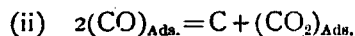
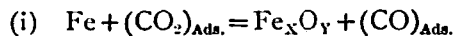


ON THE CHEMISORPTION OF CARBON DIOXIDE BY REDUCED IRON. (II)*

The Influence of the Chemisorption on van der Waals'
Adsorption of Carbon Dioxide at 0°C.

By KIMIO KAWAKITA.

In a study of the catalytic decomposition of carbon monoxide, the author found an interesting phenomenon at 300°–400°C. that, carbon dioxide (the reaction product) being adsorbed on reduced iron, the final pressure of the reacting system became nearly zero. In his preceding report¹⁾ the author proposed such heterogeneous chain reactions as



to be brought forth by the action of some carbon dioxide molecules on the iron atoms, and he demonstrated the reactions with some evidences. In this case, it was ascertained that reaction (i) was brought forth by the iron atoms at highly active centres, and reaction (ii) even at less active centres. The relation between activated adsorption of gases at high temperatures and their van der Waals' adsorption at low temperatures has lately been investigated by J. Howard²⁾ with the chromium oxide—hydrogen system and by R. M. Barrer and E. K. Rideal³⁾ with the charcoal—hydrogen system. In the present research, the relation between the chemisorption at high temperatures and van der Waals' adsorption at 0°C. and the influence of the chemisorption on the catalytic surface were examined, and it is the author's intention to report the experimental results and a new phenomenon which those investigators have not observed.

Experimental.

The measurement of the adsorbed amount was made by means of the pressure change statically. The main part of the apparatus used is shown in Fig. 1. Two spring manometers

* This paper is the English translation of the same article published in *Rev. Phys. Chem. Japan*, 10, 200–211 (1936).

1) K. Kawakita, *Rev. Phys. Chem. Japan*, 8, 89–116 (1934).

K. Kawakita, *Rev. Phys. Chem. Japan*, 11, 75–89 (1937).

K. Kawakita, *Proc. Imp. Acad. Tokyo*, 12, 61–63 (1936).

2) J. Howard, *Trans. Farad. Soc.*, 30, 278–287 (1934).

3) R. M. Barrer and E. K. Rideal, *Proc. Roy. Soc. [A]*, 149, 246–247 (1935).

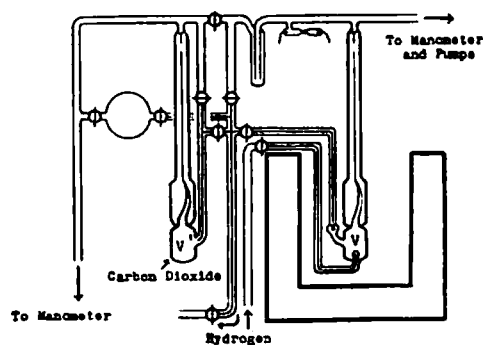


Fig. 1. Sorption Apparatus.

sorption of the gas, an electric furnace was used. The temperature of van der Waals' adsorption was kept at $0^{\circ}\text{C}.$ with ice water. The methods of preparing reduced iron and carbon dioxide are the same as described in the preceding paper.

Results.

Van der Waals' adsorption isotherms of carbon dioxide obtained at $0^{\circ}\text{C}.$ are absolutely reproducible, and the equilibrium pressure is reached within one minute. The experimental results obtained by examining the relation between the chemisorption of carbon dioxide at $300^{\circ}\text{--}400^{\circ}\text{C}.$ and its van der Waals' adsorption at $0^{\circ}\text{C}.$ are classified into three groups—[A], [B] and [C], whose most typical examples are shown in Fig. 2. In the figure, [A] is the adsorption isotherm at $0^{\circ}\text{C}.$ on the fresh surface of the catalyst; [B] that on the surface which beforehand chemisorbed a considerable amount of carbon dioxide at $300^{\circ}\text{--}400^{\circ}\text{C}.$ and was pumped off at the same temperatures; and [C] that on the surface which beforehand chemisorbed a small amount of carbon dioxide at $360^{\circ}\text{C}.$ and was not pumped off. In Fig. 2, it should be noted that the amount of van der Waals' adsorption of [B] is far greater than that of [A]. Such a phenomenon as increase in van der Waals' adsorption due to this chemical treatment of the catalyst at high temperatures has never been observed.

