

## ON THE ADSORPTION OF HYDROGEN ON POISONED NICKEL, [II].

By SHUN-ICHIRO IJIMA.

In his preceding report,<sup>1)</sup> the author investigated at low temperatures the adsorption of hydrogen on the reduced nickel poisoned with cyanogen. He made clear the relationship between the degree of poisoning and the adsorbed amount and that between the degree of poisoning and the adsorption velocity constant, and found that the poisoning of reduced nickel had tendency to start at and spread gradually from the part of the larger adsorption velocity.

The present research has been done with respect to both the adsorbed amount and the adsorption velocity of hydrogen on the reduced nickel poisoned with cyanogen, carbon monoxide, or mercury at 20°C.

### Experimental.

The apparatus used and the procedure were the same as those mentioned in the preceding report.<sup>2)</sup>

#### Materials.

(a) Reduced nickel and hydrogen. The method of preparing these two were reported in another paper.<sup>2)</sup>

(b) Mercury. Mercury was fully washed by the ordinary method and purified by vacuum distillation.

(c) Cyanogen and carbon monoxide. Cyanogen was prepared by the method mentioned in Report (I),<sup>1)</sup> and carbon monoxide from oxalic acid and concentrated sulphuric acid by Moser's method.<sup>3)</sup>

### Experimental Results.

#### (I) Influence of the Poisoning with Cyanogen.

In order to poison reduced nickel with cyanogen, hydrogen adsorbed on it was desorbed at 280°C. and over it a known small quantity of cyanogen was passed.

#### Pressure-Time Curve.

The adsorption velocity of hydrogen on a new reduced nickel at 20°C. was

1) Iijima, *Rev. Phys. Chem. Japan*, 12, 148 (1938).

2) Iijima, *ibid.*, 12, 1 (1938).

3) Moser, "*Die Reindarstellung von Gasen.*"

measured and then, the nickel being poisoned with a known small quantity of cyanogen, similar measurements were done. Hereafter, every time the poisoning with a known small quantity of cyanogen was increased, similar measurements were repeated. The adsorption velocity, in this case, is that of the decrease in the pressure of hydrogen on nickel. Measurements were made at adequate intervals 1 minute after hydrogen had been introduced over nickel. The results obtained are shown in Fig. 1. In the figure, O is the curve of a new reduced nickel and the curves indicated by the figure 1 and upwards are those obtained in the case of gradual increase in the amount of cyanogen. The quantities<sup>4)</sup> of cyanogen poisoning nickel are given in Table I. Nickel used was prepared from 8.8439 g. of nickel oxide and the pressure of hydrogen was about 22.3 cm. 1 minute after the introduction of hydrogen.

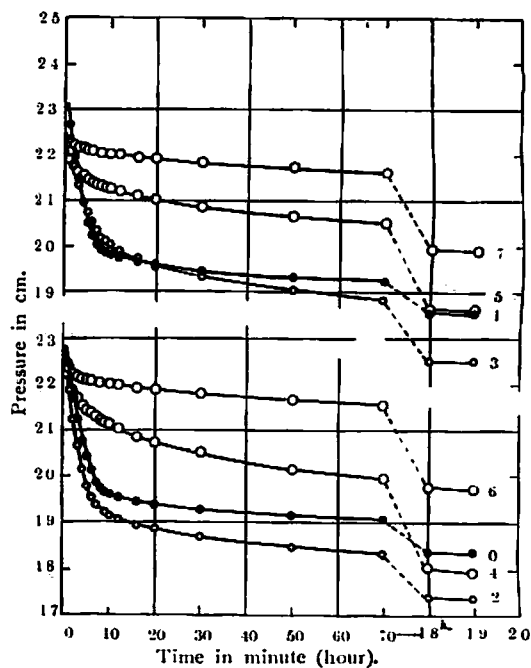


Fig. 1.

Table I.

Reduced nickel.....Prepared from 8.8439 g. of nickel oxide.

$k' = 1.580 \times 10^{-5}$ ,  $k'' = 2.189 \times 10^{-7}$ .

