom. It was constant within $\pm 0.3^\circ\text{C}$.

Results and their Considerations.

Pressure—Time Curves:

The reduced nickel was desorbed and kept at a constant temperature and a

2) Hydrogen in the reservoir B was kept at 20°C. In the apparatus, though hydrogen was not kept at the same temperature, it was observed that the temperature of hydrogen had no influence on the change of pressure of hydrogen in A 1 minute after the start in the experiment.

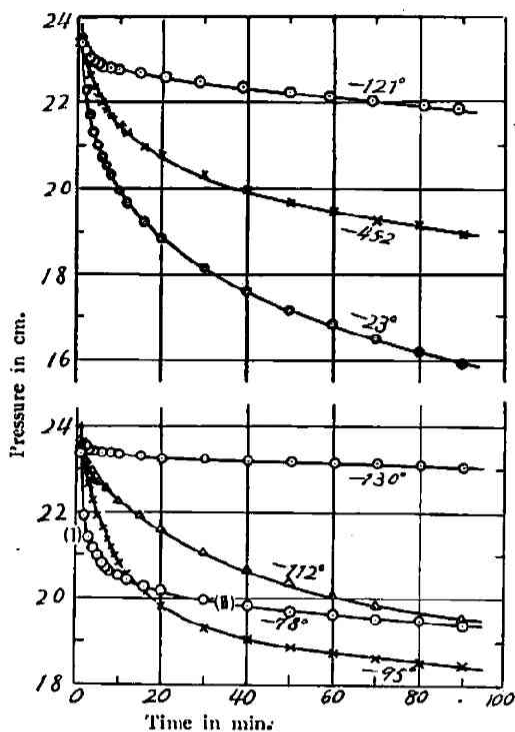


Fig. 2.

known quantity of hydrogen was introduced over it as described above. The pressure was observed 1 minute after the start of the introduction and then at suitable intervals. The pressure was gradually decreased by adsorption. The results are shown in Figs. 2 and 3. In Fig. 3 can be seen an entire process of adsorption at -78°C . The reduced nickel used was prepared from 10.0253 g. of nickel oxide.

Adsorbed Amount-Time Curves :

The quantity of hydrogen introduced over the nickel was known and the quantity of hydrogen remaining over the nickel at the time when the pressure was observed was calcu-

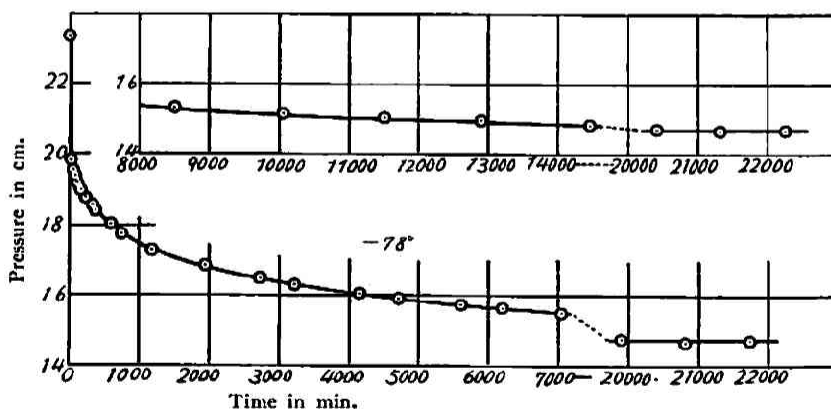


Fig. 3.

lated by equation (3). Thus, the total quantity adsorbed, at each time the pressure was observed, was calculated. The results are shown in Fig. 4.

The Rate of Adsorption :

When the values of $\log \frac{p}{p-p_e}$ (p is the pressure t minutes after the start and p_e the pressure at the time when the adsorption has reached an equilibrium) are plotted as ordinate and the time as abscissa, a nearly straight line save both

