ON THE CHEMISORPTION OF CARBON DIOXIDE
BY REDUCED IRON. [I]*

The Interaction of Carbon Monoxide and Carbon Dioxide with
the Reduced Iron.

By Kimio Kawakita.

The author found unexpectedly, during the course of his study on the decomposition of carbon monoxide by reduced iron used as a catalyst, an interesting phenomenon at 300°C. to 400°C. that the resultant pressure of the reacting system became nearly zero.[1] This was due to the chemisorption of carbon dioxide by the catalyst at these temperatures.[2] In this paper it is his intention to report this phenomenon and to discuss it from the standpoint of surface chemistry.

Experimental.

The action of carbon monoxide and carbon dioxide upon the reduced iron was examined by means of the pressure change statically. The pressure change of the reacting gases was read simultaneously by means of a mercury manometer and a spring manometer[3] of Pyrex glass. The latter was used as the zero point instrument to avoid the dead space and the direct contact of mercury vapour with the catalyst. The lower part of this spring manometer was used as a reaction vessel filled with the catalyst.[4] The apparatus employed in this work was similar to that used by Horiba and Ri[5] in the decomposition reaction of carbon monoxide in the presence of reduced nickel.

A Cenco Hyvac pump and a mercury diffusion pump were used to evacuate the whole system to about 10^{-4}—10^{-5}mm.Hg. The change of temperature during the experiment could be limited within 0.1°C. by the temperature regulator[6] specially constructed.

*) This paper is the English translation of the same article published in *Rev. Phys. Chem. Japan*, 8, 89–116 (1934).

1) As the catalytic decomposition reaction of carbon monoxide is irreversible at 300°–400°C., it will be evident that the final pressure should be one half of the initial pressure when the reaction comes to an end, if there is no action of carbon dioxide on the catalyst.

2) As to the sorption of carbon dioxide by iron at temperatures lower than 500°C. no report is found in the literature, except the experiments by N. Nikitin (*Z. anorg. Chem.*, 154, 130–143 (1926)) and T. G. Finzel (*J. Am. Chem. Soc.*, 52, 142–149 (1930)) at temperatures below 100°C. But in these there was no report as the final pressure of carbon dioxide, which was observed to be nearly zero at 300°–400°C.

3) S. Horiba, *Rev. Phys. Chem. Japan*, 1, 269–273 (1927).

4) K. Kawakita, *Rev. Phys. Chem. Japan*, 8, 94 (1934).

5) S. Horiba and T. Ri, *Rev. Phys. Chem. Japan*, 4, 75–78 (1930).

6) K. Kawakita, *Rev. Phys. Chem. Japan*, 8, 95 (1934).

The catalyst used was iron reduced by purified hydrogen for more than twenty four hours from ferric oxide[7] which was denitrated at 400°C. from ferric nitrate obtained from Kahlbaum. Adsorbed hydrogen on the surface of the catalyst was desorbed by evacuation for more than twenty four hours.

Carbon monoxide was generated by dropping pure formic acid on concentrated sulphuric acid at 120°C. It was purified by passing successively through potassium hydroxide solution (55%), pyrogallol potassium hydroxide solution (55% KOH+3.4% pyrogallic acid), concentrated sulphuric acid, and phosphorus pentoxide.

Carbon dioxide was generated by heating sodium bicarbonate obtained from Kahlbaum. It was dried initially by calcium chloride and concentrated sulphuric acid, and to remove any trace of oxygen it was passed through a Pyrex tube filled with reduced copper heated to about 300°C., and then passed through concentrated sulphuric acid and phosphorus pentoxide tubes for the final drying.

Results.

§I. Typical Examples of Summarized Results.

(A) Action of Carbon Monoxide.

Conditions of the Preparation of Catalyst.

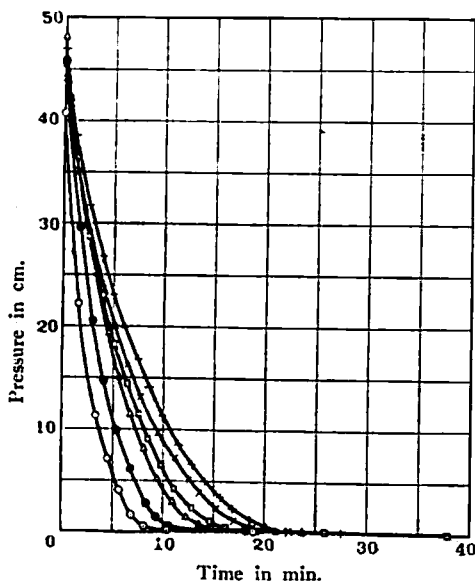| Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacuation after Reduction
4.7085gms.	362°C.	35 hrs.	24 hrs. at 362°C.

Fig. 1.

⊙ Exp. (a)   ● Exp. (b)   △ Exp. (c)
▫ Exp. (d)   × Exp. (e)   + Exp. (f)

The decrease in the pressure of *carbon monoxide* with the time at 367°C. is shown in Fig. 1. Experiments (a), (b), (c), (d), (e), and (f) are in their order of procedure. The final pressure was always between 0.02 and 0.04 cm. Hg., while the initial pressure was 40 to 50 cm. Hg. in every case.

As to the causes of such a phenomenon, namely the final pressure approaching nearly zero, the following may be taken into consideration :

(1) the strong adsorption of carbon monoxide on the surface of iron without

---

7) It was quite free from nitrate when tested by acetic acid solution of nitron.

decomposition ;.