V and V' were used. The lower part of one of the manometers V was the reaction vessel to hold the catalyst and that of the other V' the vessel to hold the gas, and the capacities of V (excluding the catalyst) and V' had been previously measured. The gas was introduced from the latter to the former. The adsorbed amount was given by deducting the amount of gas left in the reaction vessel from the gas introduced. At high temperature experiments, the reduction and degassing of the catalyst, and the chemi-

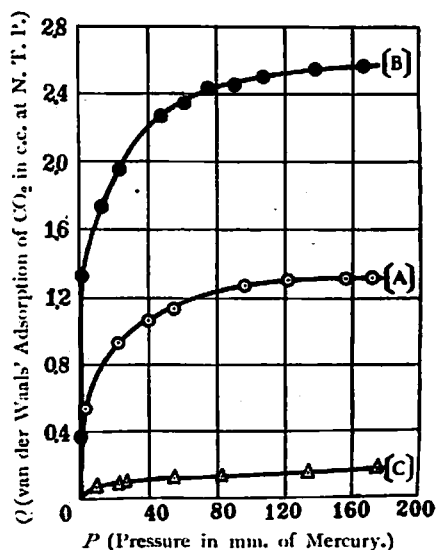


Fig. 2. Influence of the Chemisorption on the Isotherm for van der Waals' Adsorption of Carbon Dioxide at $0^{\circ}\text{C}.$

§ 1. [A]. The isotherms at 0°C . on the *fresh surface* were obtained with two catalysts. The conditions of preparing these catalysts are given in Table 1.

Table 1.
Conditions of the Preparation of the Catalyst.

Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacuation after Reduction
Catalyst 1.			
6.4088 g.	440°C .	24 hrs.	24 hrs. at 440°C .
Catalyst 2.			
3.2868 g.	440°C .	24 hrs.	24 hrs. at 360°C .

The results with Catalysts 1 and 2 are shown in Fig. 3 (Expt. 1) and Fig. 4 (Expts. 1 and 1') respectively.

§ 2. [B]. Employing Catalyst 1, van der Waals' adsorption at 0°C . was observed after carbon dioxide had been chemisorbed at 360° – 440°C . and the reaction vessel evacuated *at various temperatures*. The experiments were carried out 16 times, the experimental conditions being given in Table 2. The results obtained are shown in Fig. 3.

Table 2.
Experimental Conditions.

Expt. No.	Chemisorption of Carbon Dioxide c.c. at N. T. P.	Temperature of Chemisorption ($^{\circ}\text{C}$.)	Temperature of Evacuation ($^{\circ}\text{C}$.)	Time of Evacuation (hrs.)
1	0			
2	0.103	360	200	24
3	0.426	360	360	24
4	0.609	360	100	24
5	1.166	360	360	5
6	1.877	360	360	10
7	5.687	360	100	24
8	74.609	420	0	24
9	74.609	420	360	24
10	82.324	430	0	24
11	82.324	430	360	8
12	82.324	430	360	77
13	82.324	430	450	24
14	82.324	430	460	24
15	421.345	440	0	24
16	421.345	440	460	24