Experiment No.	Quantity, $x$ , of cyanogen (cc.)	$K$	$C$	$P_e$ (cm.)	$7 + \log k_1$
0	0	0.0850	0.695	18.83	1.094
1	0.09	0.0747	0.677	18.71	1.061
2	0.41	0.0634	0.656	17.68	1.008
3	0.88	0.0689	0.824	19.31	0.845
4	1.72	0.0930	1.210	21.03	0.552
5	2.82	0.0897	1.377	21.16	0.359
6	4.27				

#### Adsorbed Amount-Time Curve.

The relation between the adsorbed amount and the time was obtained from

4) As to the quantities, see Report (I) (This Journal, 12, 148 (1938)).

that between the pressure and the time shown in Fig. 1 by the method already mentioned.<sup>2)</sup> The relation obtained is shown in Fig. 2. The total adsorbed amount after 19 hours is decreased with increasing poisoning.

#### The Rate of Adsorption.

It has been already reported<sup>2)</sup>, by the author that in the case of adsorption of hydrogen on reduced nickel the following relation holds:

$$\log \frac{p}{p-p_e} = Kt + C, \dots \dots \dots (1)$$

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

$$K = \frac{k_1 p_e}{2.303} \times \frac{1}{[k' + k''(p_0 + p_e)](p_0 - p_e)}, \dots \dots \dots (2)$$

and

$$C = \log \frac{p_0}{p_0 - p_e}, \dots \dots \dots (3)$$

where  $p_e$  is the equilibrium pressure,  $p_0$  the pressure when  $t=0$ , and  $k_1$  the velocity constant of adsorption, and  $k'$  and  $k''$  the constants concerning the space and the temperature in the vessel.

Whether this relation held or not in the case of the adsorption of hydrogen on reduced nickel at 20°C. was examined by the method already mentioned, i.e. the presence of  $p_e$  to satisfy the linear relation between  $\log \frac{p}{p-p_e}$  and  $t$  was examined. In fact the value of  $p_e$  satisfying the required linear relation was obtained regardless of the amount of cyanogen (Table I, the 5th column). The linear relation thus obtained is shown in Fig. 3. This fact proves the applicability of equation (1) in the present case.<sup>5)</sup>

#### The Velocity Constant of Adsorption.

From the values of  $K$  and  $C$  obtained from the diagrams showing the linear

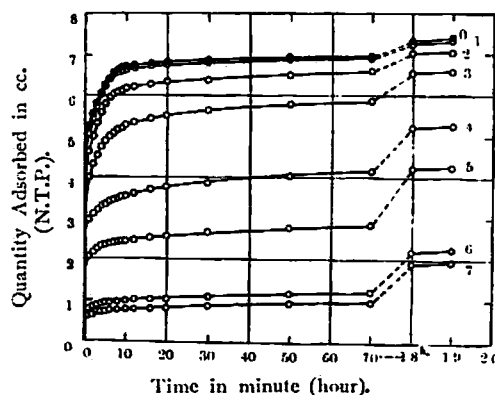


Fig. 2.

5) The applicability of equation (1) was examined by the adsorption which lasted for 7-9 minutes after the start. The velocity of the adsorption lasting further is so small that it is inappropriate to regard the decrease in pressure at 20°C. as adsorption only. Therefore, it has been omitted to examine the applicability to the adsorption lasting further after 7-9 minutes.

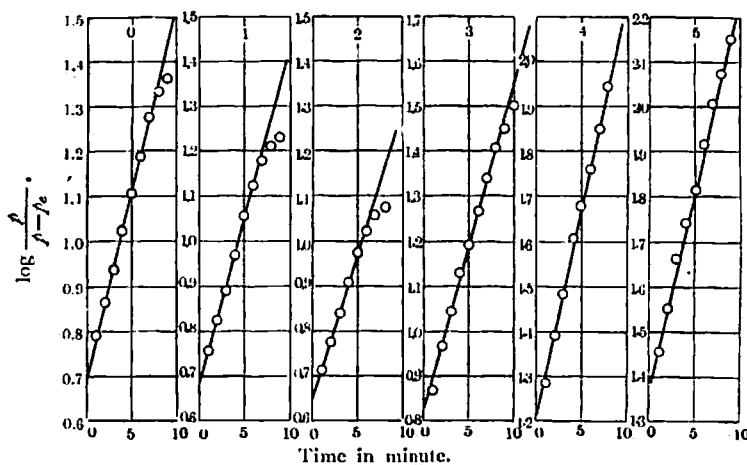


Fig. 3.

relation between  $\log \frac{p}{p-p_e}$  and  $t$ , the velocity constant of adsorption  $k_1$  was calculated according to equations (2) and (3), which is given in Table I.