(2) the formation of a solid compound of carbon monoxide and iron with small vapour pressure or decomposition pressure ;

(3) the strong adsorption of an iron compound such as a volatile carbonyl, say $Fe(CO)_5$[8], formed by the reaction of carbon monoxide upon iron ;

(4) the action between iron and carbon dioxide formed from the decomposition of carbon monoxide.

In preliminary experiments, however, it was indicated from the analysis of the reaction products in the gaseous and solid phases that most of carbon monoxide was decomposed into carbon dioxide and carbon, and no trace of carbonyl compound was detected. It seems to eliminate the third case, and with the additional reasons given in the later part of this paper, makes (1) and (2) improbable and leaves the fourth as the most probable explanation of the above phenomenon.

(B) Action of Carbon Dioxide.

Conditions of the Preparation of Catalyst.

Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacuation after Reduction
1.0019gms.	420°C.	24 hrs.	24 hrs. at 360°C.

The intensive sorption of carbon dioxide by the catalyst was observed and the typical example of the pressure change of carbon dioxide with the time at 360°C. is shown in Table 1 and Fig. 2. As a nature of this sorption, the

Table 1.

CO_2 Sorption at 360°C.

Time (t_{min}).	Pressure (p_{cm}).	$\sqrt{t}$	Pressure Decrease (x_{cm}).	Time (t_{min}).	Pressure (p_{cm}).	$\sqrt{t}$	Pressure Decrease (x_{cm}).
0	18.05	0	0	10.04	15.29	3.17	2.76
0.50	17.92	0.71	0.13	11.70	14.90	3.42	3.15
1.00	17.81	1.00	0.23	12.90	14.46	3.59	3.59
2.00	17.76	1.41	0.29	14.00	14.17	3.74	3.88
2.52	17.71	1.59	0.34	15.75	13.62	3.97	4.43
3.10	17.56	1.76	0.49	17.33	13.15	4.16	4.90
3.99	17.33	1.99	0.72	18.40	12.77	4.39	5.28
6.30	16.65	2.51	1.40	20.00	12.30	4.47	5.75
7.61	16.15	2.76	1.90	21.00	12.05	4.60	6.00
8.88	15.77	2.98	2.28	22.15	11.71	4.71	6.34

8) $Fe(CO)_5$ is decomposed instantly above 180°C. into carbon monoxide and iron.

|							
23.46	11.30	4.84	6.75	55.04	4.11	7.42	13.94
24.98	10.95	4.99	7.10	57.80	3.72	7.60	14.33
26.10	10.58	5.11	7.47	59.25	3.51	7.70	14.54
27.30	10.25	5.23	7.80	63.20	2.94	7.94	15.11
28.50	9.95	5.34	8.10	65.75	2.62	8.11	15.43
30.37	9.42	5.51	8.63	67.20	2.43	8.20	15.62
31.88	9.03	5.65	9.02	69.25	2.20	8.32	15.85
33.50	8.62	5.79	9.43	70.75	2.05	8.41	16.00
35.05	8.23	5.92	9.82	73.25	1.81	8.56	16.24
36.80	7.80	6.07	10.25	74.80	1.66	8.65	16.39
38.30	7.49	6.19	10.56	76.50	1.52	8.75	16.53
39.40	7.18	6.28	10.87	79.10	1.32	8.89	16.73
41.00	6.84	6.40	11.21	80.70	1.20	8.98	16.85
42.38	6.55	6.51	11.50	83.35	1.02	9.13	17.03
43.40	6.32	6.59	11.73	86.25	0.82	9.29	17.23
44.60	6.06	6.68	11.99	89.50	0.67	9.46	17.38
46.50	5.70	6.82	12.35	93.80	0.49	9.69	17.56
48.30	5.36	6.95	12.69	96.52	0.40	9.82	17.65
50.04	5.00	7.07	13.05	101.60	0.28	10.08	17.77
51.70	4.77	7.19	13.28	107.00	0.13	10.34	17.92
53.00	4.51	7.28	13.54	118.35	0.08	10.88	17.97
54.25	4.32	7.37	13.73				
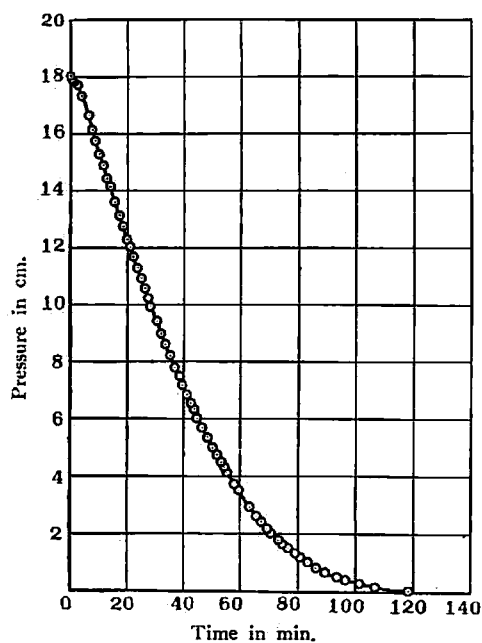
Fig. 2.
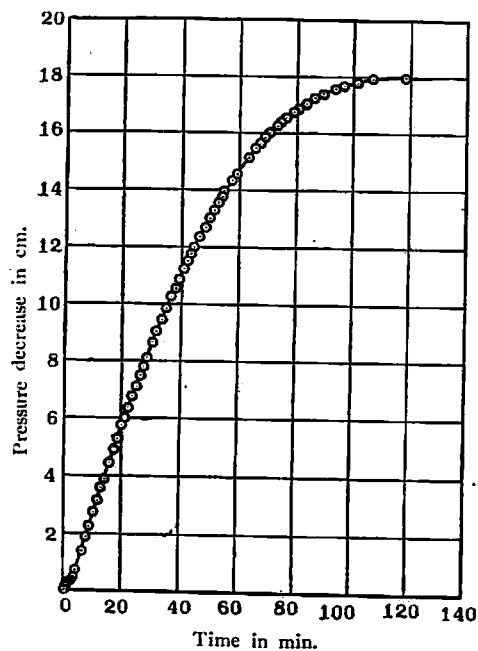
Fig. 3.

