

# ON THE ADSORPTION OF HYDROGEN ON POISONED NICKEL. [I].

Studies at Low Temperatures.

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It is well known that the activity of a catalyst is remarkably diminished by the poisoning<sup>1)-7)</sup> of the catalyst by the adsorption of a certain substance, or by the auto-poisoning of it by the adsorption of the reactants. So the adsorption rate or adsorption amount of a gas on a catalyst will be also much affected by its poisoning.

Many investigators<sup>8)-25)</sup> investigated the adsorption rate or adsorption amount on a poisoned catalyst or on a catalyst which is regarded as poisoned by other substances because of insufficient desorption before the adsorption. All of them except Maxted, however, studied qualitatively and only reported both the adsorption rate and the adsorption amount were diminished by poisoning. Maxted studied rather quantitatively the influence of hydrogen sulphide on the adsorption rate of hydrogen on platinum, measuring the apparent adsorption rate without any reference to their rate constant.

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- 3) Whitesell and Frazer, *ibid.*, **45**, 2841, (1923).
- 4) Pease, *ibid.*, **45**, 2296, (1923).
- 5) Lamb and Vail, *ibid.*, **47**, 123, (1925).
- 6) Pease and Stewart, *ibid.*, **47**, 1235, (1925).
- 7) Griffin, *ibid.*, **49**, 2136, (1927).
- 8) Harned, *J. Am. Chem. Soc.*, **42**, 372, (1920).
- 9) McGaveck and Patrick, *ibid.*, **42**, 946, (1920).
- 10) Davidheiser and Patrick, *ibid.*, **44**, 1, (1922).
- 11) Coolidge, *ibid.*, **46**, 596, (1924).
- 12) Gregg, *J. Chem. Soc.*, 1494, (1927).
- 13) McBain, *J. Phys. Chem.*, **34**, 1439, (1930).
- 14) Allmand and Chaplin, *Proc. Roy. Soc. London*, **129**, [A], 235, 252, (1930).
- 15) Maxted, *J. Chem. Soc.*, 2203, (1931).
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- 17) Foote and Dixon, *J. Am. Chem. Soc.*, **53**, 55, (1931).
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- 19) Imai, *J. Chem. Soc. Japan*, **54**, 1145, (1933).
- 20) Burrage, *Trans. Farad. Soc.*, **28**, 192, (1932); *ibid.*, **29**, 677, (1933); *J. Phys. Chem.*, **37**, 41, (1933).
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- 22) Griffin, *ibid.*, **56**, 845, (1934).
- 23) Chaplin, *Trans. Farad. Soc.*, **30**, 249, (1934).
- 24) Robert, *Proc. Roy. Soc. London*, **152**, [A], 477, (1935).
- 25) Robert, *Nature*, **137**, 659, (1936).

The present author had already proposed an equation for the adsorption velocity of hydrogen on reduced nickel.<sup>26)</sup> From the physicochemical meaning of the equation it is assumed that it is applicable to the adsorption rate of hydrogen on poisoned nickel. The object of the present research is to ascertain this assumption experimentally and if applicable, to examine the relation between the quantity of poisons and the velocity constant of adsorption calculated.

When a catalyst is active for several kinds of reactions, its poisoning action is rather selective. For example, when a catalyst which is active for three different kinds of reactions is slightly poisoned, the catalyst loses its activity for one kind of the reactions; when the catalyst is further poisoned, it loses its activity for two kinds of the reactions, but remains still active for the last one. This fact<sup>27)</sup> and those<sup>29)-31)</sup> similar to this have already been observed by many investigators. From his quantitative study of the relation between the poisoning and the catalytic activity of catalysts, Maxted<sup>32)-35)</sup> observed that if there were some parts differing in their activities the highest active part is poisoned first. Kubokawa<sup>36)</sup> also discussed the energy distribution of a catalyst through this phenomenon. The fact that there was a maximum on the curve showing the relation between the quantity of hydrogen adsorbed on a catalyst and its molal heat of adsorption<sup>37)38)</sup> and no maximum on the same curve for the catalyst preliminarily poisoned with oxygen<sup>38)</sup> has been ascribed to the phenomenon that the gas was first adsorbed on the highest active part. To ascertain the fact that the poisoning of a catalyst proceeds first from its most active part to the less active part is also the aim of the present research.