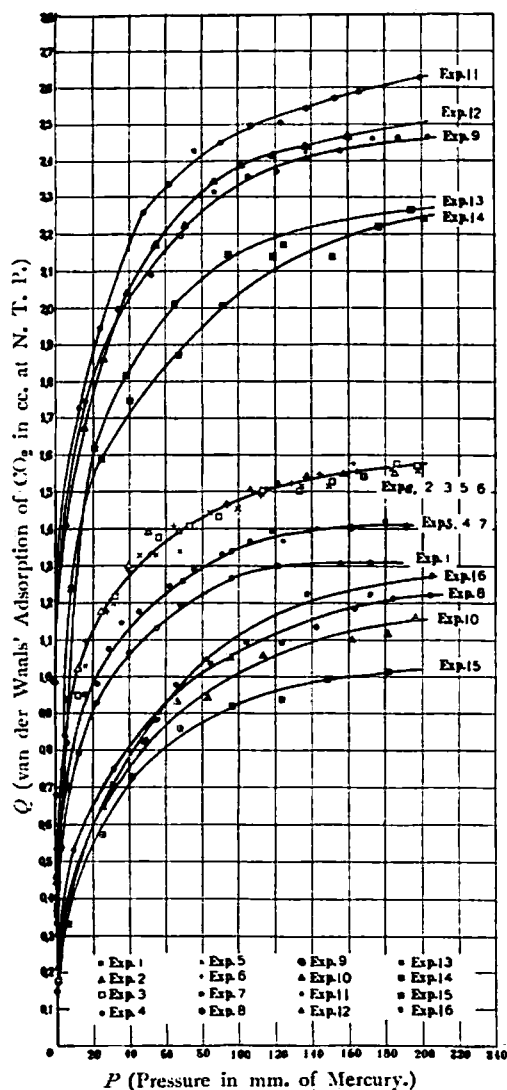


Fig. 3. Isotherms for the Adsorption of Carbon Dioxide by Reduced Iron at 0°C. The Relation between the Chemisorption and van der Waals' Adsorption.

In Fig. 3 the increase in the amount of van der Waals' adsorption at 0°C. due to the chemisorption at higher temperatures should be noted except Expts. 8, 10, 15 and 16. The adsorption isotherms of Expts. 2, 3, 5 and 6 (temperature of chemisorption, 360°C.) rise a little higher than that of Expt. 1, and it is to be noted that the amounts of van der Waals' adsorption are nearly the same. This shows that van der Waals' adsorption is not so much influenced by a little increase in the amount of chemisorption, if the same catalyst is employed and the pretreatment is the same in every experiment. The isotherm of Expt. 4 is almost the same as that of Expt. 7. The temperature of evacuation in this case is 100°C., so that the isotherm slightly declines as compared with that of Expt. 2 and others. The temperatures of chemisorption of Expts. 9 and 11 are 420° and 430°C. respectively and in this case the isotherm of Expt. 11 rises higher than that of Expt. 9. The time of evacuation of Expt. 12 is longer than that of Expt. 11 and in this case the isotherm of Expt. 12 declines as compared with that of

Expt. 11. The temperatures of evacuation of Expts. 11, 13 and 14 are 360°, 450° and 460°C. respectively. With rising temperature activity gradually falls and the isotherms decline in the order of Expts. 11, 13 and 14. In Expt. 16, carbon dioxide was chemisorbed nearly to saturation so that a number of the activated iron atoms are considered to be lost. In this case the isotherm rather declines as compared with that of Expt. 1. The isotherms of Expts. 8, 10 and

15, whose temperature of evacuation is $0^{\circ}\text{C}.$, decline as compared with that of Expt. 1. This result of the experiments (temperature of evacuation, $0^{\circ}\text{C}.$) is similar to the result gained by J. Howard on the chromium oxide—hydrogen system and that by R. M. Barrer and E. K. Rideal on the charcoal—hydrogen system.

In short, as shown in Fig. 4, when evacuation was done at $360^{\circ}\text{--}440^{\circ}\text{C}.$ after the chemisorption, the amount of van der Waals' adsorption in the case of (ii) is markedly greater than that in the case of the fresh surface (i). When evacuation was done at $0^{\circ}\text{C}.$ after the chemisorption, van der Waals' adsorption in the case of (iii) is less than that in the case of the fresh surface (i).

§ 3. [C]. Employing Catalyst 2 van der Waals' adsorption at $0^{\circ}\text{C}.$ was observed, after carbon dioxide had been chemisorbed at $360^{\circ}\text{C}.$ and the reaction vessel *not evacuated*. The experiments were carried out 4 times. The results are shown in Fig. 5. Expt. 1 in Fig. 5 is the isotherm at $0^{\circ}\text{C}.$ on the fresh surface of the catalyst; Expt. 1' is the isotherm at $0^{\circ}\text{C}.$ in 24 hours' evacuation at $0^{\circ}\text{C}.$ after Expt. 1, and it shows that the isotherms are reproducible. The reaction vessel being fully evacuated after Expt. 1', carbon dioxide was chemisorbed at $360^{\circ}\text{C}.$ and when the final pressure approached zero, van der Waals' adsorption was measured at $0^{\circ}\text{C}.$ without evacuation. The result is shown in Expt. 2. Expt. 3 was carried out in the same way after Expt. 2. The chemisorbed amounts of Expts. 2

