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# ON THE CHEMISORPTION OF CARBON DIOXIDE BY REDUCED IRON. [IV].

## Kinetics of the Chemisorption.

By Kimio Kawakita.

This paper is the fourth report on a series of investigations[1] conducted under the direction of Professor S. Horiba dealing with the chemisorption of carbon dioxide by reduced iron which is expressible by the consecutive reactions,

$$\text{(i)}\quad Fe+(CO_2)_{Ads.}=Fe_XO_Y+(CO)_{Ads.},$$

$$\text{(ii)}\quad 2(CO)_{Ads.}=C+(CO_2)_{Ads.}.$$

Here from theoretical considerations several plausible mechanisms and the rate of the chemisorption have been proposed, the validity of which has been tested by the experimental results obtained.

## Experimental Details.

The reaction rate of the chemisorption was determined by the pressure changes measured statically in employing a Pyrex "Spring manometer" and a mercury manometer simultaneously. The capacity of the reaction chamber was 50.97 c.c.; but, as to the rest, the apparatus employed and its manipulation were similar to those described in the first report. And besides,

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[1] In the first report [K. Kawakita, *This Journal*, 8, 89~116 (1934); 11, 75~89 (1937).], evidences leading to the proposal of the consecutive reactions for the chemisorption were given. Also it was shown that reaction (i) took place at highly activated points and that reaction (ii) might occur at less active centres as well. In the second report [K. Kawakita, *ibid.*, 10, 200~211 (1936); 12, 105~114 (1938); *Proc. Imp. Acad. Tokyo*, 12, 61~63 (1936).], it was pointed out that the hither-to undetected increase in van der Waals' adsorption of carbon dioxide at 0°C. due to the chemisorption at 300°C.~400°C. was brought about by the increase in the total number of the elementary spaces caused by the chemisorption reactions. In the third report [K. Kawakita, *This Journal*, 13, 87~95 (1939).], the identification of carbon monoxide formed by reaction (i) was made by the reduction of a palladous salt solution. There some thermodynamic considerations and calculations were also made and the following reactions were proposed for the chemisorption reactions:

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\begin{array}{lll}
(1) & Fe+CO_2=FeO+CO & \Delta F^{\circ}_{633}=+1.09\ \text{Kcal.},\\
(2) & 3\,FeO+CO_2=Fe_3O_4+CO & \Delta F^{\circ}_{633}=-1.41\ \text{Kcal.},\\
(3) & 3Fe+4CO_2=Fe_3O_4+4CO & \Delta F^{\circ}_{633}=+1.86\ \text{Kcal.},\\
(4) & 2CO=C+CO_2 & \Delta F^{\circ}_{633}=-14.73\ \text{Kcal.},\\
(5) & 3Fe+2CO_2=Fe_3O_4+2C & \Delta F^{\circ}_{633}=-27.60\ \text{Kcal.},
\end{array}
$$

and it is inferred that reaction (1) is the primary surface process, (2) the successive reaction, (3) the resultant primary reaction, (4) the secondary surface process which is catalytic and irreversible, and (5) the resultant reaction caused by both carbon dioxide and reduced iron in the temperature range between 300°C. and 400°C.

the purification and preparation of the experimental materials used were also the same as given there. In this investigation reduced iron catalysts supported on silica gel as well as those of non-supported iron were used. By impregnating silica gel sticks of appropriate length and of about 5 mm. diameter with an aqueous nitrate solution of iron, the supported catalyst was prepared and dried at 300°C. and reduced with hydrogen. The silica gel used was prepared by introducing an equivalent amount of 1.08N sodium silicate solution into 1N hydrochloric acid while stirring; the silica gel thus formed was washed continuously for several days; it was then formed into sticks and dried and the final traces of water were eliminated by evacuation at 300°C.~400°C. The catalysts used in the present investigation are given in Table 1.

Table 1.