relation between the time t and the decrease in the pressure x is as follows:

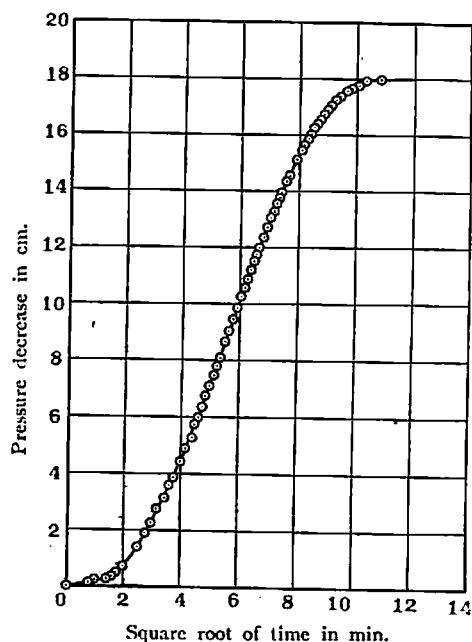(1) when t is small x is proportional to t;

Square root of time in min.

Fig. 4.

(2) when t is moderate x is a linear function of $t^{\frac{1}{2}}$,

(3) when t is large x is an exponential function of t.

In Fig. 3 the x-t curve is plotted and similarly the $x - \sqrt{t}$ curve in Fig. 4. In the latter the curve is linear except at the initial and final stages.

§ II.   The Irreversible Sorption of Carbon Dioxide.

The sorption of carbon dioxide took place irreversibly at $300° - 400°C$. One of the experimental results at $326°C$. is given in Fig. 5., and the $x - \sqrt{t}$ curve of which is shown in Fig. 6. The activity of reduced iron decreases and the inclination of the linear part of each curve in Fig. 6 becomes more and more gentle as the experiment is repeated.

Conditions of the Preparation of Catalyst.

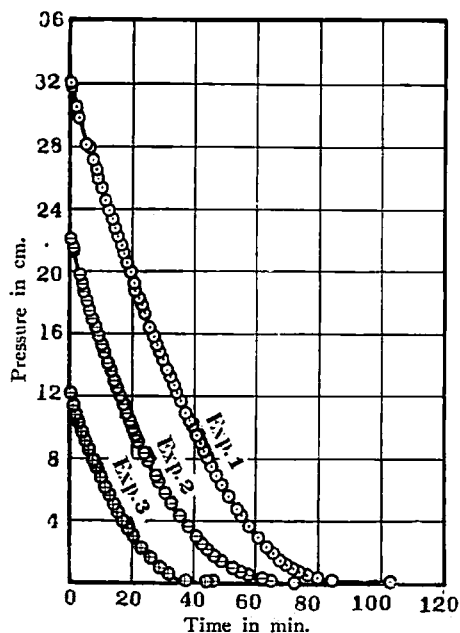| Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacuation after Reduction
4.1721gms.	420°C.	48 hrs.	22 hrs. at 420°C.

Time in min.

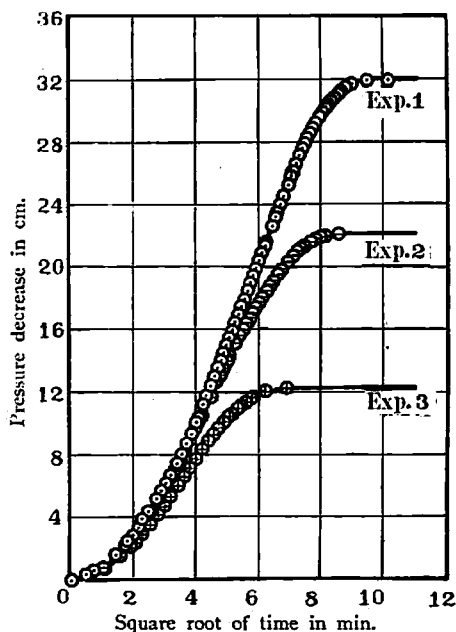Fig. 5.

Square root of time in min.

Fig. 6.

§ III.   The Relation between Equilibrium Pressure and Temperature.

The following experiments were carried out in order to observe the change of equilibrium pressure of sorption over the temperature range between 20°C. and 250°C. The adsorption of carbon dioxide by reduced iron at 20°C. reached equilibrium instantaneously. The temperature was then raised from 20°C. up to 50°C., 100°C., 150°C., 200°C., and 250°C., and at each temperature the sorption equilibrium was measured.

Conditions of the Preparation of Catalyst.

Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacuation after Reduction
6.204gms.	430°C.	24 hrs.	24 hrs. at 430°C.

The experimental results are shown in Table 2. Fig. 7 is the equilibrium

Table 2.

