ON THE ADSORPTION OF NITROGEN ON REDUCED NICKEL.

By Shun-ichiro Iijima.

The adsorption of nitrogen has not been investigated very much ; especially, investigations concerning its adsorption on metallic catalysts are rather few.[1]~[7] As far as the adsorption on nickel is concerned, studies are fewer. The principal work recently done in this line is the work of Schmidt[2] on the small adsorbed amount at 76 cm. pressure and 25°~300°C. And Taylor[8] and Gauger[9] considered that the adsorbed amount may be regarded as zero above room temperature.

As for adsorbents other than nickel, studies at low temperatures are incomplete and most of them are on the adsorbed amount at liquid air temperature. As regards the rate of adsorption, there are no reports except the work of Emmett[4] concerning the adsorption on an iron catalyst for ammonia synthesis.

In order to examine the difference between the adsorptions of hydrogen[10] and nitrogen on reduced nickel, the author studied the rate and the amount of adsorption of nitrogen at low temperatures.

Experimental.

Materials.

Reduced Nickel : It was prepared by the same method as used in the previous experiments[11].

Nitrogen : It was prepared from ammonium sulphate and sodium nitrite by Moser's method[12] and dried over phosphorus pentoxide.

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1) Pease, *J. Am. Chem, Soc.*, 45, 2296 (1923).

2) Schmidt, *Z. phys. Chem.*, 133, 263 (1928).

3) Benton & White, *J. Am. Chem. Soc.*, 54, 1373 (1932).

4) Emmett, *ibid.*, 56, 35 (1934).

5) Howard & Taylor, *ibid.*, 56, 2259 (1934).

6) Roberts, *Nature*, 137, 659 (1936).

7) Wilkins, *Proc. Roy. Soc., London*, [A], 164, 496 (1938).

8) Taylor & Burns, *J. Am. Chem. Soc.*, 43, 1273 (1921).

9) Gauger & Taylor, *ibid.*, 45, 920 (1923).

10) Studies on the adsorption of hydrogen on reduced nickel by the present author have been reported in this Journal, 12, 1, 83, 148 (1938) and 13, 1 (1939).

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

12) Moser, "*Die Rein Darstellung von Gasen,*"

Apparatus and Procedure.

The apparatus and the procedure were the same as in a study of hydrogen adsorption.[11] In the temperature range of the present experiment all the results obtained were reproducible.

Experimental Results.

Pressure-Time Curve.

Fig. 1.

The fact that the curve at −112°C. is above that at −78°C. is ascribed to the experimental condition at −112°C. that the initial pressure was higher because of a little excess in nitrogen.

When nitrogen was introduced over reduced nickel after it had been desorbed, the pressure gradually fell in parallel with the adsorption. The change in pressure which was observed at suitable intervals after nitrogen had been introduced is shown in Fig. 1. The pressure 1 minute after the introduction was about 23.7 cm. The nickel used was prepared from 10.0273 g. of nickel oxide.

As seen in Fig. 1, equilibrium was attained within 1 minute at 0°C., and within several minutes even at other temperatures. This constitutes remarkable difference distinguishing the adsorption of nitrogen from that of hydrogen,[11] heavy hydrogen[13] or ethylene[14].

Adsorbed Amount-Time Curve.

From the pressure-time curve shown in Fig. 1, the relation between the adsorbed amount and time was obtained by the method previously described[11] and is shown in Fig. 2.

The Adsorption Isotherm.