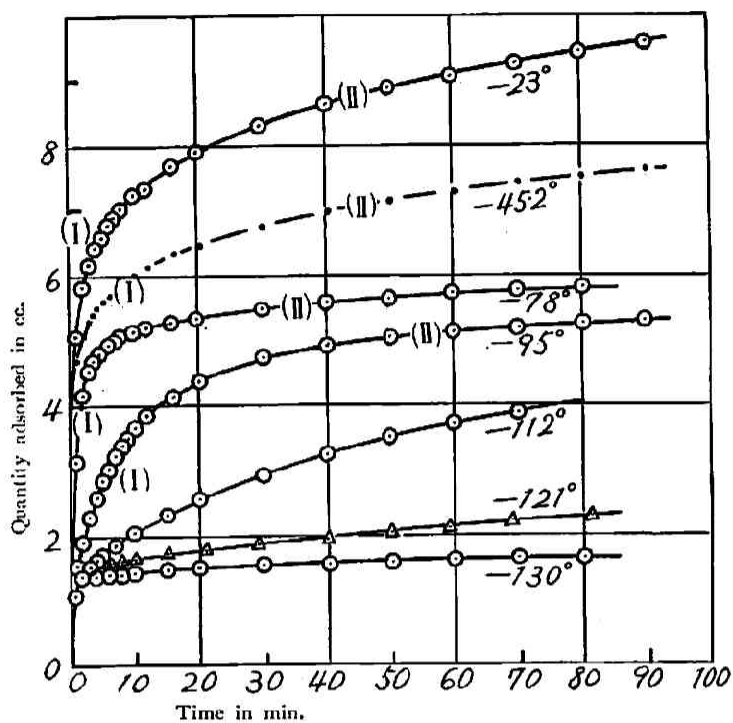


Fig. 4.

the parts near the start and near the end is obtained as shown in Fig. 5. Such

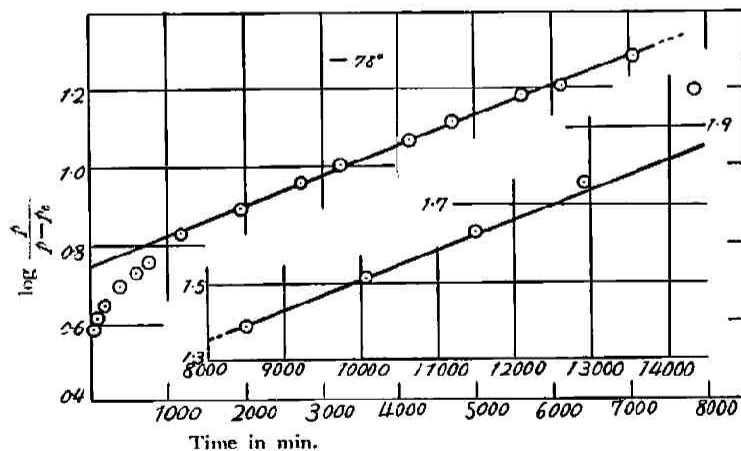


Fig. 5.

a linear relation may be represented by

$$\log \frac{p}{p-p_e} = Kt + C, \quad (4)$$

where K and C are constants. This experimental fact may be explained as follows.

Let the rate of decrease in hydrogen in the vessel be represented by $-\frac{dn}{dt}$, where n is the quantity of hydrogen in mols and t the time in minutes, then the rate at the moment when the pressure is p cm. may be expressed by

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

where k_1 is the velocity constant of adsorption of the nickel, k_2 its velocity constant of desorption, and θ the fraction of the active surface of the nickel participating in adsorption. Now if k_2 is very small compared with k_1 , then $k_2 \theta$ may be neglected in comparison with $k_1 p (1 - \theta)$ provided that θ does not approach 1 and the pressure p is within the experimental range. Then equation (5) may be simplified as follows:

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

And at the same time the following substitution may be made, assuming that k_2 is very small compared with k_1 , that is the whole active surface is almost covered with hydrogen when equilibrium has been established.

$$\begin{aligned} \theta &\doteq \frac{\text{Number of mols of } H_2 \text{ adsorbed up to the moment when the pressure is } p.}{\text{Number of mols of } H_2 \text{ adsorbed up to the time equilibrium has been established.}} \\ &= \frac{n_0 - n}{n_0 - n_e}, \end{aligned}$$

where n_0 , n , and n_e are the numbers of mols of hydrogen in the vessel at the start, at the moment when the pressure is p , and at the time equilibrium has been established. Then, equation (6) may be rewritten as

$$-\frac{dn}{dt} = k_1 p \frac{n - n_e}{n_0 - n_e}. \quad (7)$$

It can be seen from equation (3) that n and n_e are related to the pressures as follows:

$$n = k'p + k''p^2, \quad n_e = k'p_e + k''p_e^2,$$

where p and p_e are pressures corresponding to n and n_e respectively. Substituting the values of n and n_e in equation (7), we have

$$-\frac{(k' + 2k''p)dp}{dt} = k_1 p \frac{p - p_e}{n_0 - n_e} [(k' + 2k''p) - k''(p - p_e)]. \quad (8)$$

k'' being very small, in actual calculation $k''(p - p_e)$ may be neglected in comparison with $(k' + 2k''p)$. Hence,

$$-\frac{dp}{dt} = k_1 p \frac{p - p_e}{n_0 - n_e}. \quad (9)^a$$

Integrating equation (9), we have

$$\ln \frac{p}{p-p_e} = k_1 \frac{p_e}{n_0-n_e} t + c,$$

or,

$$\log \frac{p}{p-p_e} = \frac{k_1 p_e}{2.303 (n_0-n_e)} t + \frac{c}{2.303},$$

that is,

$$\log \frac{p}{p-p_e} = Kt + C, \quad (10)$$

where $K = \frac{k_1 p_e}{2.303 (n_0-n_e)}$ and $C = \frac{c}{2.303}$.

Thus the experimental fact shown in Fig. 5 or equation (4) has been explained theoretically, assuming that k_2 , the velocity constant of desorption, is very small compared with k_1 , the velocity constant of adsorption.

From the fact that such an assumption has been allowed in the explanation of the linear relationship between $\log \frac{p}{p-p_e}$ and t , it may be considered that the adsorptions observed are activated adsorptions and that in activated adsorption at low temperatures k_2 is very small compared with k_1 . It is very difficult, in practice, to desorb the gas adsorbed by what is considered to be the activated adsorption, and this indicates that the velocity constant of desorption, k_2 , is very small.

Deviation from a straight line near the end of the adsorption in the $\log \frac{p}{p-p_e} - t$ diagram (Fig. 5) is probably brought forth from the fact that $k_2\theta$ can not be neglected in equation (5), because the value of θ approaches 1 there.

Deviation from a straight line at the start in the same diagram may be explained from the following consideration. The rate of adsorption 1 minute after the start may be a resultant of several activated adsorptions, and these activated adsorptions may markedly differ from one another in their velocities and finished⁹⁾

- 3) If the experiments are carried out at constant volume, equation (3) will be as follows:

$$n = k' p, \quad 1$$

And equation (8) can be written as

$$-\frac{k' dp}{dt} = k_1 p \frac{p-p_e}{n_0-n_e} k', \quad 2$$

or

$$-\frac{dp}{dt} = k_1 p \frac{p-p_e}{n_0-n_e}. \quad 3$$

The form of equation 3 is the same as that of equation (9), but in equation (9) $n_0 = k' p_0 + k'' p_0^2$ and $n_e = k' p_e + k'' p_e^2$, while in equation 3 $n_0 = k' p_0$ and $n_e = k' p_e$.

- 4) If slower activated adsorptions are still taking place when an activated adsorption (I) has reached an equilibrium, then the pressure of hydrogen will become lower than the equilibrium pressure of adsorption (I). Accordingly the hydrogen sorbed by adsorption (I) will be desorbed gradually. But this desorption may be very slight if k_2 is very small compared with k_1 and in fact the decrease in pressure is small. Hence, adsorption (I) may be considered to finish at the time equilibrium has been established,

at different times; moreover, the velocities may be different so much that during a period in which one adsorption is taking place the quantities of adsorption of the others may be neglected, and hence it may be regarded that these adsorptions are taking place in steps. The equilibrium pressure, p_e , obtained experimentally may be the equilibrium pressure of an adsorption with the smallest measurable velocity of adsorption, and not that of the adsorption to be completed earlier. If the equilibrium pressures, p_e^* , of the adsorptions to be completed at an early period are known, straight lines with different inclinations may also be obtained with regard to these adsorptions by plotting the values of $\log \frac{p}{p-p_e}$ at different times.

Now the value of p_e , the final pressure of hydrogen for each adsorption, may be obtained by solving the simultaneous equations obtained by substituting the data observed for the period in which each adsorption mainly takes place in equation (4). But there are, in practice, mathematical difficulties⁵⁾ in solving such simultaneous equations. Therefore, the author tried to find out graphically whether or not there were values of p_e to satisfy the linear relation between $\log \frac{p}{p-p_e}$ and t and obtained the values of p_e . As an example, the graphical process for the adsorption at -78°C . will be illustrated below.

