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

Thermodynamic Consideration of the Chemisorption.

By KIMIO KAWAKITA.

Under Professor S Horiba's direction, the author has continued the investigation into a newly detected phenomenon—the chemisorption of carbon dioxide by reduced iron, and has already stated[1,2] that some of the carbon dioxide molecules adsorbed on the surface of reduced iron reacted with the active iron atoms according to the heterogeneous chain reactions:

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

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

which have been supported by a number of experimental facts. He has also shown that reaction i) took place at highly activated points and that reaction ii) might occur at less active centres as well. In his second report,[3,4,5] it has been 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 this chemisorption reaction.

In the chemisorption of carbon dioxide by reduced iron the formation of iron oxide has been observed, but neither the formation of any particular oxide nor the existence of carbon monoxide as an intermediate product has so far been ascertained. In this report it is the intention of the author, first, to consider the possibility of the formation of these products from the thermodynamic standpoint; secondly, to identify the products; and finally, to clarify the mechanism of the chemisorption reaction.

[I] Thermodynamic Consideration of the Chemisorption Reaction.

The reactions involving the three elements, *Fe*, *O*, *C*, are of high technical interest, and a number of equilibrium studies on the reactions at higher temper-

1) K. Kawakita, *Rev. Phys. Chem. Japan*, 8, 89~116 (1934).
2) K. Kawakita, *Rev. Phys. Chem. Japan*, 11, 75~89 (1937).
3) K. Kawakita, *Rev. Phys. Chem. Japan*, 10, 200~211 (1936).
4) K. Kawakita, *Rev. Phys. Chem. Japan*, 12, 105~114 (1938).
5) K. Kawakita, *Proc. Imp. Acad. Tokyo*, 12, 61~63 (1936).

atures have already been accumulated, and among them the following may be considered reasonably reliable:

$$Fe_3O_4+CO=3FeO+CO_2, \qquad FeO+CO=Fe+CO_2,$$
$$Fe_3O_4+4CO=3Fe+4CO_2, \qquad 3Fe+2CO=Fe_3C+CO_2,$$
$$Fe_2O_3+3CO=2Fe+3CO_2, \qquad Fe_2O_3+3C=3CO+2Fe,$$
$$3Fe_2O_3+CO=2Fe_3O_4+CO_2, \qquad FeO+C=Fe+CO,$$
$$3FeO+5CO=Fe_3C+4CO_2.$$

Among these reactions the following involve either Fe and CO_2 or an iron oxide and CO_2 as reactants:

$$Fe+CO_2=FeO+CO, \qquad (A)$$
$$3Fe+4CO_2=Fe_3O_4+4CO, \qquad (B)$$
$$2Fe+3CO_2=Fe_2O_3+3CO, \qquad (C)$$
$$3FeO+CO_2=Fe_3O_4+CO, \qquad (D)$$
$$2Fe_3O_4+CO_2=3Fe_2O_3+CO. \qquad (E)$$

In these reactions, when equilibrium is established both CO and CO_2 coexist. In the chemisorption reaction in question the reactants are reduced iron and CO_2, but the products formed are iron oxide and carbon.[6] This fact may be explained by the following reactions:

$$2Fe+CO_2=2FeO+C, \qquad (F)$$
$$3Fe+2CO_2=Fe_3O_4+2C, \qquad (G)$$
$$4Fe+3CO_2=2Fe_2O_3+3C, \qquad (H)$$
$$6FeO+CO_2=2Fe_3O_4+C, \qquad (I)$$
$$4Fe_3O_4+CO_2=6Fe_2O_3+C. \qquad (J)$$

The Free Energy Changes of Reactions (A) to (J)

The free energy changes as a function of the temperature in the case of the transition of $Fe(\alpha)$ to $Fe(\beta)$, the reaction $FeO+CO=Fe(\beta)+CO_2$, and the formation of FeO, Fe_3O_4, and Fe_2O_3 are given by the equations of Chipman and Murphy[7] as follows.

$$Fe(\alpha)=Fe(\beta);\ \Delta F^\circ=-2050-5.95T\ln T+0.0034T^2+39.77T. \qquad (1)$$
$$FeO+CO=Fe(\beta)+CO_2;\ \Delta F^\circ=-3850+0.65T\ln T-0.0008T^2+0.25\times10^{-6}T^3+0.85T. \qquad (2)$$
$$Fe(\beta)+1/2O_2=FeO;\ \Delta F^\circ=-63290+1.70T\ln T-0.00175T^2+6.13T. \qquad (3)$$
$$Fe(\alpha)+1/2O_2=FeO;\ \Delta F^\circ=-65340-4.25T\ln T+0.00165T^2+45.90T. \qquad (4)$$