As seen from Fig. 1 or Fig. 2, the adsorption of nitrogen reaches an equilibrium within several minutes, and since repetition is possible, the relation between the pressure and the adsorbed amount may be easily found. After the reduced nickel contained in a vessel has been desorbed, it is immersed in a bath kept at a given temperature; and after a known small quantity of nitrogen has been introduced, all that need be done
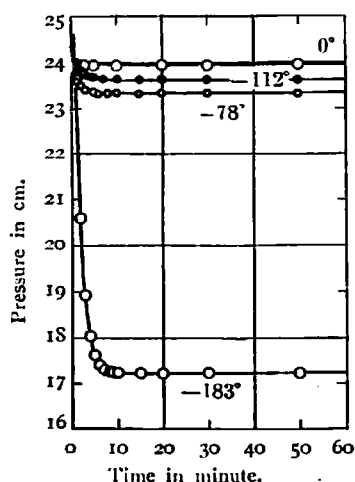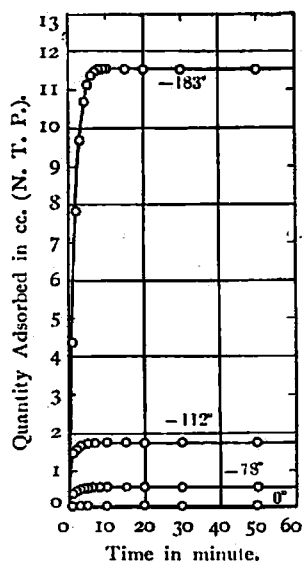

Time in minute.

Fig. 2.

13) Iijima, *Rev. Phys. Chem. Japan*, 12, 83 (1938).
14) A detailed report will be made shortly.

is to read the pressure of nitrogen every time equilibrium is reached. At 30 minutes' intervals, a known small quantity of nitrogen was successively introduced; and the equilibrium pressure being measured each time, the adsorption isotherm of Fig. 3 was obtained. From the amounts adsorbed at the same pressure it is seen that the amount is quite small at 0°C, but it increases as the temperature gets lower and becomes remarkably large at −183°C. Consequently, if adsorption isobars were to be drawn, neither maximum nor minimum should appear in them.
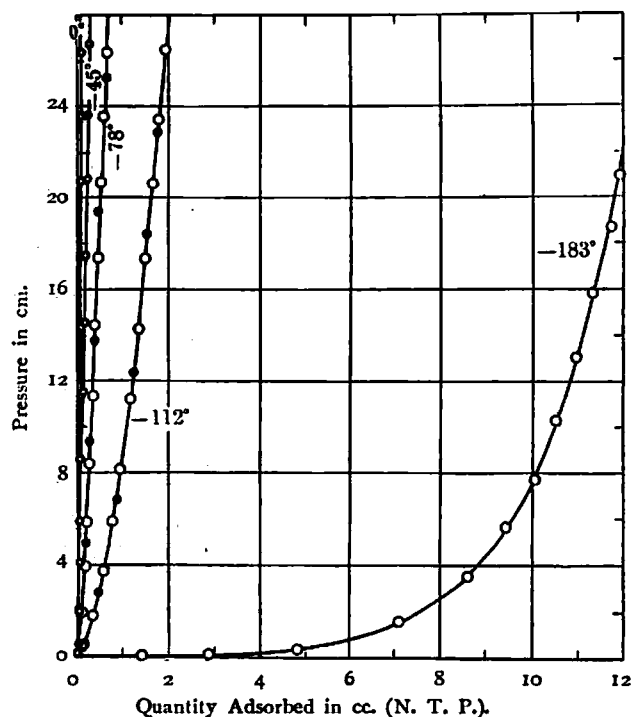

Fig. 3.

The Heat of Adsorption.

From the adsorption isotherm curves the heat of adsorption was calculated according to the Clausius-Clapeyron equation. The results obtained are given in Table I.

Table I.

Amount Adsorbed	Equilibrium Pressure		Heat of Adsorption
	−78°C.	−112°C.	
0.3 cc.	11.0 cm.	1.5 cm.	3660 cal.
0.4	16.0	2.2	3650
0.5	20.2	3.1	3450
0.6	24.4	4.1	3240
		Mean	3500 cal.

As far as the heat of adsorption of nitrogen is concerned, the value 2,000∽ 4,000 cal. was obtained by Benton[3] as the heat of adsorption on copper, and the value 35,000 cal. by Emmett[4] as the heat of adsorption on an iron catalyst for ammonia synthesis. The heat of adsorption obtained by the present author coincides with that on copper obtained by Benton.

Exchange of Baths.