Conditions for the Preparation of Catalysts.

| Catalyst Number | Weight of Catalyst | Temp. of Reduction | Time of Reduction | Time of Evacuation after Reduction |
|---|---|---|---|---|
| I | $Fe_2O_3=1.8407$ g.<br>$SiO_2=10.9802$ g. | 410°C | 24 hrs. | 24 hrs. at 360°C |
| II | $Fe_2O_3=1.8407$ g.<br>$SiO_2=10.9802$ g. | 410°C | 24 hrs. | 24 hrs. at 400°C |
| $III_1$ | $Fe_2O_3=4.0000$ g. | 420°C | 24 hrs. | 24 hrs. at 370°C |
| $III_2$ | $Fe_2O_3=4.0000$ g. | 420°C | 24 hrs. | 24 hrs. at 360°C |
| $III_3$ | $Fe_2O_3=4.0000$ g. | 420°C | 24 hrs. | 24 hrs. at 350°C |
| $III_4$ | $Fe_2O_3=4.0000$ g. | 420°C | 24 hrs. | 24 hrs. at 340°C |
| $III_5$ | $Fe_2O_3=4.0000$ g. | 420°C | 24 hrs. | 24 hrs. at 330°C |
| IV | $Fe_2O_3=0.1424$ g.<br>$SiO_2=6.6594$ g. | 400°C | 24 hrs. | 24 hrs. at 400°C |
| V | $Fe_2O_3=1.0019$ g. | 420°C | 24 hrs. | 24 hrs. at 360°C |

## Results.

### [I] Velocity of the Chemisorption.

In the consideration of the kinetics of the chemisorption the following factors are first taken into account.

(1) The velocity of the gaseous molecules reaching the surface.
(2) The velocity of adsorption.
(3) The velocity of diffusion.
(4) The velocity of reaction.

Since velocity (1) is generally regarded as very great, it can be assumed to be negligible in our present experiment of the chemisorption; hence velocity (2) can be also supposed to be extremely great.

The velocity of diffusion (3) is usually measurable in the reactions between ordinary gases and solids, and so is the velocity of reaction (4). The velocities

(3) and (4), however, can not readily be discriminated. As to the velocity (4), of the two following reactions

$$\text{(i)}\quad Fe+(CO_2)_{Ads.}=Fe_XO_Y+(CO)_{Ads.}$$

$$\text{(ii)}\quad 2(CO)_{Ads.}=C+(CO_2)_{Ads.},$$

reaction (ii) is probably of considerably rapid process, and accordingly reaction (i) is regarded as rate-determining step of the chemisorption reactions. Considerations on (3) and (4) will be mentioned later. The following discussion is made upon the assumption that the velocity of adsorption is so great as to be negligible.

If it is assumed that the adsorption equilibrium is immediately established on the surface, then the chemisorption may be considered similar to the catalytic reaction in the heterogeneous system, that is, the catalytic reaction followed by the self-poisoning action of the reaction products. It is interesting here to examine whether the unique method of velocity analysis for the heterogeneous catalytic reaction proposed by Professor S. Horiba and Dr. T. Ri[2–6] is applicable to our chemisorption.

If the velocity of the chemisorption is proportional to the fraction ($\theta_1$) of the surface covered with the adsorbed molecules, then we have

$$-\frac{dp}{dt}=k'\theta_1=\frac{kp}{1-b^*p}\,^{7)}, \qquad (1)$$

where $k'$ and $k$ are constants, and $b^*$ is a factor depending upon the difference between the adsorption coefficient of the products formed by the chemisorption and

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2) S. Horiba and T. Ri, *Bull. Chem. Soc. Japan*, 3,. 18~25 (1928).

3) S. Horiba and T. Ri, *This Journal* 4, 73~132 (1930).

4) T. Ri, *ibid.*, 5, 41~112 (1931).

5) S. Horiba and T. Ri, *Rec. trav.*, 51, 641~647 (1931).

6) S. Horiba and T. Ri, *Nippon Gakujutsu Kyokai Hokoku*, 7, 691~702 (1932).