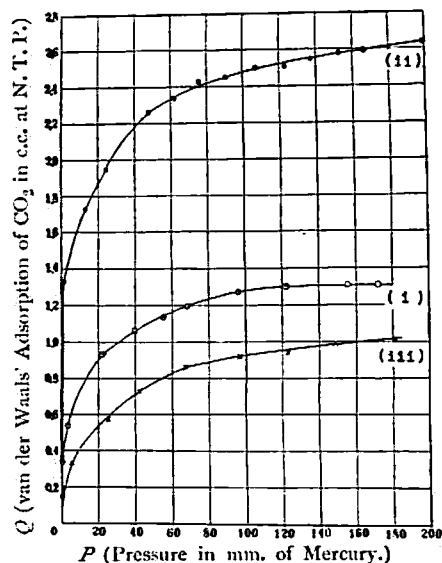


Fig. 4. Isotherms for the Adsorption of Carbon Dioxide by Reduced Iron at $0^{\circ}\text{C}.$ The Relation between the Chemisorption and van der Waals' Adsorption.

- (i) Isotherm at $0^{\circ}\text{C}.$ on the fresh surface of the catalyst.
- (ii) Isotherm at $0^{\circ}\text{C}.$ on the surface which beforehand chemisorbed a considerable amount of CO_2 at $300^{\circ}\text{--}500^{\circ}\text{C}.$ and was pumped off at $100\text{--}500^{\circ}\text{C}.$
- (iii) Isotherm at $0^{\circ}\text{C}.$ on the surface which beforehand chemisorbed a considerable amount of CO_2 at $300^{\circ}\text{--}500^{\circ}\text{C}.$ and was pumped off at $0^{\circ}\text{C}.$

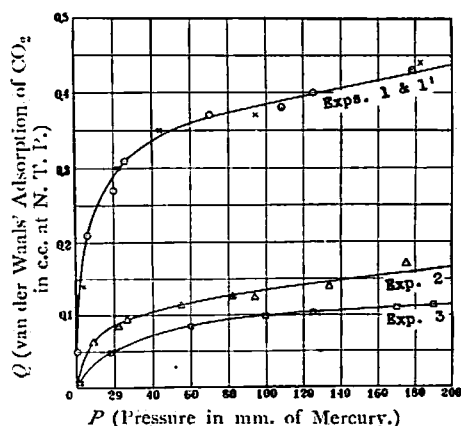


Fig. 5. Isotherms for the Adsorption of Carbon Dioxide by Reduced Iron at $0^{\circ}\text{C}.$ The Relation between the Chemisorption and van der Waals' Adsorption.

and 3 were 0.290 c.c. and 0.494 c.c. respectively. In Fig. 5 it should be noted that considerable decrease in the amount of van der Waals' adsorption is noticed when a small quantity of carbon dioxide is chemisorbed and the reaction vessel is not evacuated.

Consideration of the Experimental Results.

The fraction of the surface covered with gaseous molecules and the total number of the elementary spaces of the surface will be calculated from the results shown in Figs. 3 and 5, and then considerations on these will be made.

Calculation of the Fraction of the Surface covered with Gaseous Molecules and the Total Number of the Elementary Spaces.

Let θ_1 represent the fraction of the surface covered with the adsorbed molecules, then

$$\theta_1 = \frac{N}{N_0} \eta, \dots\dots\dots(1)$$

where N is Avogadro's constant, and N_0 the number of the elementary spaces and η that of gram molecules of the gas adsorbed per cm^2 of the surface. Equation 1 can be rewritten as

$$Q = \eta S = a \theta_1 = a \frac{N}{N_0} \eta, \dots\dots\dots(2)$$

where Q is the adsorption amount, S the whole area of the surface and a a proportional factor.

Applying Langmuir's isotherm to the value θ_1 , we have the linear relation between p/Q and p , from which we can calculate the value a , and then θ_1 and $N_0 S$ can be easily evaluated from equation (2) as will be explained below.