6) K. Kawakita, *Rev. Phys. Chem. Japan*, 11, 87 (1937).
7) J. Chipman and D. W. Murphy, *Ind. Eng. Chem.*, 25, 319~327 (1933).

$$3Fe(a)+2O_2=Fe_3O_4(a);\ \Delta F^\circ=-266570+5.30T\ lnT-0.0141T^2+57.05T. \quad (5)$$

$$2Fe(a)+3/2O_2=Fe_2O_3;\ \Delta F^\circ=-196260+0.05T\ lnT-0.00745T^2 +2.8\times10^{-6}T^3+69.30T. \quad (6)$$

From these equations the free energy changes as a function of the temperature in reactions (A) to (E) have been derived.

Combining (1) and (2), we have

$$Fe(a)+CO_2=FeO+CO;\ \Delta F^\circ=+1800-6.60T\ lnT+0.0042T^2 -0.25\times10^{-6}T^3+38.92T. \quad (A)$$

From (4) and (5),

$$3FeO+1/2O_2=Fe_3O_4(a);\ \Delta F^\circ=-70550+18.05T\ lnT-0.01905T^2-80.65T. \quad (7)$$

From (7) and (A),

$$3Fe(a)+3CO_2+1/2O_2=Fe_3O_4(a)+3CO;\ \Delta F^\circ=-65150-1.75T\ lnT -0.00645T^2-0.75\times10^{-6}T^3+36.11T. \quad (8)$$

From (2) and (3),

$$CO+1/2O_2=CO_2;\ \Delta F^\circ=-67140+2.35T\ lnT-0.00255T^2 +0.25\times10^{-6}T^3+6.98T. \quad (9)$$

From (8) and (9),

$$3Fe(a)+4CO_2=Fe_3O_4(a)+4CO;\ \Delta F^\circ=+1990-4.10T\ lnT-0.0039T^2 -1.0\times10^{-6}T^3+29.13T. \quad (B)$$

From (5) and (6),

$$2Fe_3O_4(a)+1/2O_2=3Fe_2O_3;\ \Delta F^\circ=-55640-10.45T\ lnT+0.00585T^2 +8.4\times10^{-6}T^3+93.80T. \quad (10)$$

From (B) and (10),

$$6Fe(a)+8CO_2+1/2O_2=3Fe_2O_3+8CO;\ \Delta F^\circ=-51660-18.65T\ lnT -0.00195T^2+6.4\times10^{-6}T^3+152.06T. \quad (11)$$

From (9) and (11),

$$2Fe(a)+3CO_2=Fe_2O_3+3CO;\ \Delta F^\circ=+5160-7.00T\ lnT+0.0002T^2 +2.05\times10^{-6}T^3+48.36T. \quad (C)$$

From (7) and (9),

$$3FeO+CO_2=Fe_3O_4(a)+CO;\ \Delta F^\circ=-3410+15.70T\ lnT-0.0165T^2 -0.25\times10^{-6}T^3-87.63T. \quad (D)$$

From (10) and (9),

$$2Fe_3O_4(a)+CO_2=3Fe_2O_3+CO;\ \Delta F^\circ=+11500-12.80T\ lnT+0.0084T^2 +8.15\times10^{-6}T^3+86.82T. \quad (E)$$

ΔF° for the reaction

$$C(graph.)+CO_2=2CO$$

is given by Lewis and Randall[8] as

8) G. N. Lewis and M. Randall, "*Thermodynamics and the Free Energy of Chemical Substances*," New York, p. 574 (1923).

$$\Delta F^\circ = +40910 - 4.90 T \ln T + 0.00495 T^2 - 0.51 \times 10^{-6} T^3 - 12.66 T. \quad (12)$$

From (A) and (12), we have

$$2Fe(a) + CO_2 = 2FeO + C;\ \Delta F^\circ = -37310 - 8.30 T \ln T + 0.00345 T^2 + 0.01 \times 10^{-6} T^3 + 90.50 T. \quad (F)$$

From (B) and (12),

$$3Fe(a) + 2CO_2 = Fe_3O_4(a) + 2C;\ \Delta F^\circ = -79830 + 5.70 T \ln T - 0.0138 T^2 + 0.02 \times 10^{-6} T^3 + 54.45 T. \quad (G)$$