7) Let $\theta_1$ represent the fraction of the surface covered with the adsorbed molecules, we have

$$\theta_1=\frac{b_1p}{1+b_1p+b_2x+b_3x+\dots\dots\dots},$$

where $b_1$, $b_2$, $b_3$, etc. are adsorption coefficients of reacting substance and reaction products respectively and they are proportional to the life remaining on the surface; $p$ is the pressure of the gas, and $x$ is the amount of the reaction product which is proportional to the amount of the chemisorption. If $p_0-p$ ($p_0$ is the initial pressure of the reacting gas and $p$ is the pressure of the gas at any time) is substituted for $x$ in the equation, it becomes

$$\theta_1=\frac{b_1p}{\{1+(b_2+b_3+\dots\dots)p_0\}-(b_2+b_3+\dots-b_1)p}.$$

If we put

$$\frac{b_1}{1+(b_2+b_3+\dots\dots\dots)\,p_0}\equiv b', \quad \frac{b_2+b_3+\dots\dots\dots-b_1}{1+(b_2+b_3+\dots\dots\dots)\,p_0}\equiv b^*,$$

then equation becomes

$$\theta_1=\frac{b'p}{1-b^*p}.$$

[redacted]

that of the reacting substances, and it is a constant at a fixed temperature. When equation (1) is integrated and the initial conditions are introduced, it becomes;

$$k_m - b^* v = k \qquad (2)$$

where

$$k_m = \frac{1}{t} \ln \frac{p_0}{p} \quad (p_0 \text{ is the initial pressure})$$

and

$$v = \frac{p_0 - p}{t}.$$

Let us examine the relationship given in equation (2) from the experimental results obtained with two different kinds of catalysts—non-supported catalysts and supported catalysts.

**Experiments on the Supported Catalyst.**— The supported catalyst in many cases shows the retardation type. For example, the case where the experiment was made at 360°C. with catalyst I is shown in Fig. 1, which clearly indicates the retardation type.

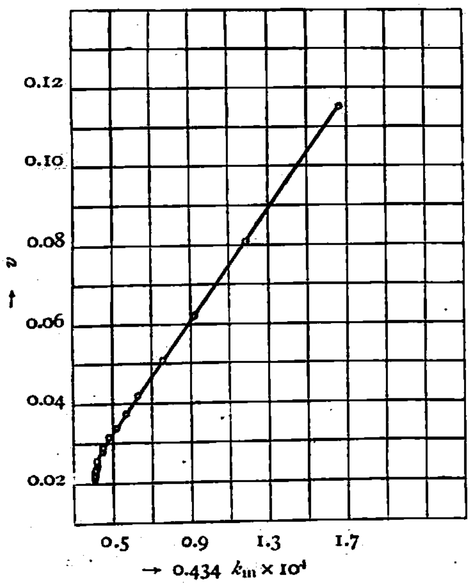

Fig. 1. Chemisorption of carbon dioxide by catalyst I at 360°C.

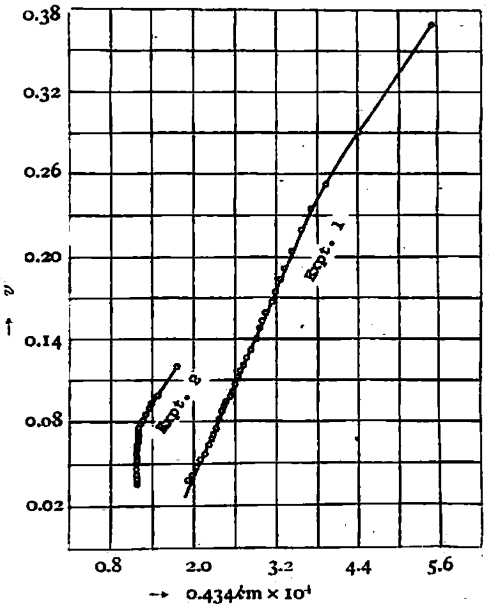

Fig. 2. Chemisorption of carbon dioxide by catalyst II at 400°C.

Fig. 2 shows the result of the experiment made at 400°C. with catalyst II, which likewise indicates this retardation type.

Here it must be noted that in Expt. 2 the first order type somewhat makes its appearance after the retardation type as shown in Fig. 2. As to the most highly active supported catalyst, the type changes from the retardation to the first order type according as the most highly active centre disappears. In this respect both theory and experiment agree with each other.

**Experiments on the Non-supported Catalyst.**—The non-supported catalyst is somewhat different from the above catalyst. It sometimes shows the retardation type, but sometimes does not.