Plotting the values of  $\log k_1$  (ordinate) and the quantities,  $x$ , of cyanogen poisoning the nickel (abscissa), a graphical relation was obtained as shown in Fig. 4. In case of a small quantity of cyanogen, each point is nearly on a straight line. In other words, the following relation holds between  $x$  and  $k_1$ :

$$\log k_1 = a - \beta x, \dots \dots \dots (4)$$

where  $a$  and  $\beta$  are constants. As already mentioned,<sup>11</sup> the same relation held in the adsorption of hydrogen on reduced nickel poisoned with cyanogen at low temperatures.

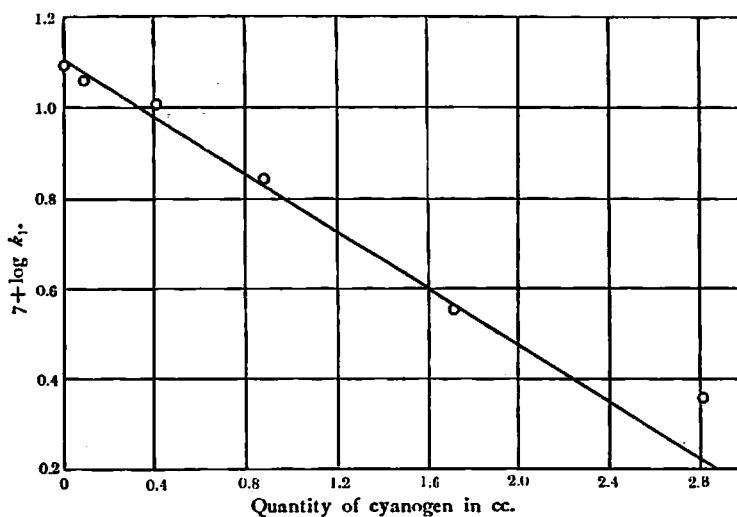


Fig. 4.

**The Adsorbed Amount and the Degree of Poisoning.**

The above-mentioned measurement was made with respect to an adsorption velocity favourable to the measurement. It is evident from Fig. 2, however, that there is any instantaneous adsorption (activated adsorption)<sup>6)</sup> which has much larger adsorption velocity. The adsorbed amount,  $a$ , of this instantaneous adsorption were calculated as in report (I), which are given in the sixth column of Table II.

The sums of the amount of the instantaneous adsorption and the amount,  $x$ , of cyanogen are given in the last column of Table II.

Table II.

Reduced nickel.....Prepared from 8.8439g. of nickel oxide.

$k' = 1.580 \times 10^{-6}$ ,  $k'' = 2.189 \times 10^{-7}$ .

Experiment No.	Quantity, $x$ , of cyanogen (cc.)	$P_0$ (cm.)	$a_0$ (cc.)	$a_0'$ (cc.)	$a = a_0' - a_0$ (cc.)	$a + x$ (cc.)
0	0	23.58	11.08	15.60	4.52	4.52
1	0.09	23.70	11.15	15.55	4.40	4.49
2	0.41	22.69	10.56	14.68	4.12	4.53
3	0.88	22.72	10.58	14.28	3.70	4.58
4	1.72	22.41	10.40	13.17	2.77	4.49
5	2.82	22.09	10.22	12.13	1.91	4.73
6	4.27				0.60*	4.87

\* Obtained directly from Fig. 2.

The relation between poisoning and the total adsorbed amount after 19 hours is given in Table III.

Table III.