From (C) and (12),

$$4Fe(a) + 3CO_2 = 2Fe_2O_3 + 3C;\ \Delta F^\circ = -112410 + 0.70 T \ln T - 0.01445 T^2 + 5.63 \times 10^{-6} T^3 + 134.80 T. \quad (H)$$

From (D) and (12),

$$6FeO + CO_2 = 2Fe_3O_4(a) + C;\ \Delta F^\circ = -47730 + 36.30 T \ln T - 0.03795 T^2 + 0.01 \times 10^{-6} T^3 - 162.60 T. \quad (I)$$

From (E) and (12),

$$4Fe_3O_4(a) + CO_2 = 6Fe_2O_3 + C;\ \Delta F^\circ = -17910 - 20.70 T \ln T + 0.01185 T^2 + 16.81 \times 10^{-6} T^3 + 186.30 T. \quad (J)$$

The free energy changes in reactions (A) to (J) at 360°C. calculated from the above equations are given in Table 1.

When ΔF° is minus, the system of products is considered more stable than the reactants from the standpoint of thermodynamics. As readily seen from the table, ΔF°_{633} is minus for those of (D), (F), (G), (H), and (I), and among these only (D) contains CO as one of the products. Whether CO is actually formed in the chemisorption reaction or not will be discussed below

Table 1.

Calculation of ΔF° at 360°C.

Reaction.		ΔF°_{633}(Kcal.)
$Fe(a)+CO_2=FeO+CO$	(A)	+ 1.09
$3Fe(a)+4CO_2=Fe_3O_4(a)+4CO$	(B)	+ 1.86
$2Fe(a)+3CO_2=Fe_2O_3+3CO$	(C)	+ 7.77
$3FeO+CO_2=Fe_3O_4(a)+CO$	(D)	− 1.41
$2Fe_3O_4(a)+CO_2=3Fe_2O_3+CO$	(E)	+ 19.59
$2Fe(a)+CO_2=2FeO+C$	(F)	− 12.55
$3Fe(a)+2CO_2=Fe_3O_4+2C$	(G)	− 27.60
$4Fe(a)+3CO_2=2Fe_2O_3+3C$	(H)	− 28.58
$6FeO+CO_2=2Fe_3O_4(a)+C$	(I)	− 17.54
$4Fe_3O_4(a)+CO_2=6Fe_2O_3+C$	(J)	+ 24.45

[II] Identification of *CO* as the Intermediate Product.

If CO is formed on the surface of the catalyst by the chemisorption of CO_2, it is conceivable that some of the CO molecules formed may decompose while some others may acquire sufficient energy to escape undecomposed from the surface. The identification of CO was made by the reduction of a palladous salt solution.[9]

9) J. Schmidt, "Das Kohlenoxyd seine Bedeutung und Verwendung in der technischen Chemie", Leipzig, s. 186, 194 (1935).

(1) **Experimental Details.**

A schematic drawing of the reaction vessel is shown in Fig. 1. A is the Pyrex glass vessel of 2.8 cm. in inside diameter and 14 cm. high, in the bottom of which was placed the catalyst. The temperature was raised to about 300°C.~400°C. and a steady stream of CO_2 was introduced, and finally the gas passed through the catalyst was washed with 50 cc. of 0.2% aqueous solution of palladous chloride. CO_2 from a commercial cylinder was purified before being used; reduced iron was prepared by the same method as mentioned in the first report.

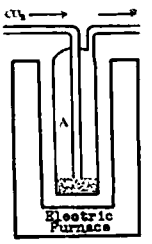

Fig. 1.

(2) **Results.**

The presence of CO can be chemically determined by the reaction

$$PdCl_2 + CO + H_2O = Pd + CO_2 + 2HCl.$$

When the rate of gas flow was 1~10 liters per hour there was no change in the palladous chloride solution, but when the rate was increased (about 40 lit./hr.) a precipitation of metallic palladium was observed. A typical example will be given below. The preparation of the catalyst and the experimental conditions are shown in Table 2.

Table 2.

Preparation of the Catalyst.

Weight of Ferric Oxide Used.	Temp. of Reduction.	Time of Reduction.	Time of Evacuation after Reduction.
5.89 g.	380°C.	24 hrs.	24 hrs. at 380°C.

Experimental Conditions.

Temperature of Chemisorption.	Rate of Flow of Carbon Dioxide.	Time of Reaction.	Weight of *Pd.* Precipitated.
380°C.	700 cc./min.	24 hrs.	0.06005 g.

In a blank test with CO_2 in the absence of the catalyst no changes were observed in the solution even when the gas was introduced continuously for three days. In another run a completely chemisorbed catalyst was re-reduced with hydrogen and when CO_2 was passed over this catalyst the palladium precipitation was again observed.