The velocity of adsorption at -78°C . is remarkably diminished at a point 6-7 minutes after the start as shown in Fig. 2, and therefore it may be considered that the main adsorption is different at both sides of this point. The velocity is large at one side (I) and at the other side (II) it is small. As to part (I), a value of p_e to satisfy the linear relation between $\log \frac{p}{p-p_e}$ and t was found graphically by trial, and the value obtained was 20.83 cm. with which the linear relation as shown in Fig. 6 (I) was obtained. It may be concluded, therefore, that the final pressure of the main adsorption at the stage is 20.83 cm. and this main adsorption takes place according to equation (4).

As to part (II), similarly $p_e=19.38$ cm. was obtained, with which the linear relation was obtained as shown in Fig. 6 (II). The linear relation holds only up to about 70 minutes after the start. In the period between $t=70-600$, however, a linear relation was also obtained with $p_e=17.50$ cm. as shown in Fig. 7.

Now, in the light of Figs. 5, 6, and 7 which show the linear relations, it may be concluded that the adsorption at -78°C . 1 minute after the start is at

5) These difficulties are dependent upon the fact that the values of p_e/p are not small enough compared with 1.

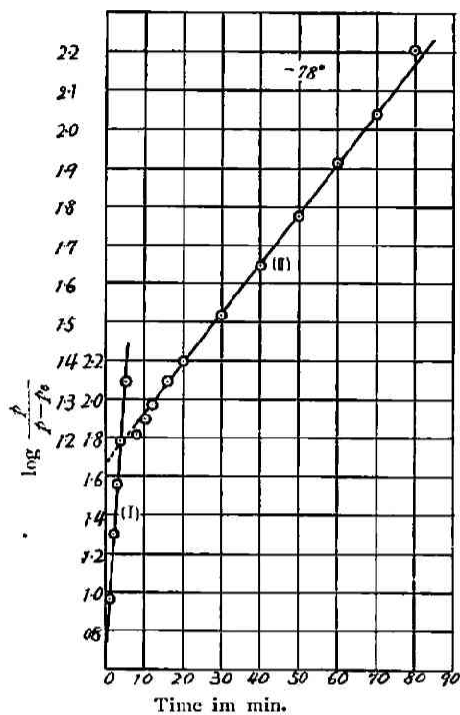


Fig. 6.

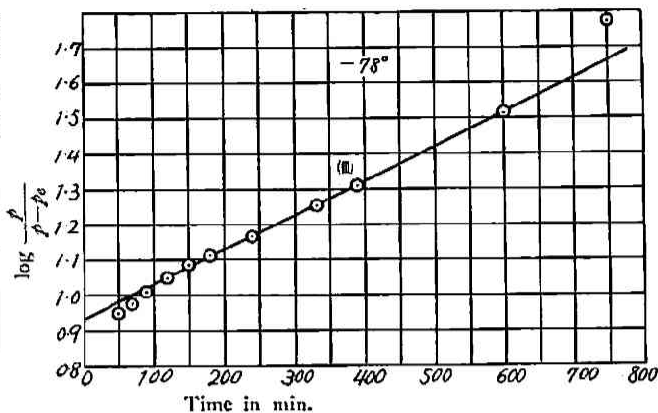


Fig. 7.

least composed of four kinds of adsorptions varying markedly in their velocities, namely, (I) an adsorption with a large velocity, and nearly completed 6-7 minutes after the start, (II) an adsorption nearly completed some 70 minutes after the start, (III) an adsorption with a small velocity and nearly completed

about 600 minutes after the start, and (IV) an adsorption with a very small velocity and lingering even 600 minutes after the start.

Similar relations were obtained also for adsorptions at -23° , -45.2° , -95° , -112° , -121° , and -130°C . The linear relations between $\log \frac{p}{p-p_e}$ and t for the period $t=1-70$ at these temperatures are shown in Figs. 8, 9, 10, 11, 12 and 13.

After all, if we assume that the adsorption of hydrogen by reduced nickel at low temperatures 1 minute after the start is composed of several kinds of activated adsorption varying markedly in their velocities, all of these adsorptions are represented by equation (4).