Experiment No.	Quantity, $x$ , of cyanogen (cc.)	Total adsorbed amount after 19 hours.		$A + x$ (cc.)
		Adsorbed amount $A$ (cc.)	Pressure (cm.)	
0	0	7.40	18.39	7.40
1	0.09	7.35	18.60	7.44
2	0.41	7.07	17.40	7.48
3	0.88	6.59	17.56	7.47
4	1.72	5.28	17.93	7.00
5	2.82	3.88	18.63	6.70
6	4.27	2.24	19.75	6.51

The total adsorbed amount after 19 hours decreased as the amount of

6) A greater part of this instantaneous adsorption is an activated adsorption, but van der Waals' adsorption is included in it.

cyanogen was increased. Each sum of the adsorbed amount and the amount of cyanogen was nearly equal to one another so long as the amount of cyanogen was small. This fact and the fact shown in the last column of Table II show that decrease in the adsorbed amount of hydrogen due to poisoning is limited only to the amount of the instantaneous adsorption in that case.

## (II) Influence of the Poisoning with Carbon Monoxide.

The poisoning of reduced nickel with carbon monoxide was made thus: reduced nickel, being desorbed at  $280^{\circ}\text{C}$ ., was cooled and over it was a known small amount of carbon monoxide introduced.

### Pressure-Time Curve.

The relation between the pressure and the time is shown in Fig. 5. In the figure, 0 indicates the curve for a new reduced nickel and the figure 1 and upwards indicate the curves obtained with increasing amounts of carbon monoxide. The total quantities of carbon monoxide which has poisoned nickel are given in the second column of Table IV. It must be considered, however, that

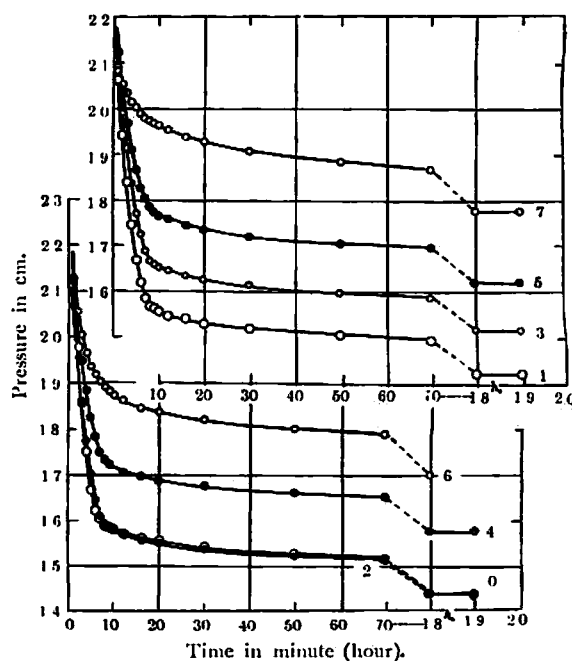


Fig. 5.

Table IV.

Reduced nickel.....Prepared from 10.0291 g. of nickel oxide.

$$k' = 1.574 \times 10^{-6}, \quad k'' = 2.189 \times 10^{-7}.$$

Experiment No.	Quantity, $x$ , of carbon monoxide (cc.)	$k'$	$C$	$P_0$ (cm.)	$7 + \log k_1$
0	0	0.0910	0.388	14.29	1.645
1	0.07	0.0905	0.390	14.27	1.539
2	0.32	0.0868	0.402	14.50	1.503
3	0.79	0.0881	0.462	15.51	1.415
4	1.77	0.0858	0.521	16.15	1.327
5	3.45	0.0908	0.595	17.00	1.194
6	6.97	0.1109	0.781	18.52	1.097
7	13.13	0.1070	1.092	19.48	0.728

the amount of carbon monoxide which has poisoned nickel is in practice smaller than these, because carbon monoxide is gradually desorbed by degassing at  $280^{\circ}\text{C}$ . prior to the experiment, as will be mentioned later. The nickel used was prepared from 10.0291 g. of nickel oxide and pressure was about 20.9 cm. 1 minute after the start.

#### Adsorbed Amount-Time Curve.

From the relation shown in Fig. 5, the relation between the adsorbed amount and the time was obtained, which is shown in Fig. 6.