No.	Temp. (°C.)	Equilibrium Press. (cm.)	Thermal Expansion Providing no Occurrence of Sorption[9] (cm.).	Initial Press. (cm.)[10]	Pressure Decrease with Sorption (cm.).
1	20	13.71	13.71	14.01 (obs.)	0.3 (obs.)
2	50	14.93	15.11	15.44 (calc.)	0.51 (calc.)
3	100	16.51	17.45	17.83 (calc.)	1.32 (calc.)
4	150	17.37	19.79	20.22 (calc.)	2.85 (calc.)
5	200	0.02	22.13	22.61 (calc.)	22.59 (calc.)
6	250	0.02	24.47	25.01 (calc.)	24.99 (calc.)

—○— represents equilibrium pressure-temperature curve·
—·—·— represents the thermal expansion.
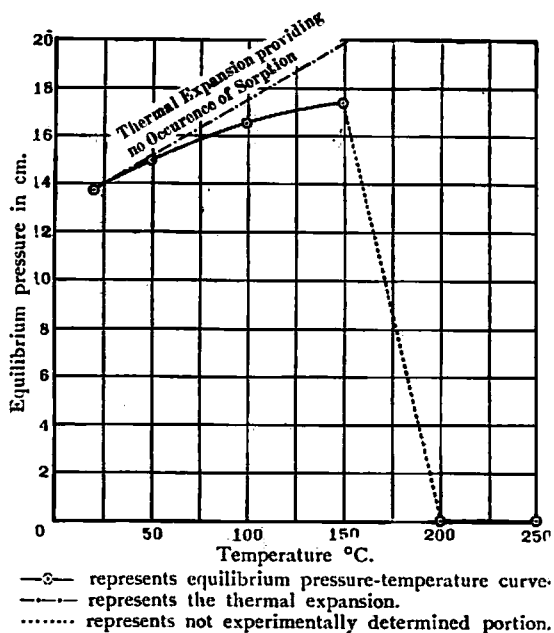········ represents not experimentally determined portion.
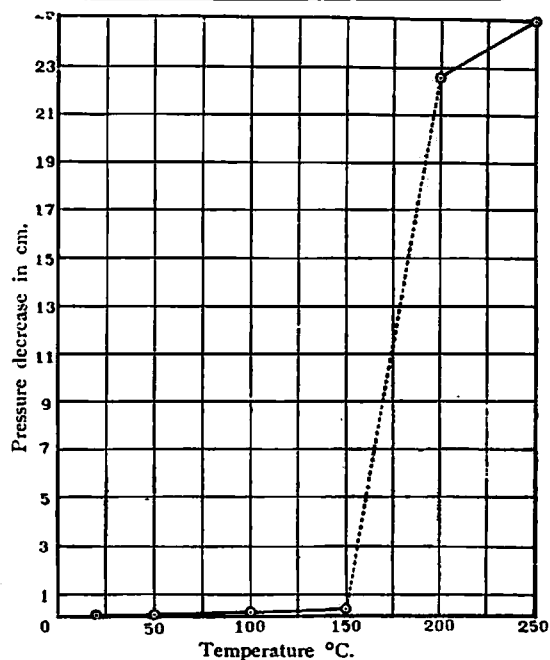
Fig. 7.

Fig. 8.

9) This means the thermal expansion without taking into consideration the occurrence of sorption for equilibrium pressure, 13.71 cm. Hg. at 20°C.

10) The initial pressure above 50°C. was calculated from the observed value at 20°C.

pressure-temperature curve, and Fig. 8 is the pressure decrease-temperature curve drawn from the data in Table 2. The difference between the equilibrium pressure and the thermal expansion calculated on the assumption that there is no sorption above 20°C., was small in the temperature range from 20° to 150°C., while a sudden change broke out in the range between 150°C. and 200°C. Thus the sorption phenomenon in which the resultant pressure of carbon dioxide became nearly zero was observed to begin at about 150°—200°C.

§ IV. The Relation between Sorbed Amount and Equilibrium
Pressure at 360°C.

So long as the quantity of catalyst was large and the sorbed amount of carbon dioxide was small, the final pressure became practically zero at 300°C.,—400°C. But when a small quantity of the catalyst was used, a kind of equilibrium pressure was observed as the sorption increased and approached to saturation. In the presence of 6.672×10^{-3} gram mol of iron, the relation between the sorbed amount and the equilibrium pressure was measured. The experimental results are shown in Table 3 and Fig. 9.

Table 3.

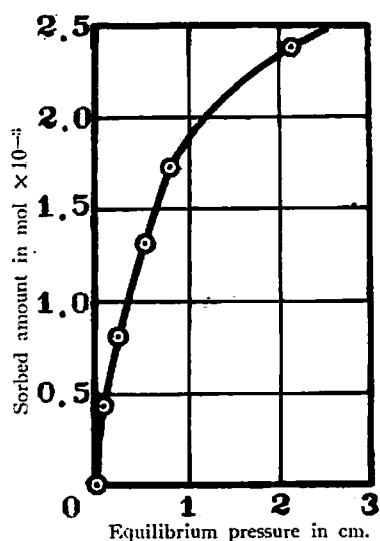| No.	Equilibrium Pressure P(cm.)	Sorbed Amount (mol) M (obs.)
1	0.08	0.4271×10^{-3}
2	0.23	0.8059×10^{-3}
3	0.53	1.3073×10^{-3}
4	0.79	1.7273×10^{-3}
5	2.14	2.3802×10^{-3}

Fig. 9.

§ V. On the Catalyst saturated with Carbon Dioxide.

The actions of carbon dioxide (Exp. 3) and *carbon monoxide* (Exp. 4) upon the catalyst saturated with carbon dioxide were examined.

