

THE ADSORPTION OF ETHYLENE ON REDUCED NICKEL.

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Many studies have been reported concerning the adsorption of ethylene,¹⁾⁻¹³⁾ but only a few of them were made at low temperatures, e. g. Steacie and Stovel's adsorption experiment on nickel⁷⁾, Turkevich's on copper,⁸⁾ Howard's on chromic oxide gel⁹⁾ and Hansford's on iron.¹¹⁾ Almost all these deal with the adsorbed amount at the temperature of solid carbon dioxide, and as for the adsorption velocity, there is no report except that of the apparent velocity at -80°C . measured by Steacie and his coworker⁷⁾.

Now that the hydrogenation of ethylene has frequently been made an object of studying the mechanism of a contact action, a detailed report on the adsorption of ethylene will be necessarily required. The present author investigated precisely the relationship between the velocity of adsorption of ethylene by reduced nickel and the temperature and also that between its adsorbed amount and the pressure, especially at low temperatures.

Experimental.

Materials.

Ethylene was prepared from ethyl alcohol and phosphoric acid by Moser's method¹²⁾. It was purified for use by repeated distillation after being passed through a series of the glass tubes cooled down to -78°C . Reduced nickel was prepared in the same way as before¹³⁾.

Apparatus and Method.

The apparatus used and the method applied were the same as those in the

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- 1) Taylor and Burns, *J. Am. Chem. Soc.*, **43**, 1273 (1921).
 - 2) Leese, *ibid.*, **45**, 2296 (1923).
 - 3) Griffin, *ibid.*, **49**, 2136 (1927).
 - 4) Foresti, *Gazz. Chem. Ital.*, **59**, 243 (1929).
 - 5) McBain and Britton, *J. Am. Chem. Soc.*, **52**, 2198 (1930).
 - 6) Schuster, *Z. Physik. Chem. B*, **14**, 249 (1931).
 - 7) Steacie and Stovel, *J. Chem. Phys.*, **2**, 581 (1934).
 - 8) Turkevich and Taylor, *J. Am. Chem. Soc.*, **56**, 2254, (1934).
 - 9) Howard and Taylor, *ibid.*, **56**, 2259 (1934).
 - 10) Maxted and Moon, *Trans. Farad. Soc.*, **32**, 1375 (1936).
 - 11) Hansford and Emmett, *J. Am. Chem. Soc.*, **60**, 1185 (1938).
 - 12) Moser, *Die Reindarstellung von Gasen*.
 - 13) Iijima, *This Journal*, **12**, 1 (1938).

case of the hydrogen adsorption on reduced nickel¹³). Such is also the case with the baths used at -95° , -78° , -45° and -23°C . Besides these, the following baths or furnaces were used:

At -63°C ., a mixture of liquid and solid chloroform which was prepared by dropping liquid air little by little into chloroform.

At 0°C ., a mixture of water and ice.

At 20° and 50°C ., a water thermostat, whose temperature was kept constant within $\pm 0.2^{\circ}\text{C}$.

At 100° , 150° and 200°C ., an electric furnace, whose temperature was kept constant within $\pm 1^{\circ}\text{C}$.

Both the adsorbed amount and the adsorption velocity were reproducible at low temperatures, but above 50°C ., they became slightly smaller every time the measurement was repeated.

Experimental Results.

The Relation between the Pressure and Time.

When ethylene is introduced over the reduced nickel which has been desorbed, it is adsorbed and the pressure gradually falls. The change in pressure