(a) **The case where the retardation type does not appear:** This case is recognized in the experiments made with the less active catalysts or at relatively high reaction temperature. Fig. 3 indicates the result of the experiment made with catalyst III at 370°C.

The available surface of the non-supported catalyst is clearly small as compared with that of the supported catalyst, and accordingly the process of the gaseous molecules diffusing as far as the available surface of the catalyst must be simultaneously considered.

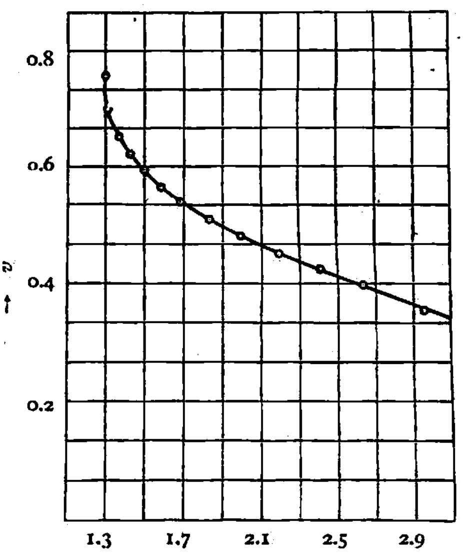

Fig. 3. Chemisorption of carbon dioxide by catalyst $III_1$ at 370°C.

In fact it has been recognized by many investigators that Fick's diffusion law is well applicable to the sorption between metals and gases.[8–13] Ward[12] derived, from Fick's diffusion law, the following equation

$$S = 2ac_0\sqrt{\frac{Dt}{\pi}} \qquad (3)$$

and showed that the equation explains the results of the experiments. In equation (3) $S$ is the amount of diffusion of the gas, being proportional to the square root of time at a given temperature and a given surface concentration ($c_0$). $a$ and $D$ are constants. By examining whether the relationship given in equation (3) is applicable to the chemisorption, we find that the relationship is fairly satisfied,

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8) E. M. Johnson and P. Larose, *J. Am. Chem. Soc.*, **46**, 1377 (1924).
9) M. V. Lombard, *Compt. rend.*, **177**, 116 (1923).
10) J. E. Lennard-Jones, *Trans. Farad. Soc.*, **28**, 333 (1932).
11) I. Langmuir and J. B. Taylor, *Phys Rev.*, **40**, 463 (1932); **44**, 423 (1933).
12) A. F. H. Ward, *Proc. Roy. Soc.* [A], **133**, 522 (1931).
13) C. J. Smithells, "*Gases and Metals*," pp. 77～136 (1937).

for example, as indicated by Fig. 4 except at the first and last parts.

As the velocity of diffusion between metals and gases, Richardson and other investigators have proposed the following equation:

$$D'=\frac{k}{d}\sqrt{p}\,\sqrt{T}e^{-\frac{b}{T}} \tag{4}$$

where $D'$ is the diffusion velocity, $p$ the pressure, $d$ the thickness of the metal, and $k$ and $b$ are constants. The diffusion velocity is thus proportional to the square root of the pressure at a given temperature. Being applied to the chemisorption, this relationship holds good except at the last part for example, as shown in Fig. 5.

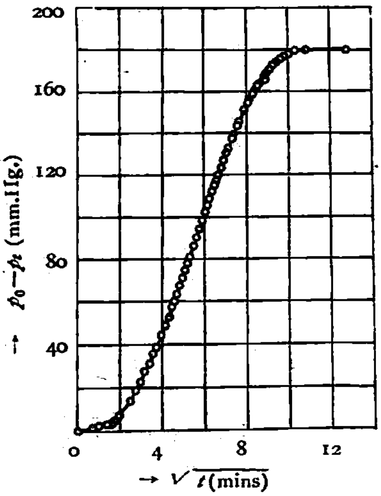

Fig. 4. $(p_0-p_t)\sim\sqrt{t}$ curve for the chemisorption of carbon dioxide by catalyst V at 360°C.