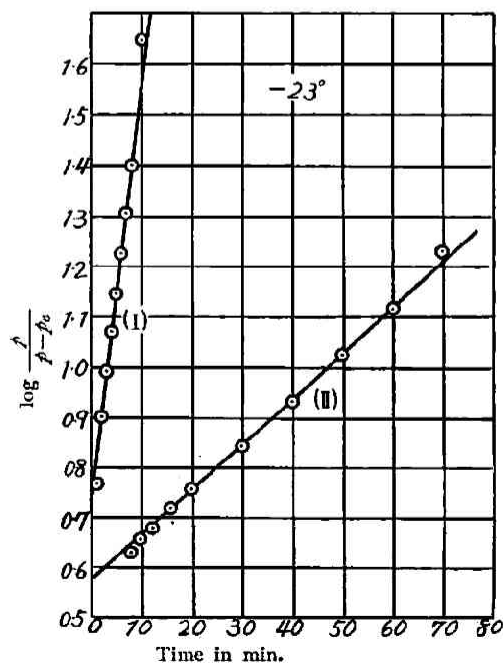


Fig. 8.

The Velocity Constant of Adsorption:

In equation (10) let $p=p_0$ when $t=0$, then C , a constant, is given by $C=\log \frac{p_0}{p_0-p_e}$. Substituting this in equation (10), we have

$$\log \frac{p}{p-p_e} = Kt + \log \frac{p_0}{p_0-p_e}. \quad (11)$$

From the diagram showing the linear relation between $\log \frac{p}{p-p_e}$ and t , the values of $\log \frac{p_0}{p_0-p_e}$ and K are obtainable, and the value of p_0 can be calculated from the value of $\log \frac{p_0}{p_0-p_e}$.

Now, from the earlier discussion

$$K = \frac{k_1 p_0}{2.303 (n_0 - n_e)} = \frac{k_1 p_0}{2.303} \times \frac{1}{[k' + k''(p_0 + p_e)](p_0 - p_e)},$$

$$\text{then } k_1 = \frac{2.303 K [k' + k''(p_0 + p_e)] (p_0 - p_e)}{p_0}. \quad (12)$$

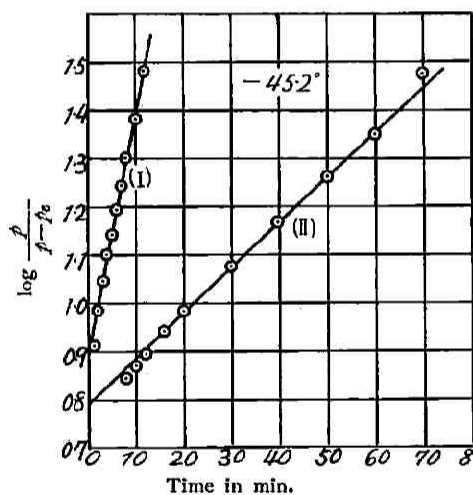


Fig. 9.

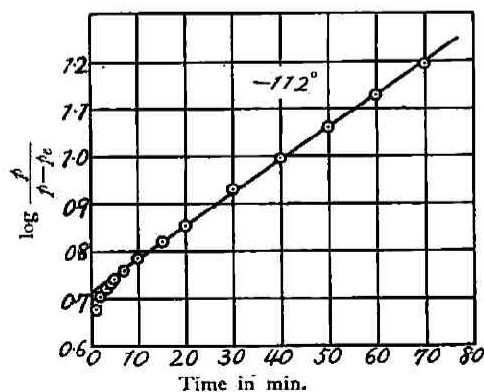


Fig. 11.

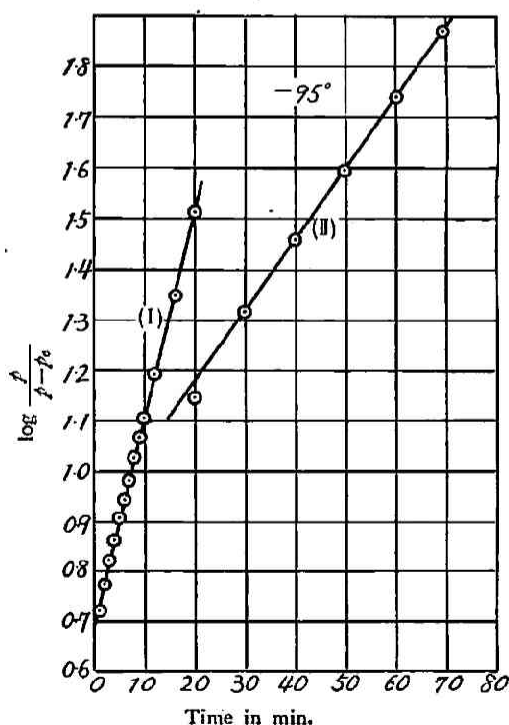


Fig. 10.