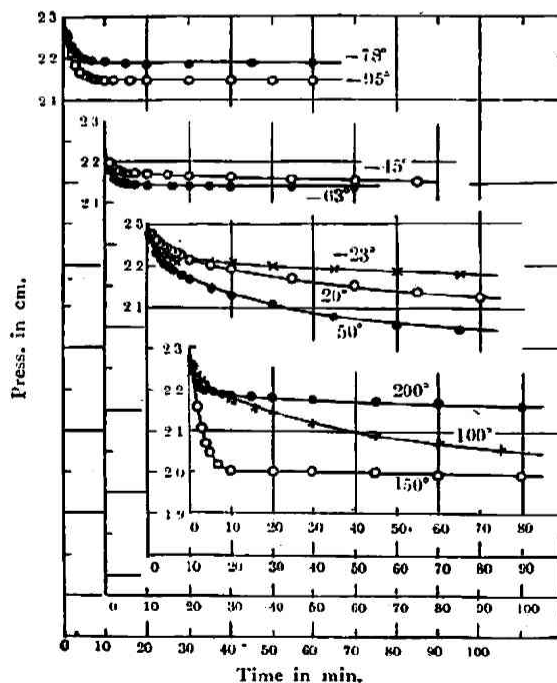


Fig. 1

which was measured at suitable intervals after the gas had been introduced is shown in Fig. 1. The pressure 1 minute after the introduction was 22.5 cm. at

every measurement. The nickel used was prepared from 11.0352 g. of nickel oxide.

As seen in Fig. 1, the duration of adsorption is short at very low and very high temperatures, e. g. equilibrium is established within 10 minutes at both -95°C. and 150°C. * In the temperature range, $-45^{\circ}\sim 150^{\circ}\text{C.}$, the duration is comparatively long, e. g. at 0°C. equilibrium is established in several days. Fig. 2

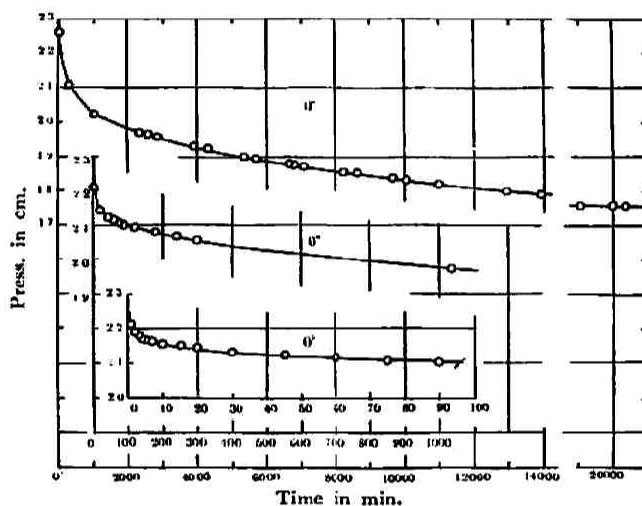


Fig. 2

shows the relation between the pressure of the adsorption at 0°C. and time.

The fact that adsorptions taking place below -45°C. reach equilibrium in a short time suggests that most of those adsorptions are the van der Waals' adsorption. As to the adsorptions above -45°C. , the higher the temperature is, the velocity of the adsorption which lasts long becomes larger. This fact indicates that the activated adsorption gradually becomes faster with the rise of temperature. That the adsorption at 150° and 200°C. reaches equilibrium only in several minutes suggests that only the activated adsorption, which reaches equilibrium in several minutes, takes place at such temperatures.

The Relation between the Adsorbed Amount and Time.

The relation between the pressure and time shown in Figs. 1 and 2 leads to that between the adsorbed amount and time,¹³⁾ which is shown in Fig. 3. This figure shows that at 100°C. both van der Waals' adsorption and the activated

* At 200°C. equilibrium is established in several minutes, and then extremely slow fall of pressure lasts long.

adsorption are small in amount. Consequently it is supposed that the minimum

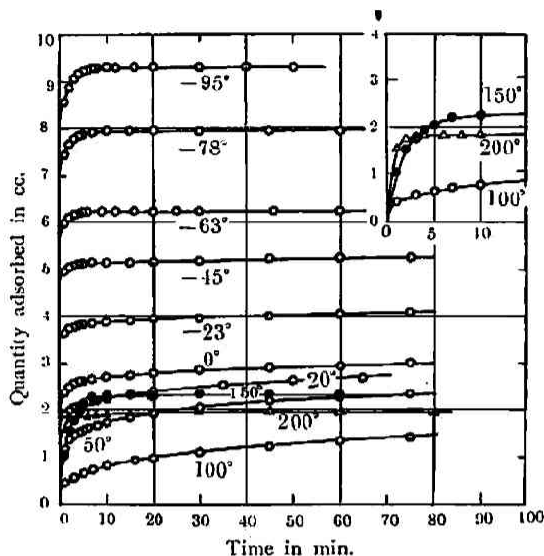


Fig. 3

point on the adsorption isobar lies in the neighbourhood of 100°C. And the figure also shows that the maximum point lies in the neighbourhood of 150°C.