#### The Rate of Adsorption and the Velocity Constant of Adsorption.

To the adsorption velocity of hydrogen on the reduced nickel poisoned with carbon monoxide equation (1) is applicable. The relation between  $\log \frac{p}{p-p_e}$  and  $t$  is shown in Fig. 7. The velocity constant of adsorption  $k_1$ , calculated as before, using the values of  $K$  and  $C$  of equation (1) obtained from Fig. 7 is tabulated in Table IV. As seen in the table,  $k_1$  becomes smaller with increasing poisoning.

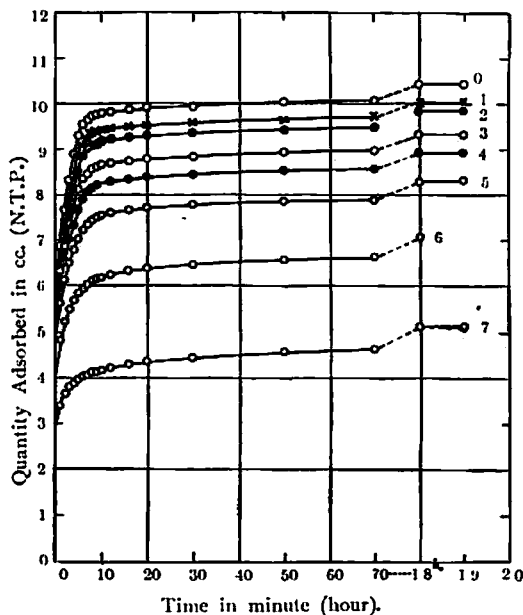


Fig. 6.

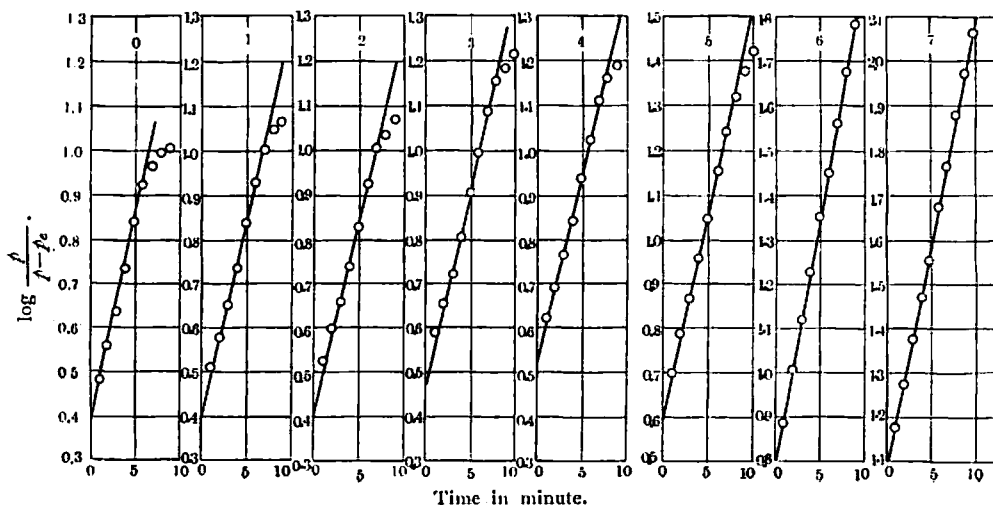


Fig. 7.

### The Desorption of Carbon Monoxide.

Carbon monoxide poisoning reduced nickel is slowly desorbed by degassing at  $280^{\circ}\text{C}$ . This fact is proved from the comparison of the adsorption velocity of hydrogen measured after the degassing of the poisoned nickel and that before