### Experimental.

The rate of the adsorption of hydrogen on nickel poisoned by cyanogen was determined. The apparatus used and the procedure were the same as described in the preceding paper.<sup>26)</sup>

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- 26) Iijima, *Rev. Phys. Chem. Japan*, **12**, 1, (1938).
  - 27) Vavon and Hasson, *Compt. rend.*, **175**, 277, (1922).
  - 28) Willstätter and Hatt, *Ber.*, **45**, 1471, (1912).
  - 29) Kubota and Yoshikawa, *Sc. Pap. I.P.C.R.*, **3**, 223, (1925).
  - 30) Rideal and Wright, *J. Chem. Soc.*, **127**, 1347, (1925).
  - 31) Ghosh and Bakshi, *J. Ind. Chem. Soc.*, **6**, 749, (1929).
  - 32) Maxted, *J. Chem. Soc.*, **119**, 225, (1921).
  - 33) Maxted, *ibid.*, **121**, 1760, (1922).
  - 34) Maxted, *ibid.*, 1600, (1928).
  - 35) Maxted, *ibid.*, 502, (1933).
  - 36) Kubokawa, *Rev. Phys. Chem. Japan*, **11**, 452, (1937).
  - 37) Fryling, *J. Phys. Chem.*, **30**, 818, (1926).
  - 38) Taylor and Kistiakowsky, *J. Am. Chem. Soc.*, **49**, 2200, (1927).

**Materials.**

(a) Reduced nickel and hydrogen. Reduced nickel and hydrogen were prepared in the same way as described in the preceding paper.<sup>39)</sup>

(b) Cyanogen. Cyanogen was prepared from potassium cyanide and copper sulphate by Moser's method.<sup>39)</sup>

**Results and their Considerations.****Pressure-Time Curve.**

The rate of adsorption of hydrogen on pure reduced nickel was first measured at  $-78^{\circ}$  and  $-112^{\circ}\text{C}$ . and then that on the nickel poisoned with a small quantity of cyanogen. In this way, the amount of cyanogen being increased each time, a series of experiments were carried out. The results are shown in Figs. 1 and 2.

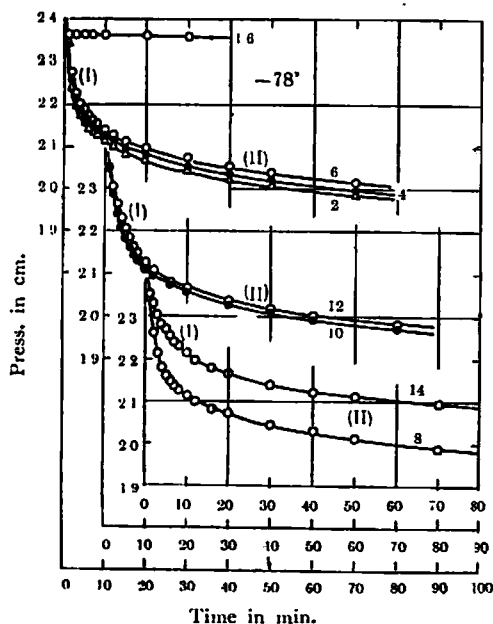


Fig. 1.

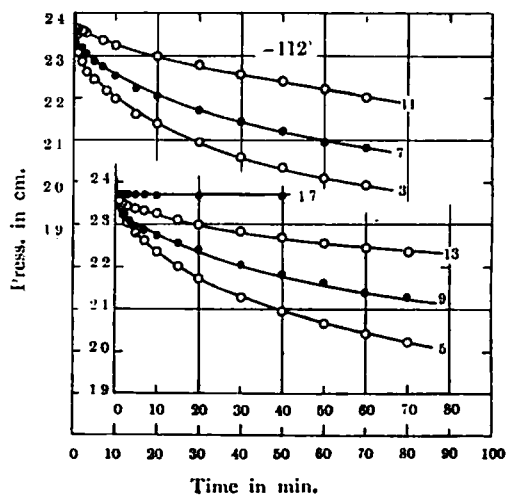


Fig. 2.