Conditions of the Experiment and of the Preparation of Catalyst.

Expt. No.	Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacuation after Reduction
	0.5054gms.	420°C.	48 hrs.	72 hrs. at 360°C.
1.	Experiment with carbon dioxide at 360°C.			
2.	Experiment with carbon dioxide——The reaction vessel was evacuated for 24 hours at 360°C. after Exp. 1.			
3.	Experiment with carbon dioxide——The reaction vessel was evacuated at 360°C. after the catalyst was left in carbon dioxide for 216 hours at 360°C. until no further sorption took place.			
4.	Experiment with *carbon monoxide*——The reaction vessel was evacuated at 360°C. after Exp. 3.			
5.	Experiment with carbon dioxide at 360°C. after re-reduction by hydrogen after Exp. 4. (Temperature of reduction was 430°C.; time of reduction was 24 hours; time and temperature of evacuation were 24 hours and 360°C. respectively.)			

The results are shown in Fig. 10. Exps. 1 and 2 in Fig. 10 may be regarded as examples of irreversible sorption. The catalyst in Exp. 3 is considered to be almost saturated with carbon dioxide. In the presence of the same catalyst as in Exp. 3, the decomposition reaction of *carbon monoxide*, however, took place at a moderate velocity (Exp. 4). When the catalyst, thus saturated with carbon
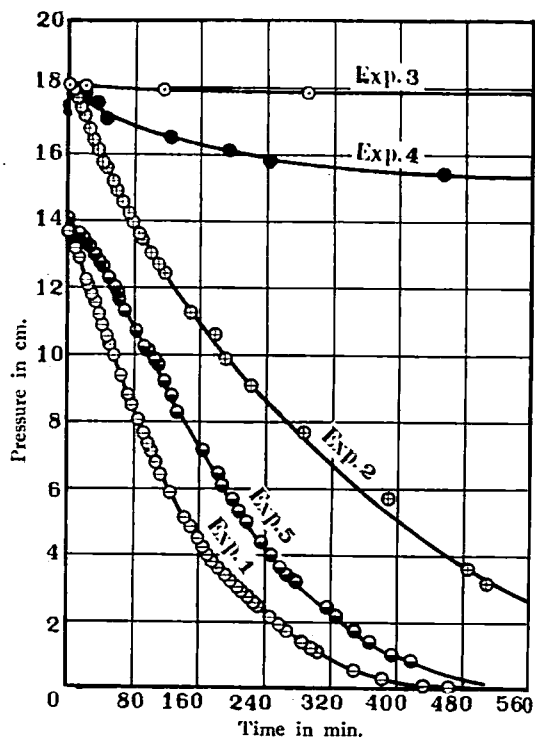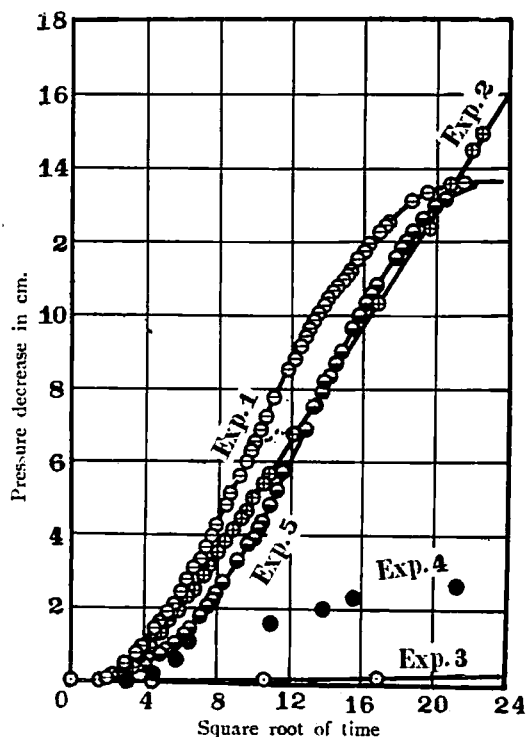

Fig. 10.

Fig. 11.

dioxide after successive experiments, was re-reduced by hydrogen the formation of water was detected. After this treatment of the catalyst, the sorption of carbon dioxide took place again (Exp. 5). Fig. 11 shows the relation between the pressure decrease and the square root of time. The curves in Fig. 11 have linear stages except Exp. 4.

§ VI. On the Poisoned Catalyst.

By introducing a small quantity of grease into the reaction vessel, the poisonous effect upon the sorption of carbon dioxide (Exp. 1) and the decomposition of *carbon monoxide* (Exp. 2) was examined.

Conditions of the Preparation of Catalyst.

Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacution after Reduction
0.5319gms.	360°C.	24 hrs.	24 hrs. at 360°C.

The two experiments at 349°C. are shown in Fig. 12. It may be clearly observed that both the sorption of carbon dioxide and the decomposition of *carbon monoxide* did not occur.
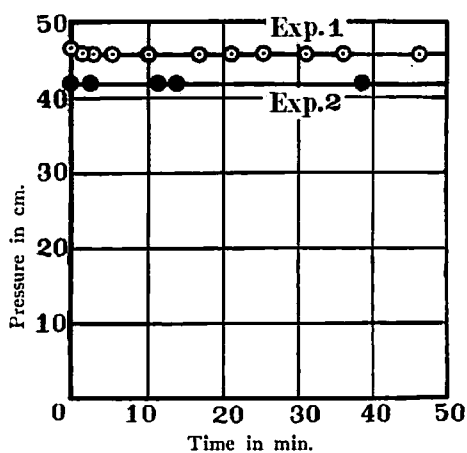
Fig. 12.