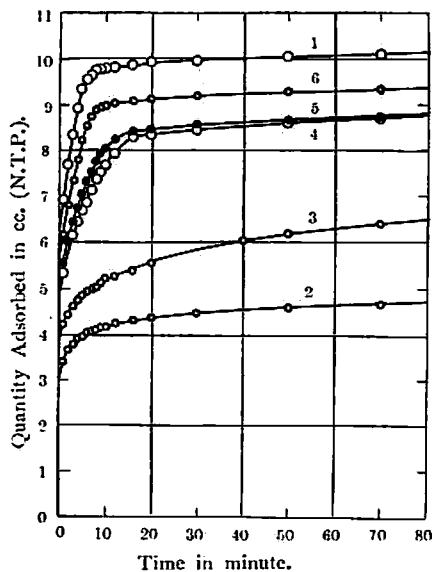


Fig. 8.

poisoning. In Fig. 8, 1 is the curve of the adsorption velocity measured before poisoning, and 2 and others are the curves of the adsorption velocity measured every time each of the under-mentioned degassing was done in order, after the reduced nickel was left alone at room temperature for one night with addition of a pretty large amount of carbon monoxide.

- 2, 0.5 hr. at  $20^{\circ}\text{C}$ .
- 3, 1 hr. at  $280^{\circ}\text{C}$ .
- 4, 5 hrs. at  $280^{\circ}\text{C}$ .
- 5, 3 hrs. at  $280^{\circ}\text{C}$ .
- 6, 1.5 hrs. at  $280^{\circ}\text{C}$ . and, after one night of standing still, for 6.5 hrs. at  $280^{\circ}\text{C}$ .

As seen in Fig. 8, according as the desorption of carbon monoxide proceeds and the amount remaining on nickel gradually decreases, the values of both the adsorbed amount and the adsorption velocity become considerably approximate to those of pure reduced nickel through a process reverse to the case of gradual increase in carbon monoxide.

### (III) Influence of the Poisoning with Mercury.

The poisoning with mercury was done thus: the particles of mercury were put in the space near the reduced nickel in hydrogen. This space and the vessel holding the nickel were heated to  $280^{\circ}\text{C}$ . to let mercury evaporate and let the vapour of mercury come in contact with the nickel. Part of the vapour of mercury condensed in the capillary tubes in room temperature of the vessel, so that the amount of mercury which had practically combined with nickel could not be measured.

#### Pressure-Time Curve.

The relation between the pressure and the time is shown in Fig. 9. In the figure, the curve indicated by o is that of new reduced nickel, and the curves



indicated by 1 and others are those in the case of gradual increase in mercury. Nickel used was prepared from 11.8643 g. of nickel oxide and the pressure was about 21 cm. 1 minute after the start.

#### Adsorbed Amount-Time Curve.

From the relation between the pressure and the time shown in Fig. 9 the relation between the adsorbed amount and the time was obtained by the method already mentioned and is shown in Fig. 10.

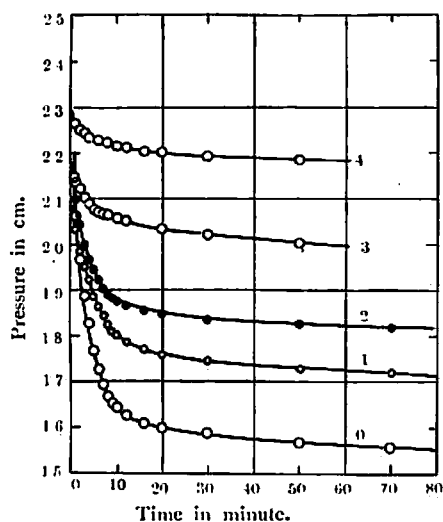


Fig. 9.

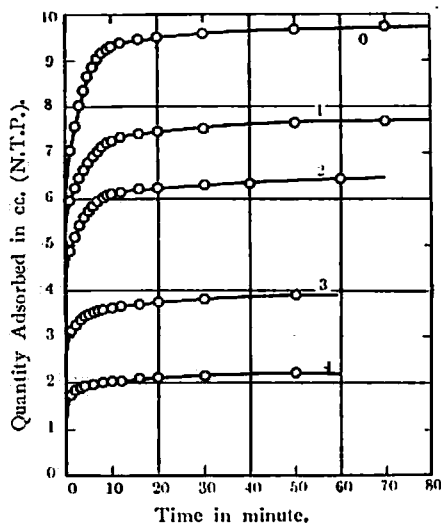


Fig. 10.