In this case the rate of adsorption of hydrogen meant the rate of decrease in the pressure of hydrogen in the adsorption vessel. The pressure 1 minute after the introduction of hydrogen was always about 23.5 cm. The nickel used was prepared from 10.5361 g. of nickel oxide. The amount of cyanogen poisoning the nickel was calculated under the assumption that the cyanogen was not removed by the desorption prior to the adsorption or, if removed, it was of so small quantity as to be negligible, and the values obtained are tabulated in the first column in Table I.

39) Moser, *Die Reindarstellung von Gasen*, (1920).

Table I.

Quantity of cyanogen (cc.)	Velocity constant of adsorption ( $\log k_1 + 8$ )				
	Experimental No.	-78°(I)	-78°(II)	Experimental No.	-112°
0.00	2	2.470	0.907	3	1.074
0.12	4	2.418	0.885	5	1.032
0.49	6	2.329	0.852	7	0.884
1.09	8	2.244	0.810	9	0.738
1.70	10	2.045	0.772	11	0.591
2.29	12	1.941	0.721	13	0.396
3.89	14	1.587	0.496	15	—
Large quantity	16	—	—	17	—

**Adsorbed Amount-Time Curve.**

The number  $n$  of mols of the gas in the vessel at the pressure  $p$  is expressed by the equation<sup>39)</sup>;

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

where  $k'$  and  $k''$  are known constants dependent on both 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 the pressure in the vessel at a given time is known, the total amount of the gas adsorbed during the time—from the start to the given time—can be calculated. The amount thus calculated is shown in Fig. 3.

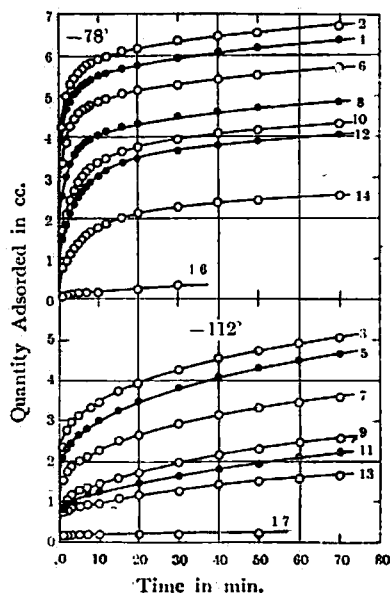


Fig. 3.

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

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

40) Iijima, *Rev. Phys. Chem. Japan*, 12, 83, (1938).

and 
$$C = \log \frac{p_0}{p_0 - p_e}, \quad (4)$$

where  $p_0$  is the pressure at  $t=0$ , and  $k_1$  the velocity constant of adsorption.

Whether or not the relation represented by equation (2) held in the case of the adsorption of hydrogen on poisoned nickel was examined as described in the preceding paper.<sup>30)</sup> In other words, whether the value of  $p_e$ , which satisfied the linear relation between  $\log \frac{p}{p-p_e}$  and  $t$  for the adsorption in the early part, existed or not was examined. In fact the value of  $p_e$  satisfying the required linear relation was obtained in each case (In the adsorption at  $-78^\circ\text{C}$ . the values of parts (I) and (II) differed from each other). This justifies the applicability of equation (2) to the present case. Some examples of the linear relation obtained are shown in Figs. 4, 5, 6 and 7.

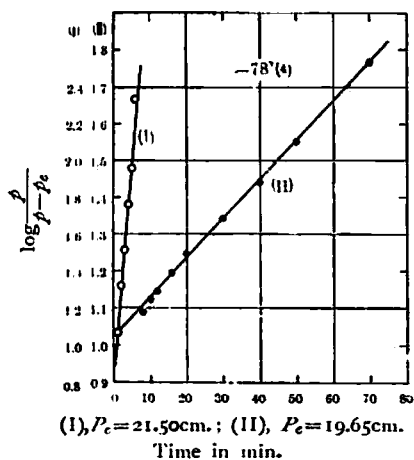


Fig. 4.