§ VII. On the Sintered Catalyst.

The effect of sintering upon the sorption of carbon dioxide (Exp. 1) and the decomposition of *carbon monoxide* (Exp. 2) was examined.

Conditions of the Preparation of Catalyst.

Weight of Ferric Oxide	Temp. of Reduction	Time of Reduction	Time of Evacuation after Reduction
0.5396gms.	500°C.	48 hrs.	36 hrs. at 500°C.

Table 4 gives the results of the two experiments at 340°C. Fig. 13 is the pressure-time curve drawn from the data in Table 4. As seen from the curve of Exp. 1 in Fig. 13, the sorption of carbon dioxide scarcely occurred, and this is probably due to the sintering of catalyst at 500°C. But *carbon monoxide* was decomposed by the same catalyst, as shown by the curve of Exp. 2. The final pressure in Exp. 2 is indicated by the isolated point in Fig. 13. The dotted line in the same figure shows the theoretical value of the final pressure in the decomposition of *carbon monoxide*.

Table 4.

| Exp. 1 CO$_2$		Exp. 2. CO			
t_{min}	Pcm	t_{min}	Pcm	t_{min}	Pcm
0	19.64	0	27.05	82.50	20.85
3.5	19.44	3.20	26.70	94.00	20.51
7.5	19.44	5.28	26.44	98.82	20.29
15.00	19.44	7.00	26.13	105.22	20.10
20.00	19.32	9.68	25.85	113.72	19.89
110.00	19.32	12.62	25.52	127.13	19.56
125.00	19.32	17.58	25.08	138.58	19.26
161.00	19.32	24.50	24.49	164.72	18.51
250.00	19.32	29.68	24.07	171.60	18.18
300.00	19.32	37.58	23.48	194.27	17.71
∞	19.32	44.15	23.01	217.60	17.32
		50.13	22.61	237.93	17.28
		57.68	22.05	249.93	17.17
		62.60	21.82	969.93	14.15
		72.20	21.33		
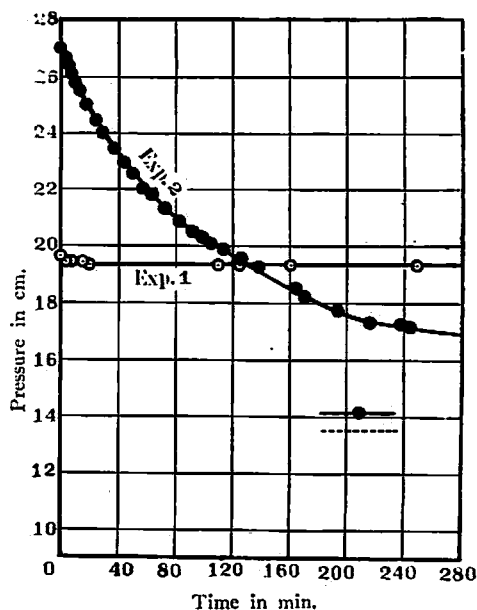
Fig. 12.

It was indicated that the sintering effect upon the sorption of carbon dioxide was remarkably greater than that upon the decomposition of *carbon monoxide*. It was observed, however, that when the temperature of reduction was comparatively low, the catalyst was very active for the sorption of carbon dioxide as well. For example, the catalyst, reduced for ninety six hours at 330°C., was catalytically active and the catalyst itself was pyrophoric.[11]

Considerations on Experimental Results.

Summary of Experimental Results.

In the case of carbon dioxide acting on reduced iron at 300°—400°C., it was found, in the measurement of sorption velocity, that (1) an irreversible sorption always took place in the normal state of the activity of the catalyst; (2) the sorbed amount was proportional to the square root of time in the intermediate stage of the sorption; (3) the pressures attained at the end of the experiments were always practically zero; (4) this sorption was observed to begin at 150°—200°C; (5) when the catalyst was used in a minute quantity, a definite equilibrium pressure, not practically zero as in case (3), was observed, which gradually increased with the repetition of experiments; (6) the activity of the catalyst, weakened by repeated usage was recovered by re-reduction with hydrogen, water being produced; (7) the sorption occurred slightly with the catalyst saturated with the gas, and also with the sintered catalyst, while the decomposition of *carbon monoxide* took place with both of them; (8) finally it was

11) T. G. Finzel, *J. Am. Chem. Soc.*, **52**, 142–149 (1930).

found .that the poisoned catalyst had no action upon *carbon monoxide* and carbon dioxide. A further explanation of the experimental results will be given below.

[A] On the Proportionality of the Sorbed Amount to the Square Root of Time.

Many investigators[12] pointed out that the proportionality of the sorbed amount to the square root of time was due to the diffusion of the adsorbed molecules into the interior of metal catalyst.   So the diffusion of the adsorbed carbon dioxide molecules may be the main process of the chemisorption in question (§I. (B)).

[B] On Possibility of Chemisorption.

(a)   *Applicability of Sieverts' Formula.*

Our case (§IV) was not applicable to Henry's formula, $M = kP$, where M is the sorbed amount, P the pressure, and k the proportionality factor. In Table 5 the sorbed amount M_H calculated by Henry's formula is compared with

Table 5.