The reduction to Pd of $PdCl_2$ may be accounted for either by (i) the desorbed hydrogen or by (ii) the presence of CO produced in the chemisorption reaction.

Since the catalyst was evacuated at the temperature of reduction it is improbable that a large amount of hydrogen still remained adsorbed[10] after 24 hours' evacuation. This consideration makes (i) factor unreasonable, and leaves (ii) factor as the cause of the reaction with $PdCl_2$. From these experiments it may be said that the proposed consecutive reaction mechanism.

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

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

is justified.

[III] Thermodynamic Consideration of the Primary Reaction (*CO* Formation).

According to Table 1 the free energy changes at 360°C. are +1.09, +1.86, +7.77, and −1.41 Kcal. for reactions (A), (B), (C), and (D) respectively. Their heats of reaction will be calculated using the heat capacity equations given in Table 3 and equation (13), where ΔC_p, ΔH_o, and ΔH_T have their usual significance.[11]

$$\Delta H_T=\Delta H_o+\int_o^T \Delta C_p \cdot dT \qquad (13)$$

If the heats absorbed at the absolute zero for reactions (A), (B), and (D) are $\Delta H_{oA}=+1800cal.$, $\Delta H_{oB}=+1990cal.$, and $\Delta H_{oD}=-3410cal.$ respectively, then the

Table 3.
Heat Capacity Equations.

Substance.	Range (K°).	Equation.
$Fe(a)$	273～1033	$3.90+0.0068T$
FeO	298～1630	$11.4+0.004T$
$Fe_3O_4(a)$	293～858	$19.4+0.0506T$
CO(gas)	298～2300	$6.50+0.0010T$
CO_2(gas)	298～2300	$7.40+0.0066T-1.5\times10^{-6}T^2$

Table 4.
ΔH at 360°C.

Reaction.	*Kcal.*
(A)	+4.42
(B)	+6.66
(D)	−6.61

heats of reaction at 360°C. will be as given in Table 4. It is found as shown in Table 4 that reactions (A) and (B) are endothermic. For reaction (A) Chaudron[12]

10) According to A. Sieverts (*Z. Metallkunde*, 21, 40 (1929)), at about 400°C. less than 0.1 mg. of H_2 is adsorbed at one atmosphere per 100 grams of iron; N. I. Nikitin (*Z. anorg. u. allgem. Chem.*, 154, 134 (1926)) states that at 380°C. 5 grams of pyrophoric iron absorbs less than 6cc. (N.T.P.) of H_2 at 700 mm. Hg.—J. W. McBain, "*The Sorption of Gases and Vapours by Solids*", London, p. 306～321 (1932).

11) G. N. Lewis and M. Randall, "*Thermodynamics and the Free Energy of Chemical Substances*" New York, (1923).

12) G. Chaudron, *Ann. Chim.*, 16, 253, 268 (1921).

has calculated $\Delta H = +3.4$ *Kcal.* (17°C.) from the thermodynamic data and $\Delta H = +2$ *Kcal.* (650°C.) from the equilibrium determinations; while Tigerschiöld[13] gives $\Delta H = +1.8$ *Kcal.* (17°C.). Similarly, Chaudron obtains $\Delta H = +1.2$ *Kcal.* (17°C) from the thermodynamic data, $\Delta H = +2$ *Kcal.* (650°C.) from the equilibrium determinations for reaction (B); Tigerschiöld's calculation from the thermodynamic data gives $\Delta H = +1.4$ *Kcal.* (17°C.). For reaction (D) Chaudron obtains $\Delta H = -9$ *Kcal.* (17°C.) and $\Delta H = -6.8$ *Kcal.* (650°C.) from the thermodynamic data and the equilibrium determinations respectively; and Tigerschiöld gives $\Delta H = -4$ *Kcal.* (17°C.).

From the results of Tables 1 and 4, it is thermodynamically considered that reaction (D) should occur most readily. If the catalyst is assumed to be completely reduced, (D) can not be initiated; but (D) always follows the occurence of (A). Although $\Delta F°$ for (A) is $+1.09$ *Kcal.*, the circumstances that the existence of active iron atoms on the surface of the catalyst is certain and that one of the products, *CO*, is continuously taken away by its decomposition make the occurrence of reaction (A) plausible. Since reaction (A) and (D) are thought of as coexisting, and *FeO* is unstable as compared with Fe_3O_4 at temperatures below 570°C.,[14] it is not amiss to assume the existence of reaction (B).