Calculation of the Proportional Factor a .

Let us see whether the isotherm experimentally obtained at 0°C . satisfies the equation of Langmuir's adsorption isotherm:

$$Q = a \theta_1 = \frac{abp}{1 + bp}, \dots\dots\dots(3)$$

or

$$p/Q = \frac{1}{ab} + \frac{1}{a} p, \dots\dots\dots(4)$$

Applying equation (4) to the results of Figs. 3 and 5, it was found that the relation between p and p/Q is linear as shown in Figs. 6 and 7.

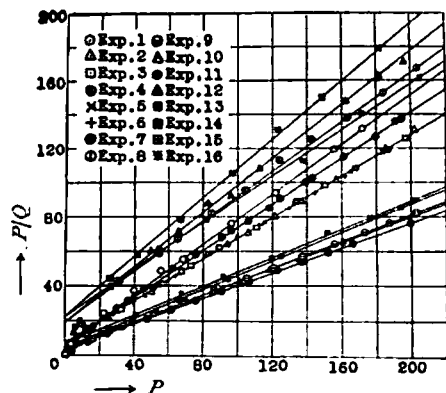


Fig. 6. Data for the Adsorption of Carbon Dioxide by Reduced Iron at 0°C. graphed according to the Langmuir equation.

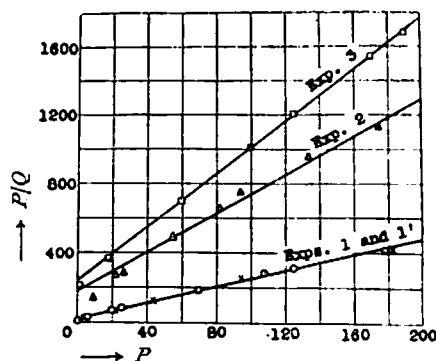


Fig. 7. Data for the Adsorption of Carbon Dioxide by Reduced Iron at 0°C. graphed according to the Langmuir equation.

From these inclinations the values $1/a$ are given and hence the values a are obtained. The values a of Expts. 1-16 in Fig. 6 are given in Table 3 and those of Expts. 1, 1', 2 and 3 in Fig. 7 are tabulated in Table 4. Q in Figs. 6 and 7 is expressed by cubic centimeter and so is a in Tables 3 and 4. Therefore a in equation (2) corresponds to $a/22412$.

Table 3.

Expt. No.	a	Expt. No.	a
1	1.364	9	2.583
2	1.655	10	1.269
3	1.655	11	2.738
4	1.480	12	2.635
5	1.655	13	2.421
6	1.655	14	2.423
7	1.480	15	1.170
8	1.381	16	1.474

Table 4.

Expt. No.	a
1 & 1'	0.440
2	0.179
3	0.130

Calculation of θ_1 and N_0S for van der Waals' adsorption at 0°C.

Using the value a obtained, θ_1 can be calculated from the following equation:

$$\theta_1 = Q/a \quad \dots\dots\dots(5)$$

And N_0S is obtained from equation (2) as follows:

$$N_0S = aN, \dots\dots\dots(6)$$

or

$$N_0S = \frac{6.06 \times 10^{21}}{22412} \times a = 27.0276 \times 10^{18} \times a. \dots\dots\dots(7)$$

θ_1 and N_0S calculated from Table 3 are given in Table 5 and those from Table 4 are in Table 6.

Table 5.
Fraction covered with Adsorbed Molecules, θ_1 , and Total Number of Elementary Spaces, N_0S .

Expt. No.	Q (c.c.) (at 150 mm.)	θ_1 (at 150 mm.)	N_0S $10^{18} \times$	Increase \oplus or decrease \ominus in N_0S compared with the fresh surface
1	1.306	0.957	36.877	
2	1.545	0.933	44.743	\oplus
3	1.545	0.933	44.743	\oplus
4	1.400	0.946	40.001	\oplus
5	1.545	0.933	44.743	\oplus
6	1.545	0.933	44.743	\oplus
7	1.400	0.946	40.001	\oplus
8	1.173	0.849	37.333	\oplus
9	2.426	0.939	69.821	\oplus
10	1.110	0.875	34.297	\ominus
11	2.568	0.938	74.014	\oplus
12	2.458	0.933	71.216	\oplus
13	2.232	0.922	65.435	\oplus
14	2.181	0.900	65.490	\oplus
15	0.995	0.851	31.614	\ominus
16	1.223	0.830	39.830	\oplus

Table 6.
Fraction covered with Adsorbed Molecules, θ_1 , and Total Number of Elementary Spaces, N_0S .