The Adsorption Velocity.

The $\log \frac{p}{p-p_e} - t$ curve¹³⁾ drawn with respect to the adsorption at 0°C. is linear except at the earlier and later stages as shown in Fig. 4 (III). In this case p is the pressure at a time t which has elapsed from the beginning; p_e is the equilibrium

pressure obtained experimentally. Deviation from the linear part at the later stage of adsorption has already been discussed¹³⁾. On the other hand, if we put $p_e = 21.12$ cm.,* then deviated part at the earlier stage of adsorption will also become linear as shown in Fig. 4 (II). As for the initial part of adsorption, such

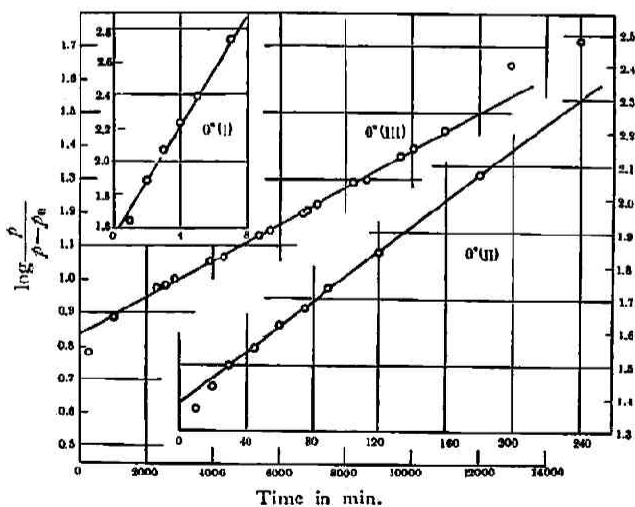


Fig. 4

a straight line as shown in Fig. 4 (I) is obtained when we put $p_e = 22.10$ cm. These linear relations prove that there holds the following relation at each part:

* As for the calculation of p_e see the preceding report¹³⁾.

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

As already pointed out,¹³⁾ the fact that the whole process consists of three linear parts suggests that practically three adsorptions of markedly different velocities proceed stepwise. Here, K and C in equation (1) are the constants to be expressed as follows:

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

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

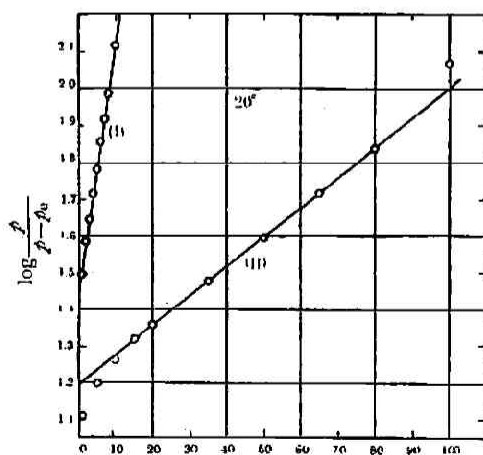
where k_1 is the velocity constant of adsorption, p_0 the pressure when $t=0$, k' and k'' known constants with respect to the size of the vessel and temperature.

Calculating the velocity constant k_1 of each adsorption from equations (2) and (3), Table I was obtained. K and C used in this calculation are what were obtained from the $\log \frac{p}{p-p_e} - t$ diagram.