No.	M_H (calculated from Henry's formula, $M_H = 2.92P \times 10^{-3}$)	Δ_H M (obs.)$-M_H$
1	0.2336×10^{-3}	$+0.1935 \times 10^{-3}$
2	0.6716×10^{-3}	$+0.1343 \times 10^{-3}$
3	1.5476×10^{-3}	-0.2403×10^{-3}
4	2.3068×10^{-3}	-0.5790×10^{-3}
5	6.2488×10^{-3}	-3.8686×10^{-3}

$$\Sigma \Delta_H = -4.3601 \times 10^{-3}$$

12) Kitagawa (*Rev. Phys. Chem. Japan*, 6, 106–126 (1932)) has observed in the case of the sorption of hydrogen by reduced copper that the sorbed amount was proportional to the square root of time, and Iijima (*Rev. Phys. Chem. Japan*, 7, 3-36 (1933)), using reduced nickel, obtained the same results. Both of them considered as Ward (*Proc. Roy. Soc.* [A], 133, 506–522 (1931)), that it was due to the diffusion of adsorbed hydrogen into the interior of metal catalyst. Such a phenomenon was also observed in the oxidation of a metal, which was nothing but what is called Parabolic Law established by such investigators as Dunn (*Proc. Roy. Soc.* [A], 111, 203–219 (1926)), Feitknecht (*Z. Elektrochem.*, 35, 142-151 (1929)), Wilkins (*Proc. Roy. Soc.* [A], 128, 407–417 (1930)) and Rideal (*Proc. Roy. Soc.* [A], 128, 394–406 (1930)). This phenomenon is brought about by the lattice diffusion of gas through the crystal lattice or by the grain boundary diffusion of gas through oxide film, that is, the boundary of microcrystals of oxide. Lennard-Jones (*Trans. Farad. Soc.*, 28, 333–359 (1932)) has pointed out that the surface of reduced copper was full of minute cracks of molecular dimensions and that the hydrogen atoms adsorbed on the surface diffused into those cracks or small fissures by two-dimentional thermal motion, and he has given a probable explanation to Ward's experimental results. As to the cracks, see Lennard-Jones and Dent, *Proc. Roy. Soc.*, [A], 121, 247 (1928); Smekal, *Physik. Z.*. 27, 837 (1926); *Ann. Phys. Chem.*, 83, 1202 (1927); *Z. Elektrochem.*, 34, 477 (1928); Zwicky, *Proc. Nat. Acad. Sci.*, 15, 253, 816 (1929); Kapitza, *Proc. Roy. Soc.* [A], 119, 358 (1928); Quinney, *Proc. Roy. Soc.* [A], 124, 591 (1929); Griffith, *Phil. Trans.* [A], 221, 163 (1920).

the observed value $M_{(obs.)}$. The difference between $M_{(obs.)}$ and M_H is comparatively large.

Sieverts and his school hold that, in the case of dissolution of a gas in such metals as copper, iron, nickel, tantal, etc. at high temperatures, the sorbed amount M is proportional to the square root of pressure P. Applying the Sieverts formula, $M = kP^{\frac{1}{2}}$, to the present case, it was found as shown in Table 6 that

Table 6.

No.	M_s (calculated from Sieverts' formula, $M_s = 1.71\sqrt{P} \times 10^{-3}$)	Δ_s $M\,(obs.) - M_s$
1	0.4839×10^{-3}	-0.0563×10^{-3}
2	0.8208×10^{-3}	-0.0149×10^{-3}
3	1.2449×10^{-3}	$+0.0624 \times 10^{-3}$
4	1.5202×10^{-3}	$+0.2076 \times 10^{-3}$
5	2.5017×10^{-3}	-0.1215×10^{-3}

$\Sigma\Delta_s = -0.0758 \times 10^{-3}$

the difference between M_s calculated by the Sieverts formula and the observed value was smaller and the applicability of this formula is better than that of Henry's formula. As the formula, $M = kP^{\frac{1}{2}}$, is generally applicable when the gas is dissociated and dissolved on the surface of solid, it may lead to the anticipation that the sorption of carbon dioxide is preceded by its chemical transformation.

(b) Possible Chemical Reactions on the Sorption of Carbon Dioxide.

Here some material chain mechanism such as the following is most probable:

$$Fe + (CO_2)_{Ads.} = Fe_X O_Y + (CO)^{13)}_{Ads.} \qquad (1)$$

$$2(CO)_{Ads.} = C + (CO_2)_{Ads.} \cdot \qquad (2)$$
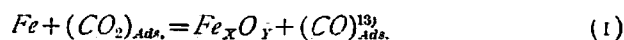
At first, the adsorbed carbon dioxide molecules acting on the active metal atoms produce an iron oxide and carbon monoxide by reaction (1). Thermodynamically, reaction (2) is practically irreversible at 300°–400°C., and carbon monoxide formed by reaction (1) is catalytically decomposed into carbon and carbon dioxide. Thus the equilibrium of reaction (1) is shifted to the right side. Carbon dioxide formed by reaction (2) reacts again, as in reaction (1), with the other active iron atoms. As considered in [A] and [B] (a), it seems probable that, as reaction (1) occurs chiefly at the active parts in the inner surface of the catalyst (§V and §VII), the carbon dioxide molecules adsorbed and activated on the outer surface

---

13). As to this reaction, the author intends to make a further thermodynamical investigation in the third report which will be published later in this journal.

diffuse into the inner surface and some of them react with the active iron atoms of the inner surface, producing carbon monoxide. The chain will be broken when the active iron atoms become deficient.

Facts indicating the Existence of the Above Chemisorption.

i) The catalyst saturated with carbon dioxide recovers its activity, forming water, by its re-reduction with hydrogen (Exp. 4 in §V). The formation of water indicates the existence of iron oxide.[14]

ii) Presence of Free Carbon.