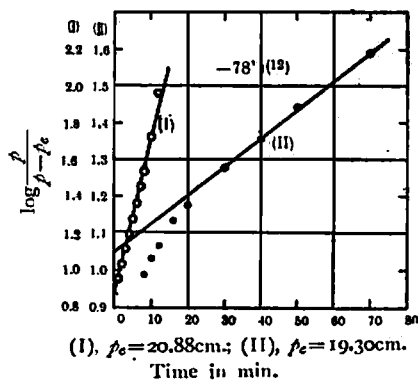


Fig. 5.

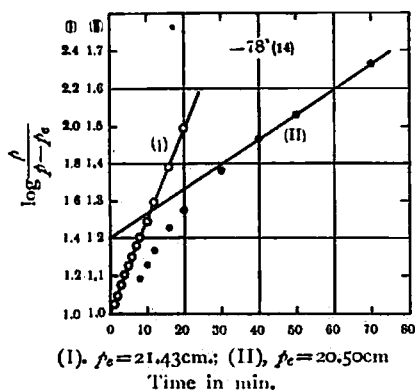


Fig. 6.

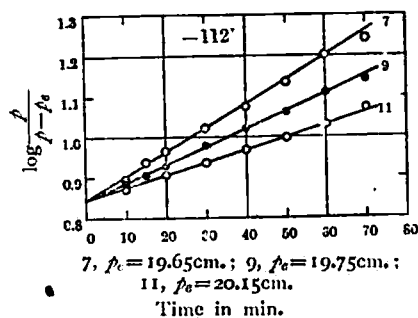


Fig. 7.

### The Velocity Constant of Adsorption.

From the values of  $K$  and  $C$  obtained from the diagrams showing the linear relation between  $\log \frac{p}{p-p_e}$  and  $t$ , the velocity constant of adsorption  $k_1$  was calculated according to equation (3) and (4), which is given in Table I.

Plotting the values of  $\log k_1$  (ordinate) and the quantities of cyanogen poisoning the nickel (abscissa), a nearly linear relation was obtained as shown in Fig. 8. This linear relation is expressed thus:

$$\log k_1 = a - \beta x, \quad (5)$$

where  $x$  is the quantity of cyanogen,  $a$  and  $\beta$  the constants varying with different adsorptions. Equation (5) is nothing but the integral form of the following equation:

$$-\frac{dk_1}{dx} = \beta k_1. \quad (6)$$

Accordingly, it may be said that the decrease in the value of the velocity constant caused by the addition of a unit quantity of cyanogen is proportional to the velocity constant itself.

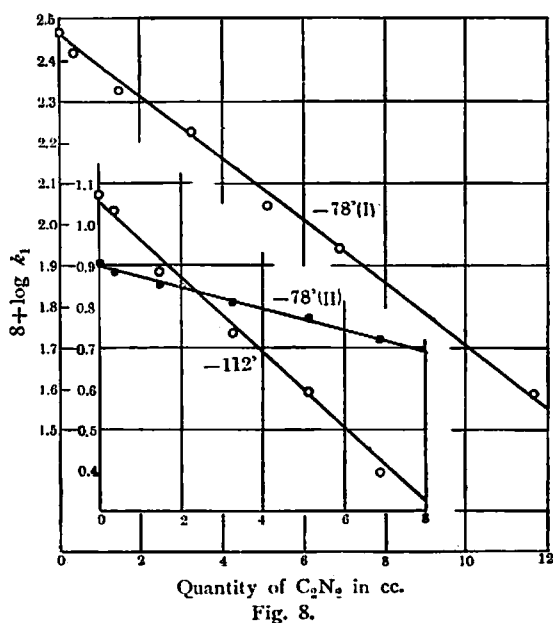


Fig. 8.

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

The value of  $C$ , a constant in equation (2), was obtained from the diagram showing the linear relation between  $\log \frac{p}{p-p_e}$  and  $t$ ; hence the value of  $p_0$ , the pressure of hydrogen at the start under the assumption that the adsorption in question alone took place. From the values of  $p_0$  and  $p_e$  (the equilibrium pressure), the quantity  $a_0$  of hydrogen in the vessel at the start under the assumed condition and that of  $a_e$  of hydrogen in the vessel at the time when the adsorption has been completed were calculated (from equation (1)). The difference between the two,  $a_0 - a_e$ , is the quantity of hydrogen adsorbed under the equilibrium pressure  $p_e$ . The values thus calculated for the adsorption in part (I) at  $-78^\circ C.$  and that at  $-112^\circ C.$  on the nickel poisoned in different degrees are given in Table II.