Expt. No.	Q (c.c.) (at 150 mm.)	θ_1 (at 150 mm.)	N_0S $10^{18} \times$	Increase \oplus or decrease \ominus in N_0S compared with the fresh surface
1 & 1'	0.413	0.939	11.892	
2	0.152	0.849	4.838	\ominus
3	0.107	0.824	3.508	\ominus

It should be noted in Table 5 that N_0S of all the experiments except Expts. 10 and 15 is larger than that of Expt. 1. In Expt. 11, the total number of the elementary spaces became about twice as many as that of the fresh catalyst. On the other hand, it is seen in Table 5 that θ_1 is not so influenced by the chemisorption, being 0.90–0.96 (at 150 mm. Hg.) except in Expts. 8, 10, 15 and 16. This shows that the increase in van der Waals' adsorption due to the chemisorption

and evacuation is attributable to the increase in the total number of the elementary spaces. The value N_0S generally decreases in the order of Expts. 8, 10 and 15 when the reaction vessel has been evacuated at 0°C . after the chemisorption and the value θ_1 of these experiments diminishes as compared with that of Expt. 1. Table 6 shows that the values N_0S of Expts. 2 and 3 markedly diminish as compared with that of Expt. 1.

All the experimental results are summarised in Table 7. As to [A], [B] and [C], the following relations hold:

$$\theta_1 \dots \dots \dots [B] \div [A] > [C]$$

$$N_0S \dots \dots \dots [B] > [A] > [C]$$

From these relations it is considered that there is little difference between [B] and [A] in the value θ_1 , and so in their adsorption ability, but the total number of the elementary spaces of [B] increases as compared with that of [A].

Summary.

(1) The chemisorption of carbon dioxide by reduced iron at $300^\circ\text{--}500^\circ\text{C}$. has been studied from the measurement of its van der Waals' adsorption at 0°C .

(2) The influence of the chemisorption on van der Waals' adsorption at 0°C . is shown in the following table.

Surface	Pretreatment	Variation in van der Waals' Adsorption at 0°C . as compared with the Surface [A]
[A]	Fresh surface without chemisorption	
[B]	When the reaction vessel is evacuated at $300^\circ\text{--}400^\circ\text{C}$. after chemisorption	+
[C]	When the reaction vessel is not evacuated or evacuated at 0°C . after chemisorption	-

(3) The fraction of the surface covered with the adsorbed molecules and the total number of the elementary spaces in van der Waals' adsorption at 0°C . have been calculated.

Table 7.

Expt.	θ_1 (at 150 mm.)	N_0S $10^{18} \times$
[A]	0.957	36.877
[B]	0.938	74.014
[C]	0.849	4.838

[A] Adsorption at 0°C . on the fresh surface of the catalyst.

[B] Adsorption at 0°C . on the surface which beforehand chemisorbed a considerable amount of CO_2 at $300^\circ\text{--}400^\circ\text{C}$. and was pumped off at the same temperatures.

[C] Adsorption at 0°C . on the surface which beforehand chemisorbed a small amount of CO_2 at 360°C . and was not pumped off.

(4) It has been found that the following relations hold between $[A]$, $[B]$ and $[C]$ in (2) with respect to the fraction of the surface covered with the adsorbed molecules and the total number of the elementary spaces.

The Fraction of the Surface covered with
the Adsorbed Molecules $[B] \doteq [A] > [C]$

The Total Number of the Elementary Spaces..... $[B] > [A] > [C]$

Thus, it has been pointed out that increase in van der Waals' adsorption due to the chemical treatment at high temperatures in the case of $[B]$ is ascribed to increase in the total number of the elementary spaces.

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