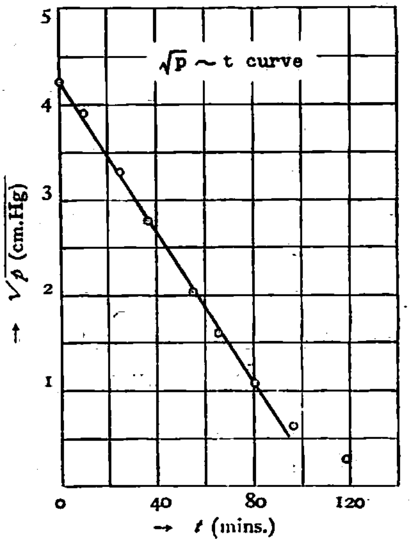

Fig. 5. $\sqrt{p}\sim t$ curve for the chemisorption of carbon dioxide by catalyst V at 360°C.

From the above considerations it can readily be supposed that the chemisorption by the non-supported catalyst simultaneously accompanies the appearance of the diffusion velocity.

b) **The case where the retardation type appears:** The retardation type makes its appearance in the experiments made with the non-supported catalysts at comparatively low reaction temperatures. For example, the result of the experiment made at 330°C. with catalyst $III_3$ is shown in Fig 6, which indicates roughly this retardation type. The case where the experiment was made at 330°C. with catalyst $III_5$ is shown in Fig. 7, which more clearly indicates the retardation type. The $\sqrt{t}$ law given in equation (3) was found to be applicable to the process following the bend $D$ of the curve in Fig. 7. This fact would most pro-

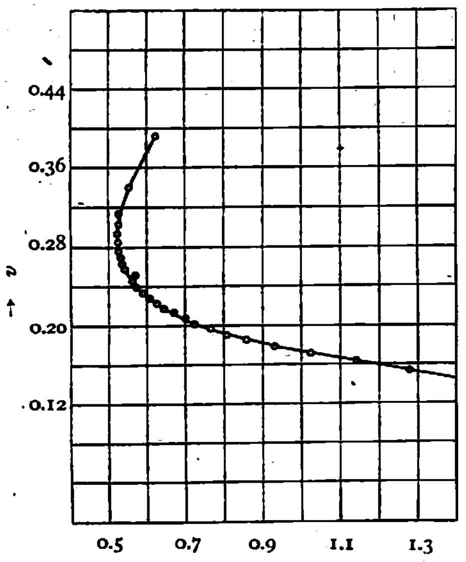

Fig. 6. Chemisorption of carbon dioxide by catalyst $III_3$ at 350°C.

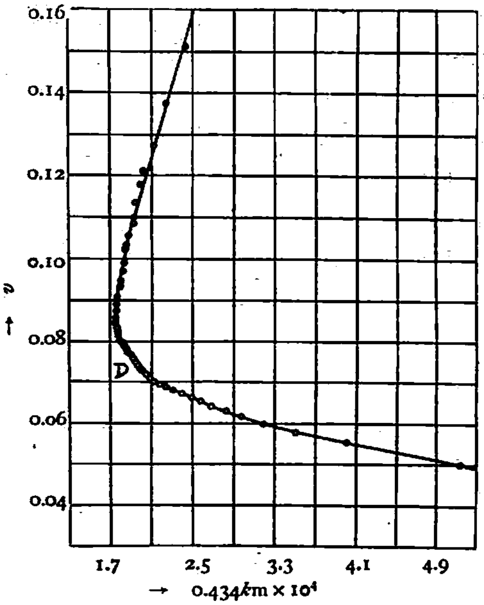

Fig. 7. Chemisorption of carbon dioxide by catalyst $III_5$ at 330°C.

perly be explained, if we consider that, at low temperatures, the self-poisoning action caused by the strong adsorption of reaction products first appears as in the experiment of the supported catalyst, and then the diffusion velocity appears simultaneously.