About 50 c.c. of hydrochloric acid (sp. gr. 1.19) obtained from Kahlbaum was added to 3 grams of the catalyst saturated with carbon dioxide, and it was carefully boiled for 160 hours with a reflux-condenser, renewing the hydrochloric acid every day in order to dissolve away a greater part of iron ; after this treatment there remained·an insoluble substance, black in colour, in the end. This insoluble residue consisted mostly of carbon (96.17%C). When the newly reduced iron, which had never reacted with carbon dioxide, was introduced into hydrochloric acid and heated, it dissolved completely in a few minutes forming a clear solution.

iii) Self-poisoning.

It was observed that, when the sorption of carbon dioxide took place with the catalyst, a kind of self-poisoning was manifested by a gradual decrease in the sorption velocity (Exps. 1, 2 and 3·in §V). This is considered to be due to the decrease in the number of active iron atoms by the reaction $Fe + (CO_2)_{Ads.} \rightarrow Fe_xO_Y + (CO)_{Ads.}$.

In such a system of iron and carbon dioxide as treated in this chemisorption, whether carbon monoxide is formed or not is an interesting question, which the author intends to investigate further ; the results of which will be published later in this journal.

[C] Action of Carbon Dioxide and Carbon Monoxide upon the catalyst with Various Activities.

(a) On the Catalyst saturated with Carbon Dioxide.

The chemisorption of carbon dioxide scarcely occurred with the catalyst which was saturated with carbon dioxide (§V. Exp. 3) ; with the same catalyst, however, the decomposition of *carbon monoxide* took place (§V. Exp. 4).

These facts show a selectivity that the chemisorption of carbon dioxide

---

14) If it is assumed that carbon dioxide molecules being adsorbed without any chemical change react with hydrogen as ordinary molecules, the reaction $CO_2 + H_2 = CO + H_2O(g)$ is conceivable, but as the free energy equation of this reaction is $\Delta F^0 = 10100 - 1.81\ T \ln T + 0.00445\ T^2 - 0.00000068\ T^3 - 0.54\ T$ (Lewis and Randall, *Thermodynamics* McGraw-Hill (1923) p. 575) ΔF^0 is +3340 at 430°C., so that the said reaction is not probable to occur at such a temperature. Moreover, the presence of an iron oxide was shown by analysis in this laboratory.

occurs only on the strong active centers of the catalyst, while the decomposition of *carbon monoxide* can take place even on the comparatively weak active centers of the catalyst.

(*b*)   On the Poisoned Catalyst.

The catalyst poisoned by a small quantity of grease had no action upon · carbon dioxide and *carbon monoxide* (§VI. Exps. 1 and 2). This indicates that the active centers on the outer surface of the catalyst is wholly covered with poisonous matter. Thus the decomposition of *carbon monoxide* is impossible, and it is probable that carbon dioxide molecules are unable to diffuse into the interior of the catalyst because of impossibility of adsorption on the outer surface.

(*c*).   On the Sintered Catalyst.

The catalyst as mentioned in (*a*) may also be obtained by sintering (§VII). The sintered catalyst was so inactive that the chemisorption of carbon dioxide scarcely occurred (§VII. Exp. 1). The decomposition of *carbon monoxide*, however, proceeded at comparatively large velocity (§VII. Exp. 2). In this case, the inactivity of the sintered catalyst is probably due to a large diminution in active surface. Though the strong active cnters—crystal edges, crystal corners, etc.—are lost owing to sintering, the weak active centers still exist, by which the decomposition of *carbon monoxide* can occur.

In short, the chemisorption of carbon dioxide is brought about by iron atoms in the strong active centers and the decomposition of *carbon monoxide* takes place even in the weak active centers on the surface of the catalyst.

Summary.

(1) The decomposition velocity of carbon monoxide in the presence of reduced iron has been measured in the temperature range between 300°C. and 400°C., and the pressures attained at the end of the experiments have been observed to be nearly zero.

(2) The sorption of carbon dioxide alone has been observed in the same temperature range and the final pressure of carbon dioxide approached practically to zero, and the sorption has been ascertained to be irreversible.

(i) The sorbed amount is proportional to the square root of time in the intermediate stage of the sorption. This is probably due to the diffusion of adsorbed carbon dioxide molecules into the inner surface of the catalyst.

(ii) Carbon dioxide molecules diffused into the inner surface of the catalyst have been considered to react on the active iron atoms giving rise to a material

chain reaction such as

$$Fe + (CO_2)_{Ads.} = Fe_xO_r + (CO)_{Ads.} \qquad \text{(a)}$$

$$2(CO)_{Ads.} = (CO_2)_{Ads.} + C. \qquad \text{(b)}$$
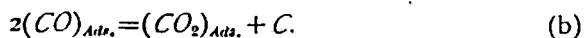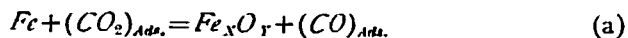
(iii) The existence of carbon which is considered to be formed by the above reaction has been ascertained.

(3) The chemisorption of carbon dioxide has been observed to begin at $150°-200°C$.

(4) Using the catalyst saturated with carbon dioxide, the poisoned-, and sintered catalyst, the sorption of carbon dioxide and the decomposition of carbon monoxide has been examined.

(5) It has been observed that the chemisorption of carbon dioxide occurs only on the strong active centers of the catalyst while the decomposition of carbon monoxide can take place even on the comparatively weak active centers of the catalyst.

The Laboratory of Physical Chemistry.
Kyoto Imperial University.