#### The Rate of Adsorption and the Velocity Constant of Adsorption.

To the adsorption velocity of hydrogen on nickel poisoned with mercury equation (1) is also applicable. The relation between  $\log \frac{p}{p-p_e}$  and  $t$  is shown in Fig. 11. The velocity constant of adsorption  $k_1$  calculated as before, using the values of  $K$  and  $C$  of equation (1) obtained from Fig. 11 are tabulated in Table V. As in the previous case,  $k_1$  becomes smaller with increasing poisoning.

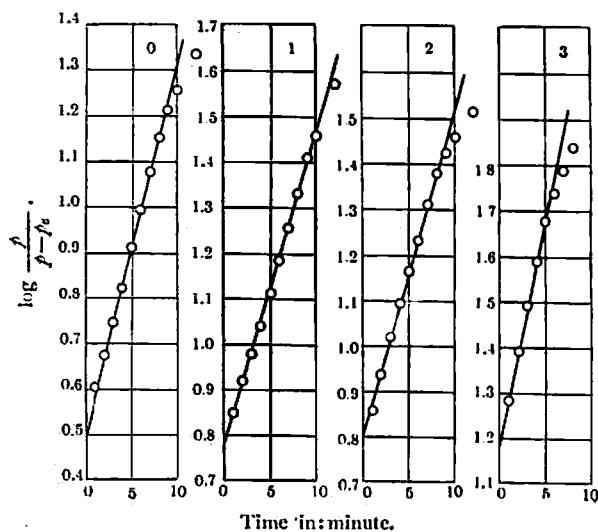


Fig. 11.

Table V.

Reduced nickel.....Prepared from 11.8643 g. of nickel oxide.

 $k' = 1.556 \times 10^{-5}$ ,  $k'' = 2.189 \times 10^{-7}$ .

Experiment No.	$A'$	$C$	$P_e$ (cm.)	$7 + \log k_1$
0	0.0830	0.495	15.52	1.333
1	0.0704	0.777	18.37	0.900
2	0.0719	0.802	18.11	0.876
3	0.0986	1.186	20.37	0.594

## Considerations.

The experimental facts above mentioned and the results<sup>1)</sup> obtained concerning the relation between the adsorption of hydrogen at low temperatures and the poisoning of nickel by cyanogen are summarised as follows:

(1) Poisons combine first with the part on the surface of nickel whose hydrogen adsorption velocity is largest and then gradually with the parts on which the velocity is smaller.

(2) In case a poison is small in amount, the amount of the instantaneous adsorption decreases by the amount of the poison, so that the total adsorbed amount decreases nearly by the amount of the poison.

(3) When a poison combines with the parts of large adsorption velocity, the adsorption velocity constant of the other parts becomes smaller due to this combination, but the adsorbed amount seldom varies.

(4) The equation of the velocity of hydrogen adsorption on pure reduced nickel which the author had proposed in his preceding paper<sup>2)</sup> is applicable to the velocity of hydrogen adsorption on poisoned nickel.

## Summary.

(1) The adsorption velocity and the adsorbed amount of hydrogen on reduced nickel poisoned with cyanogen, carbon monoxide or mercury at 20°C. have been studied.

(2) The equation of the velocity of hydrogen adsorption on reduced nickel which the author had proposed in his preceding paper has been found to be applicable in the present case.

(3) The adsorption velocity constant becomes smaller according as the increase in poison. There holds a linear relation between the logarithm of the velocity constant of adsorption and the quantity of poison.

(4) A poison has tendency to combine first with the parts where instan-

taneous adsorption takes place and then with the parts on which the velocity is smaller.

(5) When a poison is small in amount, the amount of instantaneous adsorption decreases by that of the poison and so does the total adsorbed amount.

(6) The adsorption velocity curve changes its form as a poison increases. When the poison is gradually removed, the curve approaches that of the new nickel by changing in a reverse order.

The author wishes to take this opportunity in expressing his deep gratitude to Prof. S. Horiba of the Kyoto Imperial University for his kind guidance and valuable advices.

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(Received February 8, 1938.)