Maintain desorbed reduced nickel at a temperature t_1 and introduce a desired quantity of some gas over it and seal. Then let a represent the adsorbed amount obtained thus after equilibrium has been established. Next immerse this system in another bath at a higher temperature t_2 for some time and again return to the bath at t_1. Let a' represent the adsorbed amount in this case after equilibrium has been established. If the gas used were hydrogen,[15] then

$$a < a'.$$

If, however, the gas used were nitrogen, then

$$a = a'.$$

In Fig. 4, (i) shows the change in pressure until equilibrium is first reached at −112°C., (ii) the change in pressure when it is transferred to a bath kept at 20°C., and (iii) the change in pressure when it is re-transferred to a bath kept at −112°C. The coincidence of (i) and (iii) approximately 10 minutes after the start serves to show that $a=a'$. Again, (iv) represents the change in pressure when it has been returned once more to a 20°C. bath. In short, in the system—reduced nickel and nitrogen, no matter how many times such exchange of baths may be repeated at any definite temperature the amount adsorbed is always fixed. This fact is one of the striking differences contrasting the adsorption of hydrogen and that of nitrogen.

Fig. 4.

Desorption at Low Temperatures.

The desorption at $t°$ of hydrogen adsorbed on reduced nickel at the same temperature is very difficult to make and generally only a very small portion of it may be desorbed.[15] On the contrary, nitrogen adsorbed on reduced nickel may be almost completely desorbed by exhaustion at the temperature of adsorption. The points o in the curves for the adsorption
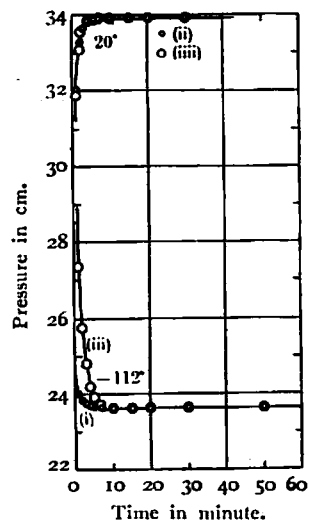
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15) A detailed report will be made shortly.

isotherm at $-78°$ and $-112°C.$ in Fig. 3 are the values observed with respect to reduced nickel to be regarded as completely desorbed by exhaustion at $280°C.$; and the points marked ● were obtained, after the observation of the points marked o, by exhaustion for 2 hours at the adsorption temperature $(-78°C.$ or $-112°C.)$ and repeating the above mentioned observations. The presence of the observed values, in the two instances, upon the same curve shows that nitrogen is completely desorbed from the nickel both at $-78°C.$ and at $-112°C.$

The Relation between the Adsorbed Amount and Pressure.

The relation between the adsorbed amount a and the equilibrium pressure p at $0°$, $-45°$, and $-78°C.$ may be represented by a straight line approximately passing through the origin (Fig. 3). Namely, taking a as the variation constant, the equation

$$a = ap \qquad\qquad (1)$$

holds. This is nothing but Henry's Law. The fact that the equation is valid in general in the case of a small adsorbed amount has already been discussed by Williams.[16][17] In the adsorption of nitrogen at the above-mentioned temperature the adsorbed amount is small and equation (1) holds well as has been discussed by Williams.

In the adsorptions at $-112°C.$ and $-183°C.$, Freundlich's equation holds fairly well. At $-112°C.$, the log a—log p diagram approximately assumes a straight line and at $-183°C.$ becomes a straight line having a break (Fig. 5).

Langmuir's equation for the adsorption isotherm is not applicable to this adsorption. For example, in constructing the p—p/a diagram for the adsorption at $-183°C.$, the relation assumes an arc of small curvature, as shown in Fig. 6, and not a straight line. But when some revision is made for the experimental results under
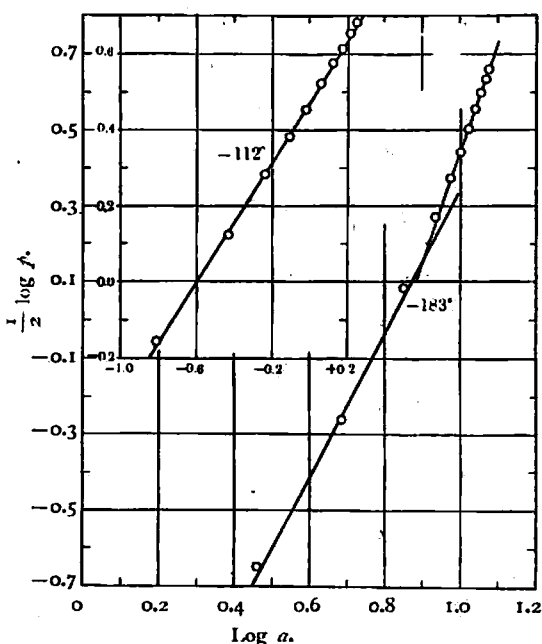