### 〔II〕 Presence of Active Centres of Different Characters.

Even when the catalyst is saturated with carbon dioxide the decomposition of carbon monoxide takes place. For example, when catalyst IV was saturated

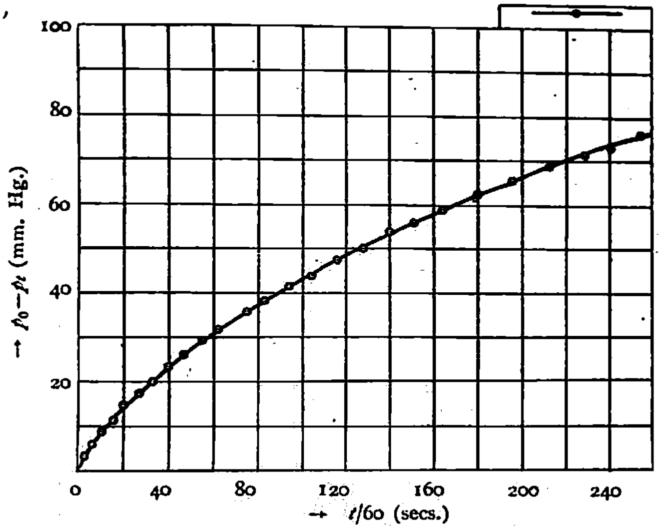

Fig. 8. Decomposition of carbon monoxide at 350°C. in the presence of catalyst IV saturated with carbon dioxide.

with carbon dioxide at 350°C. and reacted with carbon monoxide at the same temperature, the decomposition was brought about as shown in Fig. 8.

When $v \sim k_m$ is plotted according to the result, Fig. 9 is obtained, in which the appearance of the retardation type is evident.

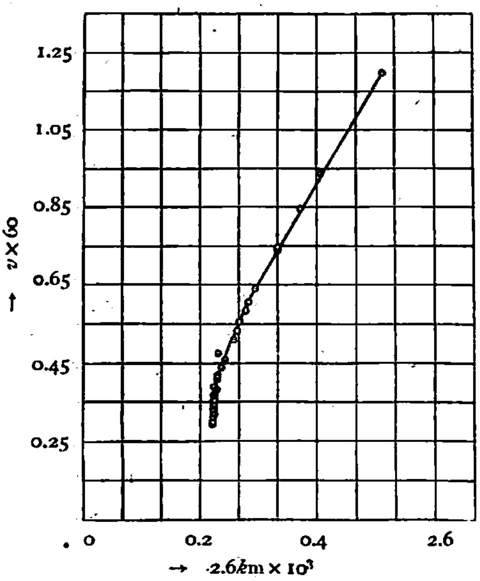

Fig. 9. Decomposition of carbon monoxide at 350°C in the presence of reduced iron saturated with carbon dioxide.

Here in this case,

$$k_m = \frac{1}{t} \ln \frac{p_0}{2p_t - p_0}$$

($p_t$ is the pressure at time $t$).

From the above experiments, it may be said that even the catalyst saturated with carbon dioxide still retains some of its active centres which can effect the decomposition of carbon monoxide. It is thus considered that on the surface of the reduced iron there exist the active centres of the following two different characters for the reactions (i) and (ii) in the chemisorption:

(i) $\mathrm{Fe} + (\mathrm{CO_2})_{\mathrm{Ads.}} = \mathrm{Fe_XO_Y} + (\mathrm{CO})_{\mathrm{Ads.}}$

(ii) $2\,(\mathrm{CO})_{\mathrm{Ads.}} = \mathrm{C} + (\mathrm{CO_2})_{\mathrm{Ads.}}$

If (i) and (ii) were to take place on the same centres, it is readily seen that the above results would never be obtained.

## [III] Activation Energy of the Chemisorption.

Employing catalyst $\mathrm{III}_{1-5}$, the effect of temperature on the chemisorption was investigated, the experimental conditions are given in Table 2 and the result is plotted in Fig. 10.