Table I

Adsorption	Velocity const. of adsorption (k_1) $\times 10^6$
0°C (I)	0.690
" (II)	0.0175
" (III)	0.00055

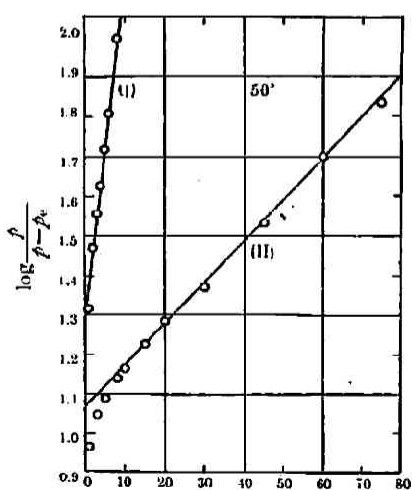
Equation (1) is applicable not only to the adsorption at 0°C., but to all the adsorption at certain temperatures which are considered, from the adsorption velocity curve, essentially composed of activated adsorption. Figs. 5, 6, and (i) and



(I), $p_e = 22.03$ cm.; (II), $p_e = 20.98$ cm.

Time in min.

Fig. 5



(I), $p_e = 21.55$ cm.; (II), $p_e = 20.19$ cm.

Time in min.

Fig. 6

(ii) in Fig. 7 show that equation (1) is applicable to the adsorptions at the temperatures of 20°, 50°, 100° and 150°C., i. e. the $\log \frac{p}{p-p_e} - t$ curve is linear.

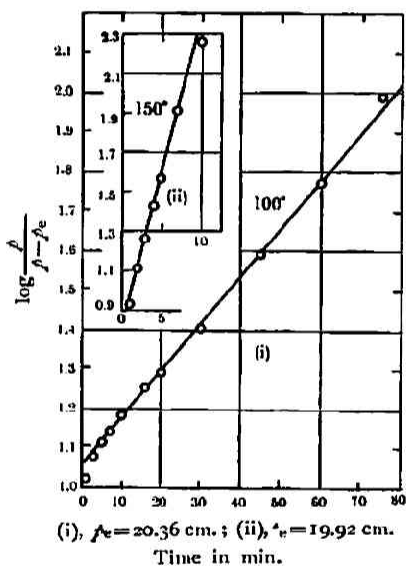


Fig. 7

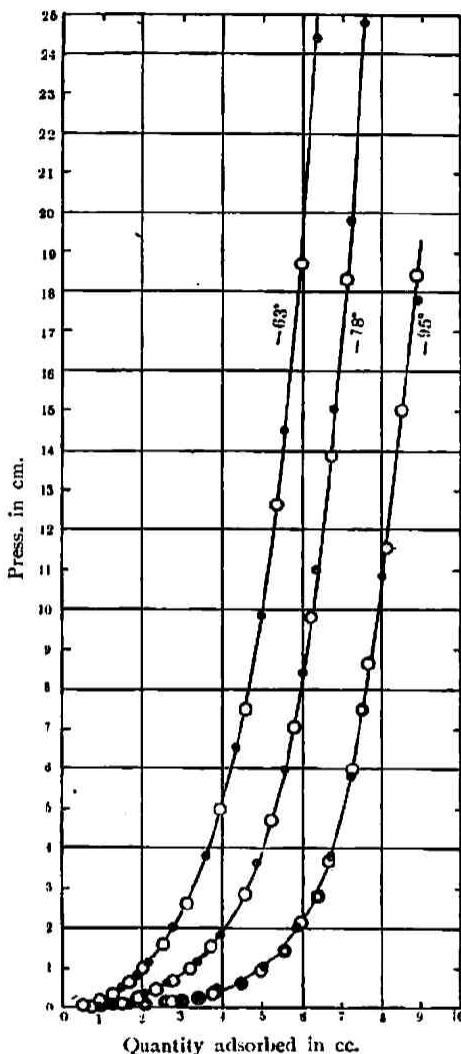


Fig. 8

Adsorption Isotherm.

As seen in Fig. 1, which shows the relation between the pressure and time, the adsorption equilibrium is established for a short time at such low temperatures as -63° , -78° and -95°C . And both the adsorption and desorption at low temperatures are, as already mentioned, reproducible. Accordingly, the relation between the pressure and the adsorbed amount at low temperatures can be easily obtained as follows: first desorb reduced nickel, put it in a thermostat to keep it at a desired temperature, introduce a known small quantity of ethylene over it, and then read the pressure every time the adsorption equilibrium is reached. Fig. 8 is the adsorption isotherm obtained by reading the equilibrium pressure

after a supply of a known small quantity of ethylene every 30 minutes.

Heat of Adsorption.