Fig. 5.

16) Williams, *Proc. Roy. Soc. Edin.*, 39, 48 (1919).

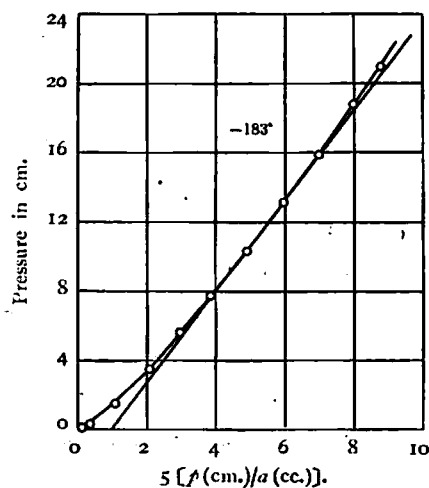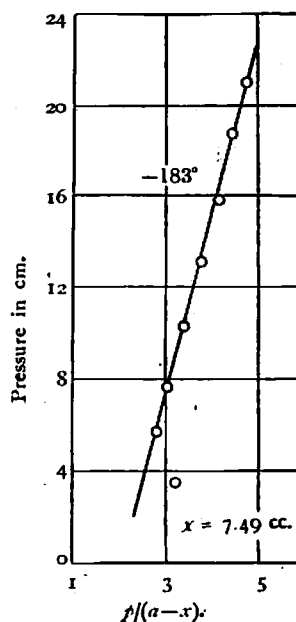17) Williams, *Proc. Roy. Soc. London*, [A], 96, 287 (1920).

Fig. 6.

Fig. 7.

certain consideration, the diagram having the same meaning becomes a straight line as shown in Fig. 7.[18]

Considerations.

The adsorption of nitrogen below 0°C. remarkably differs from that of hydrogen, namely,

(1)   Adsorption equilibrium is reached several minutes after the start.

(2)   The lower the temperature is, the greater is the adsorbed amount., i.e., in the adsorption isobar neither maximum nor minimum appears.

(3)   The adsorbed gas is almost completely desorbed by exhaustion at the temperature of adsorption (save near the boiling point of nitrogen— —183°C.).

(4)   Adsorption and desorption are reversible ; in other words, in the case of the nickel-nitrogen system at a given temperature the adsorbed amount is fixed.

(5)   Low temperature desorption is possible.

(6)   The heat of adsorption is small.

From these differences, it may be concluded that the adsorption of nitrogen on nickel below 0°C. is van der Waals' adsorption.

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18) This revision will be discussed in another report.

Summary.

(1) The adsorption of nitrogen on reduced nickel in the temperature range between 0° and −183°C. has been studied.

(2) The adsorption reaches an equilibrium in several minutes.

(3) From the adsorption isotherm obtained the heat of adsorption was found to be 3500 cal.

(4) The adsorption and the desorption accompanying temperature changes are reversible.

(5) Low temperature desorption is possible.

(6) In regard to the relation between the adsorbed amount and the equilibrium pressure, Henry's isothermal equation is applicable above −78°C. and Freundlich's equation is applicable to the temperature range between −112°C. and −183°C. The relation between $\log a$ and $\log p$ at −183°C. is indicated by a straight line having a break. Langmuir's isothermal equation is not so satisfactorily applicable.

(7) From these considerations it has been concluded that the adsorption of nitrogen on reduced nickel at temperatures below 0°C. is van der Waals' adsorption.