Table 2
Experimental Conditions.

| Expt. | Reaction Temperature | Initial Pressure |
|---|---|---|
| 1 | 370°C | 282.2 mm. Hg. |
| 2 | 370°C | 287.4 mm. Hg. |
| 3 | 370°C | 290.8 mm. Hg. |
| 4 | 350°C | 285.4 mm. Hg. |
| 5 | 350°C | 280.8 mm. Hg. |
| 6 | 330°C | 277.4 mm. Hg. |
| 7 | 340°C | 282.7 mm. Hg. |
| 8 | 360°C | 289.8 mm. Hg. |
| 9 | 370°C | 285.0 mm. Hg. |

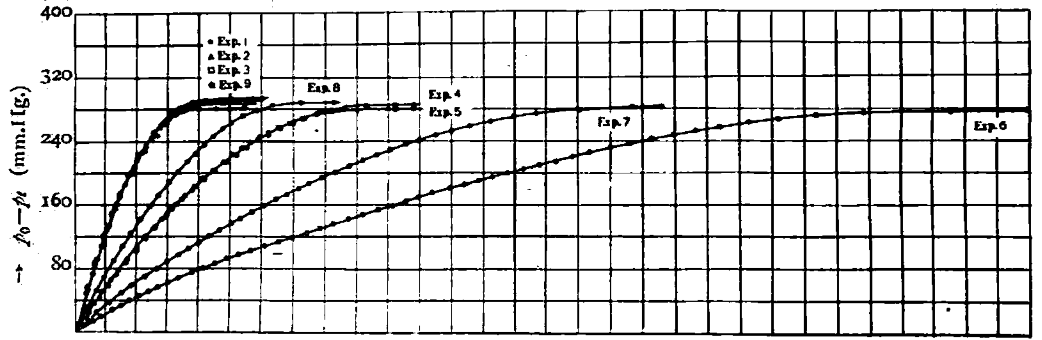

Fig. 10. Chemisorption of carbon dioxide by catalyst $III_{1-5}$ at 370°C. (Expts. 1,2,3, and 9), 360°C. (Expt. 8), 350°C. (Expts. 4 and 5), 340°C. (Expt. 7), and 330°C. (Expt. 6).

Let $t$ represent the time required to chemisorb a given amount of carbon dioxide (1 to 7 c.c. under standard conditions) and $T$ the absolute temperature. If the logarithm of $t$ is plotted on the abscissa against $1/T$ on the ordinate the relationship becomes as shown in Fig. 11

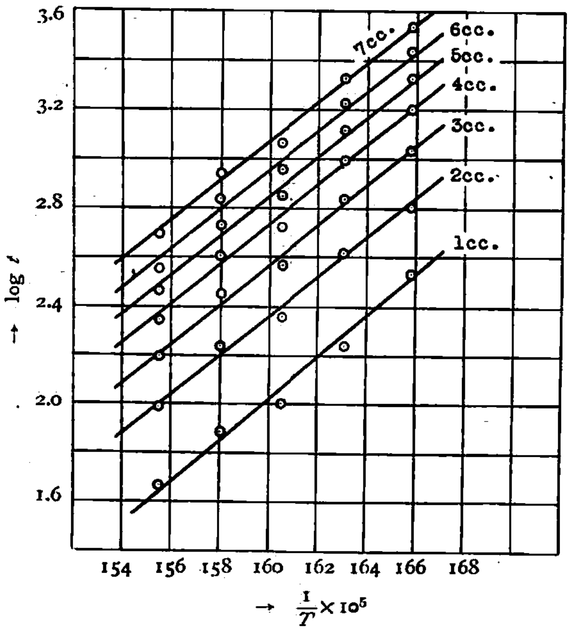

Fig. 11. Influence of temperature on the chemisorption of carbon dioxide by reduced iron (catalyst $III_{1-5}$) in the temperature range between 370°C. and 330°C.

From Fig. 11, we obtain 37.0 Kcal./g. mol for the apparent heat of activation. This value may vary slightly, depending on the conditions of the preparation of the catalysts, but it lies between 30 and 40 Kcal./g. mol for non-supported and supported catalysts when the reducing temperatures of the catalysts are of a small difference from one another.

## Summary.

1) The kinetics of the chemisorption has been studied, and it has been found that the method of analysis of the reaction velocity in the heterogeneous system first introduced by Professor S. Horiba and Dr. T. Ri is applicable in the present chemisorption phenomenon.

2) The presence of active centres of different characters on the surface of the catalysts has been observed.

3) The apparent heat of activation of the chemisorption has been found to be 37 Kcal./g. mol.

The author wishes to take this opportunity to express his thanks and appreciation to Professor S. Horiba for his guidance throughout the course of this work.

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