There are considerable differences of the value for the heat of adsorption among investigators and, moreover, remarkable disparity between the maximum and the minimum values even by the same investigator. For example, Schwab¹⁴⁾ and zur Strassen¹⁵⁾ obtained 17.3 Cal. and 9 Cal. from their study of the hydrogenation of ethylene; Maxted¹⁶⁾ obtained 9 Cal. as the observed heat of adsorption on platinum; Klar¹⁶⁾ obtained 6~15 Cal. from the study of the adsorption of ethylene on nickel; Schuster^{9) 17)} obtained 7.5 Cal. by his calculation and 7.5~16.5 Cal. by direct measurement from the study of adsorption on charcoal. Further, Hansford¹⁰⁾ has lately obtained 4.5 Cal. from the study of adsorption on iron.

From such a disparity of the value it is inferred that the adsorption of ethylene consists of two different kinds of adsorption—van der Waals' adsorption and an activated adsorption. The above mentioned heats of adsorption are either the heats of adsorption at different temperatures or those calculated from the results obtained at different temperatures. Hence, they give the heat of adsorption in the cases when the ratios of the amounts of two kinds of adsorption are different from each other. Accordingly, such a disparity must be necessarily brought forth. If it be calculated from the isotherms of the adsorption at such low temperatures as only van der Waals' adsorption takes place, a constant value which is the minimum value or one approximate to it would be obtained. To prove this assumption, the heat of adsorption was calculated from the adsorption isotherms at -63° , -78° , and -95°C . according to Clausius-Crapeyron's formula. The result obtained is given in Table II.

Table II

Adsorbed amount (cc.)	Temperatures			Mean (Cal.)
	-63° , -78°	-78° , -95°	-95° , -63°	
2.5	5.94 Cal.	6.39 Cal.	6.19 Cal.	6.17
4.0	5.40	5.65	5.55	5.53
6.0	4.60	5.59	5.17	5.12
Mean	5.32	5.88	5.64	5.6

It is seen in the table, as may be expected, that disparity in the values is relatively small and that the mean value is 5.6 Cal. This fact indicates that almost

14) Schwab, *Z. physik. Chem.*, **A**, 171, 421 (1934).

15) zur Strassen, *ibid.*, 169, 81 (1934).

16) Klar, *ibid.*, 168, 215 (1934).

17) Schuster, *Trans. Farad. Soc.*, **28**, 406 (1932).

all the adsorptions below $-63^{\circ}\text{C}.$ are van der Waals' adsorption.

Considerations.

The Relation to Freundlich's Adsorption Isotherm.

Between the logarithm of the adsorbed amount α and that of the equilibrium

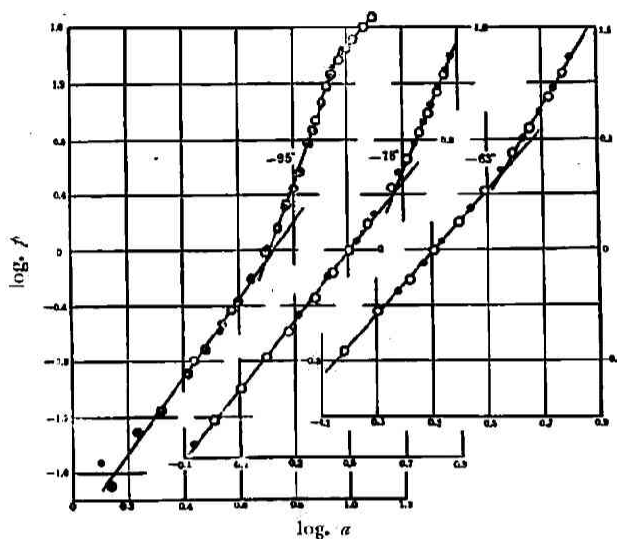


Fig. 9

pressure p corresponding to the adsorbed amount there holds a linear relation, as shown in Fig. 9 which was drawn from the observed values used for Fig. 8.

Such a linear relation as this indicates the establishment of the following relation in the case when a and n are constants:

$$\alpha = a p^{\frac{1}{n}}, \quad (1)$$

namely, Freundlich's adsorption isotherm is applicable to the adsorption in question.