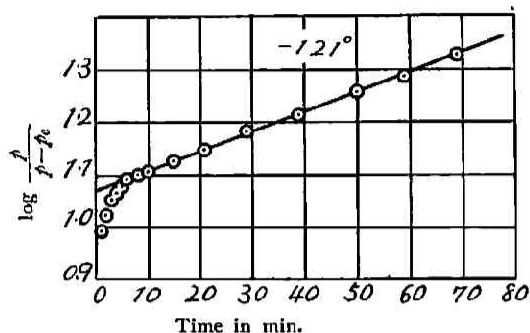


Fig. 12.

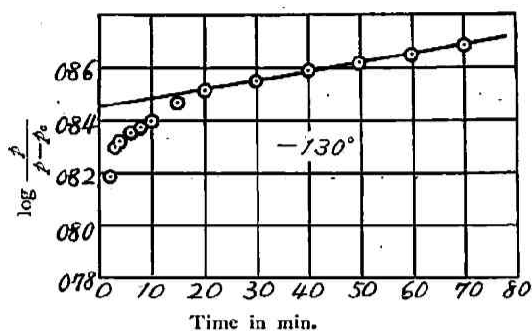


Fig. 13.

By equation (12) k_1 , the velocity constant of adsorption, was calculated. The velocity constants of the main adsorptions at each step for adsorption at -78°C . are given in Table I.

It seems in Fig. 4 that the main adsorptions indicated by (I) at -78°C . and -95°C . are correspondent to those at -112° , -121° and -130°C . The velocity constants of adsorption for these apparently corresponding adsorptions calculated for a trial are given in Table II.

Table I.
 -78°C .

Adsorption	$k_1 \times 10^6$
(I)	4.8
(II)	0.072
(III)	0.0087
(IV)	0.0011

Table II.

Temperature		$\log k_1$
$t^\circ\text{C}$.	$1/T$	
-78°	0.00513	-5.315
-95°	562	-6.128
-112°	621	-6.882
-121°	657	-7.554
-130°	699	-8.301

The relation between $\log k_1$ and $1/T$ is almost linear as shown in Fig. 14. It is probable, therefore, that they may be corresponding adsorptions.

The Heat of Activation of the Adsorption:

Regarding the adsorptions which show a nearly straight line in the $\log k_1 - \frac{1}{T}$ graph (Fig. 14) as corresponding adsorptions, the heat of activation of these adsorptions is calculated by Arrhenius' equation:

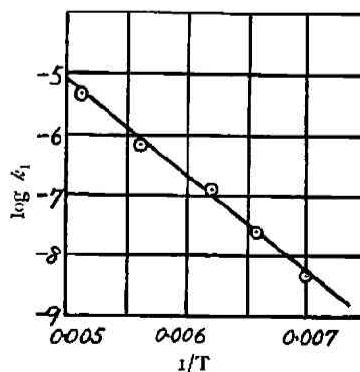


Fig. 14.

$$\frac{d \ln k_1}{dT} = \frac{Q}{RT^2} \quad \text{or} \quad \log k_1 = A - \frac{Q}{2.303 RT}, \quad (13)$$

where R is the gas constant, Q the heat of activation, and A a constant. $Q/2.303R$ can be obtained from the inclination of the straight line in Fig. 14. The calculated value of the heat of activation is 7100 cal.

The Adsorption Isotherm:

If we get the value of p_e for the main adsorption at one stage, for example, the value of p_e for the main adsorption at -78°C . during the interval $t=1$ and $t=6-7$ (p_e for adsorption (I) in Table I), the quantity of hydrogen remaining in the vessel when the adsorption has been completed may be calculated. Let it be a_e . The value of p_0 for this adsorption may be obtained by the method described in a foregoing paragraph and it is nothing but the pressure of hydrogen at the start under the assumption that this adsorption alone is taking place. From the value of p_0 , the quantity of hydrogen in the vessel at the start under the assumed condition may be calculated. Let it be a_0 . Then $a_0 - a_e$ is the total quantity of hydrogen adsorbed by this main adsorption when the equilibrium pressure is p_e .