In Table II the equilibrium pressures  $p_e$  are different from each other, but not so much. Roughly speaking, the quantity of the adsorption,  $a_0 - a_e$ , is not so

Table II.

Quantity of cyanogen (cc.)	Experimental No.	-78°(1)		Experimental No.	-112°	
		$P_0(\text{cm.})$	$a_0 - a_e(\text{cc.})$		$P_0(\text{cm.})$	$a_0 - a_e(\text{cc.})$
0.00	2	21.38	2.50	3	19.28	2.63
0.12	4	21.50	2.44	5	19.35	2.81
0.49	6	21.55	2.32	7	19.65	2.54
1.09	8	21.10	2.39	9	19.75	2.60
1.70	10	20.70	2.47	11	20.15	2.62
2.29	12	20.88	2.19	13	20.70	2.08
3.89	14	21.43	1.63	—	—	—

much affected by poisoning except in the case when poisoning is remarkable. But as is seen in Fig. 3, the total quantity of adsorption in the early part gradually diminished with increased poisoning, hence this must be ascribed to the decrease in the adsorption amount of the activated adsorption which might take place either instantaneously or nearly so, having higher adsorption velocity than that measured by the author.<sup>41)</sup>

The quantity  $a$  of this instantaneous adsorption may be approximately given thus:

$$a = a_0' - a_0. \quad (7)$$

where  $a_0'$  is the quantity of hydrogen actually introduced in the vessel. The calculated value of  $a$  gradually diminished with increasing quantity of cyanogen as seen in Table III. The sum of the quantity  $a$  of this adsorption and that  $x$  of

Table III.

Experimental No.	$x(\text{cc.})$	$a_0'(\text{cc.})$	$a_0(\text{cc.})$	$a_0' - a_0$ or $a$	$x + a$	$P_0(\text{cm.})$
2	0.00	18.32	15.17	3.15	3.15	24.99
4	0.12	18.01	15.13	2.88	3.00	24.94
6	0.49	17.46	15.04	2.42	2.91	24.81
8	1.09	16.48	14.80	1.68	2.77	24.48
10	1.70	15.78	14.62	1.16	2.86	24.23
12	2.29	15.57	14.46	1.11	3.40	24.01
14	3.89	14.89	14.27	0.62	4.51	23.76

cyanogen poisoning nickel, which is given in the sixth column of the table, is nearly constant in Expts. 2—10 regardless of the quantity of cyanogen. This shows

41) In this instantaneous adsorption van der Waals' adsorption is contained, but its quantity is considered to be extremely small compared with the activated adsorption from the author's unpublished work on the van der Waals' adsorption of nitrogen on the same adsorbent.

that cyanogen first combined with the part of the nickel surface participating in the very adsorption and that the quantity of that adsorption was decreased as much as that of cyanogen which combined. In Expts. 12 and 14, on the other hand, the sum is larger than the said constant value. This may indicate that the combination of cyanogen with the part participating in slower adsorption was remarkable.

If so, the quantity of hydrogen adsorbed by slower adsorption must be smaller than those of the others. In fact, this was proved as seen in the 4th column of Table II.

From these facts it may be understood that cyanogen combines first with the part on which the rate of adsorption of hydrogen is largest and then with the part on which the rate is less, that is, from the largest to the least in order.

### Summary.

(1) The rates of adsorption of hydrogen on reduced nickel poisoned with cyanogen have been observed at  $-78^{\circ}$  and  $-112^{\circ}\text{C}$ .

(2) The equation for the adsorption rate of hydrogen and deuterium on pure reduced nickel which the author had proposed in his preceding paper has been found to be applicable to the adsorption rate of hydrogen on reduced nickel poisoned with cyanogen.

(3) It has been found that a linear relation holds between the quantity of cyanogen poisoning reduced nickel and the logarithm of the velocity constant of adsorption of hydrogen.

(4) When a small quantity of cyanogen is introduced over reduced nickel at a time, cyanogen combines with the part on nickel in the order of the largeness of the rate of adsorption of hydrogen.

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