Each of these straight lines has a break. A break similar to this was observed in the case of the adsorption of hydrogen on reduced nickel at low temperatures¹⁹⁾. Such is also the case with the adsorptions of water vapour¹⁰⁾ and ammonia²⁰⁾ on titania gel as reported by Higuti. In his case, however, not only is the adsorbed amount remarkably large*, but also it increases markedly in the neighbourhood of the pressure corresponding to the breaking point. According to him, the break occurs at the point where the capillary condensation begins to take place. In the experimental results of Langmuir²¹⁾ there were also similar breaks found as shown

18) Iijima, *This Journal*, 7, 24 (1933); *Sci. Pap. I.P.C.R.*, 23, 34 (1933).

19) Higuti, *Bull. Inst. Phys. Chem. Research*, 16, 536 (1937).

20) Higuti, *ibid.*, 16, 42 (1937).

21) Langmuir, *J. Am. Chem. Soc.*, 40, 1361 (1918).

* For example, to 0.827 g. of titania gel 326.58 cc. (N.T.P.) of ammonia is sorbed at $-40^{\circ}\text{C}.$ under a pressure of 53.91 cm.

in (i) and (ii) in Fig. 10*. But whether Langmuir was conscious of the existence of such breaks in his own results or not is unknown, for he only pointed out that Freundlich's formula is not applicable to any observation covering a wide range of pressure.

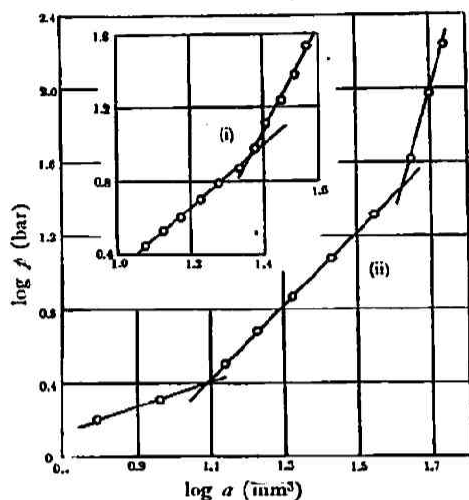


Fig. 10

What is meant by such a break as in the adsorption system of nickel and ethylene? The present author will not touch upon this question in this paper. It is asserted, however, that the said break never indicates the start of the capillary condensation. For the present case differs from Higuti's case in the direction of the break: in Higuti's case the line breaks toward the $\log a$ axis. In the present case, however, it does toward the $\log p$ axis:

the increase of the adsorbed amount with the rise of pressure becomes less after the break, and, besides, a break in the same direction as in Higuti's case is found at the pressure higher than that of the breaking point (Fig. 9, $-95^{\circ}\text{C}.$).

The Relation to Langmuir's Adsorption Isotherm.

To understand the relation of the present results to Langmuir's adsorption isotherm:

$$a = \frac{dfp}{1 + dp}, \quad (5)$$

$$\text{or} \quad \frac{p}{a} = \frac{1}{df} + \frac{p}{f}, \quad (6)$$

where d and f are constants, the $p-p/a$ diagram was drawn. The diagram shows, as a whole, a straight line, but, if fully examined, it has a tendency to form a small curvature. Fig. 11 shows this relation at $78^{\circ}\text{C}.$ ** The disparity between equation (6) and the result obtained may be expected, if the significance of the Langmuir's formula and the surface construction

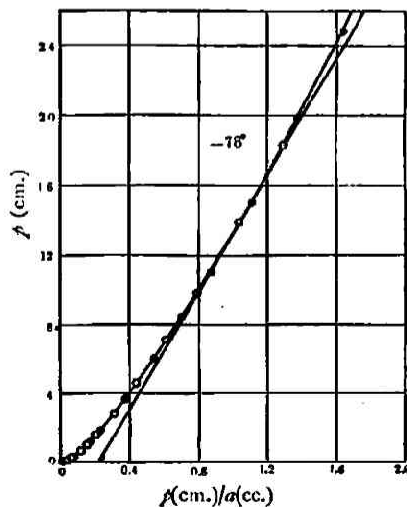


Fig. 11

* (i) and (ii) are the adsorptions of nitrogen and carbon dioxide on mica respectively.