Now, the rate of adsorption for different initial pressures of hydrogen was observed at -78°C .; and the quantities of hydrogen adsorbed, i.e., $a_0 - a_e$, by the main adsorption at the intervals $t=1$ and $t=6-7$ for different values of p_e were calculated as described above. The similar observations were made at -95° and -112°C . and the values of $a_0 - a_e$ for adsorptions apparently corresponding to adsorption (I) at -78°C ., that is, the main adsorption during the period indicated by (I) (-95°) and (-112°) in Fig. 4, were calculated for different values of p_e . The results are given in Table III.

Table III.

	p_0 (cm.)	a_0 (cc.)	p_e (cm.)	a_e (cc.)	$a_0 - a_e$ (cc.)
-78°C. (I)	17.78	10.07	13.15	7.15	2.92
	13.25	7.22	8.55	4.47	2.75
	11.67	6.27	6.83	3.51	2.76
	9.44	4.97	4.60	2.32	2.65
	6.26	3.21	1.50	0.74	2.47
	5.05	2.56	0.55	0.27	2.29
	3.36	1.67	0.03	0.01	1.66

-95°C. (I)	20.00	12.27	15.20	8.98	3.29
	15.89	9.44	10.85	6.18	3.26
	11.60	6.65	6.49	3.56	3.09
	7.67	4.26	2.50	1.33	2.93
	5.55	3.02	0.50	0.26	2.76
	4.48	2.42	0.05	0.02	2.40
-112°C.	14.63	9.24	9.75	5.94	3.30
	10.17	6.22	5.20	3.05	3.17
	6.96	4.15	1.80	1.03	3.12
	5.58	3.29	0.50	0.28	3.01
	5.16	3.05	0.10	0.06	2.97

The adsorption isotherms obtained from Table III are shown in Fig. 15.

The Heat of Adsorption:

Regarding the isotherms in Fig. 15 as those of corresponding adsorptions, the heat of adsorption was calculated by Clausius-Clapeyron's equation. The results obtained are given in Table IV.

Table IV.

Two different temperatures	Adsorbed amount (cc.)	Heat of adsorption (cal.)
-112°C. and -95°C.	2.95	11200
	3.00	11100
	3.10	9100
-95°C. and -78°C.	2.50	10300
	2.75	11000
	2.90	10700
Mean		10600

The mean value in Table IV is approximate to the values given in literature⁶⁾.

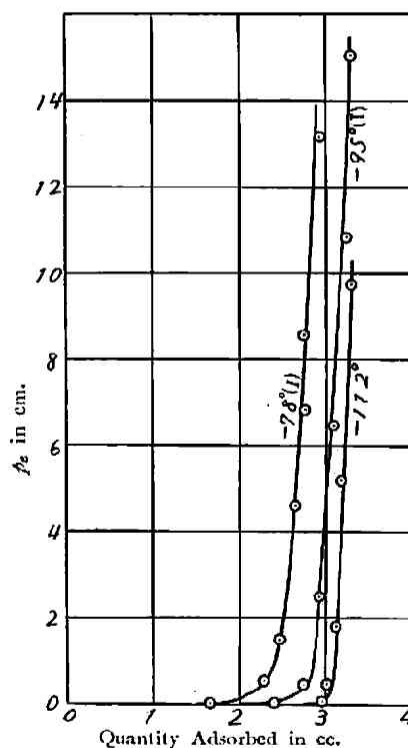


Fig. 15.

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Summary.

(1) The velocities of adsorption of hydrogen by reduced nickel at a low temperature range between -23° and -130°C . have been observed 1 minute after the start.

(2) It may be understood that the adsorption occurring 1 minute after the start consists of several activated adsorptions, whose velocities vary markedly.

(3) An equation for the adsorption velocity has been obtained and its physical interpretation is given.

(4) The velocity constants of the adsorption have been obtained.

(5) The heat of activation of a particular adsorption has been found to be 7100 calories.

(6) Adsorption isotherms for some particular adsorptions have been found.

(7) The heat of adsorption has been calculated from the adsorption isotherms and found to be 10,600 calories.

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