** In Langmuir's results there are the adsorptions having similar curvature, such as those of methane and carbon dioxide on mica (*J. Am. Chem. Soc.*, 40, 1361 (1918)).

of nickel are taken into consideration.

The Relation to Williams' Adsorption Formula.

With respect to the adsorption equilibrium at low pressures, Williams has theoretically deduced²²⁾ that the following relation holds between the adsorbed amount a and equilibrium pressure p :

$$\ln \frac{a}{p} = A \frac{B}{T}, \quad (7)$$

where A and B are constants and T is the absolute temperature. By applying this equation to the experimental results, Fig. 12 was obtained, which shows the relation between $\log p$ and $1/T$ in the case when a is constant. And the numerical values used to draw the figure, which are tabulated in Table III were calculated from the adsorption isotherm in Fig. 8. As seen in Fig. 12, at low pressures equation (7) coincides well with the results, all being straight lines of equal inclination, while at higher pressures the deviation from each other becomes noticeable.

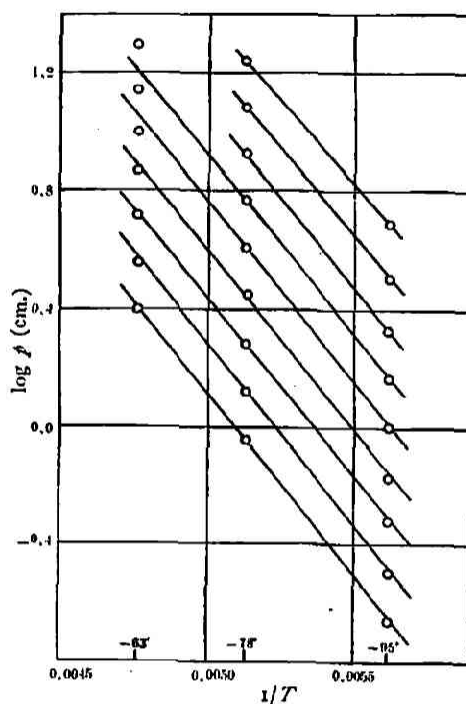


Fig. 12

Table III

Adsorbed amount (cc.)	-63°C.		-78°C.		-95°C.	
	p	$\log p$	p	$\log p$	p	$\log p$
3.0	2.50	0.398	0.90	1.954	0.22	1.342
3.5	3.60	0.556	1.32	0.121	0.32	1.505
4.0	5.22	0.718	1.91	0.281	0.48	1.681
4.5	7.40	0.869	2.79	0.446	0.67	1.826
5.0	10.01	1.000	4.05	0.607	1.00	0.000
5.5	13.90	1.143	5.82	0.765	1.46	0.164
6.0	19.80	1.297	8.45	0.927	2.12	0.326
6.5			12.10	1.083	3.20	0.505
7.0			17.40	1.241	4.88	0.688

22) Williams, *Proc. Roy. Soc., A*, 96, 287, 298 (1920).

Summary.

1) In the temperature range, $-95^{\circ}\sim+200^{\circ}\text{C.}$, the adsorbed amount and velocity of adsorption of ethylene on reduced nickel has been observed.

2) Below -63°C. and above 150°C. , adsorption equilibrium is established in several minutes, but at the intermediate temperatures, in a moderately long time.

3) To the adsorption velocity at the stage when the activated adsorption is presumably proceeding, the velocity formula already proposed by the author is applicable.

4) The adsorption isotherm of the adsorption at low temperatures has been drawn.

5) The heat of adsorption calculated from the adsorption isotherm is 5.6 Cal. This heat of adsorption is to be regarded as that of van der Waals' adsorption, and the value is far smaller than those already reported by many investigators.

6) Freundlich's adsorption isotherm can be satisfactorily applied to the observed values, but the $\log a-\log p$ diagram has a break.

7) Langmuir's adsorption isotherm is not applicable.

8) Williams' adsorption formula is applicable only to the case at low pressures.

The author wishes to express his appreciation to Prof. S. Horiba for his continued guidance throughout this research.

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(Received March 25, 1940)