The mechanism of the reaction, (A)+(D)=(B), may also be explained by the following considerations. Let the equilibrium constant of (A) be K_{pA} and that of (D) be K_{pD}, and assume that *FeO*, Fe_3O_4, *CO*, and CO_2 are confined in a closed system. Further, consider the following cases:

(1) $K_{pA} > K_{pD}$. The concentration of *CO* in (A) will be higher than that of (D), and the direction of the reaction in the closed system will be clockwise, as written,

$$\begin{array}{ccc} Fe + CO_2 & \rightarrow & FeO + CO \\ \uparrow & & \downarrow \\ 3FeO + CO_2 & \leftarrow & Fe_3O_4 + CO, \end{array}$$

and the following two conditions will be set up: (i) if the amount of *Fe* is greater than that of Fe_3O_4, the final equilibrium of the whole system will be controlled by that of (A); (ii) if the amount of *Fe* is smaller than that of Fe_3O_4, the final equilibrium will be determined by that of (D).

(2) $K_{pA} < K_{pD}$. The direction of the reaction in the closed system will be

13) M. Tigerschiöld, *Jernkontorets Ann.*, 78, 79, 104 (1923).

14) J. W. Mellor, "*A Comprehensive Treatise on Inorganic and Theoretical Chemistry*", Vol. 12, p. 622, 623; Vol. 13, p. 737 (1934).

counter-clockwise. FeO will tend to disappear, and the final equilibrium of the whole system will be determined by that of (B).

van Groningen[15] has obtained the equations $-\log K_{pA}=1000/T-1.16$ and $-\log K_{pD}=-1600/T+1.92$ for K_{pA} and K_{pD}, respectively. Hofman[16] has gained the equations $-\log K_{pA}=949/T-1.140$ and $-\log K_{pD}=-1645/T+1.935$ as well. From these equations, it is pointed out that the value of K_{pA} is smaller than that of K_{pD} in the temperature range between 300°C. and 400°C. Therefore reaction (B) will predominate in this temperature range. Thus, in the chemisorption reaction in question the formation of Fe_3O_4 is theoretically not only possible, but probable.

The presence of Fe_3O_4 was in fact confirmed thus: Magnetic and non-magnetic substances were separated from the completely chemisorbed catalyst. The magnetic substance thus isolated was treated with dilute nitric acid,[17] and the physical and chemical properties of the substance remaining insoluble in this treatment were examined.

Specific gravity of this undissolved substance was measured by the ordinary method and the value 5.04 obtained. It was observed, on the other hand, that the ferromagnetic substance insoluble in dil. HNO_3 reacts with HCl and becomes soluble and that the solution contains Fe^{++} and Fe^{+++}. These facts are considered to indicate the existence of ferrosoferric oxide.

From the identification of CO and Fe_3O_4, it now becomes certain that reaction (B), which consists of two reactions (A) and (D), is the primary reaction in the chemisorption reaction discussed in the present paper.

Finally, the reactions involving the free energy changes of the chemisorption are summarized below:

(1) $Fe+CO_2=FeO+CO$ $\quad \Delta F^\circ_{633}=+1.09$ *Kcal.*,

(2) $3FeO+CO_2=Fe_3O_4+CO$ $\quad \Delta F^\circ_{633}=-1.41$ *Kcal.*,

(3) $3Fe+4CO_2=Fe_3O_4+4CO$ $\quad \Delta F^\circ_{633}=+1.86$ *Kcal.*,

(4) $2CO=C+CO_2$ $\quad \Delta F^\circ_{633}=-14.73$ *Kcal.*,

(5) $3Fe+2CO_2=Fe_3O_4+2C$ $\quad \Delta F^\circ_{633}=-27.60$ *Kcal.*,

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

15) P. van Groningen, *Dissert. Delft*, s. 56 (1921).

16) K. Hofman, *Z. Elektrochem.*, 31, 172 (1925).

17) Pure iron is dissolved in warm dil. nitric acid, but ferrosoferric oxide formed at low temperatures is insoluble. (J. W. Mellor, "*A Comprehensive Treatise on Inorganic and Theoretical Chemistry*", Vol. 13, pp. 342, 759 (1934).)

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.

[IV] Summary.

(1) The possibility of the reactions in the chemisorption of carbon dioxide by reduced iron has been considered from the standpoint of thermodynamics, and the equations of free energy changes in the iron~carbon dioxide system have been derived and the values at 360°C. calculated.

(2) The identification of carbon monoxide as the intermediate product of the chemisorption has been made by the reduction of palladous chloride solution.

(3) It has been pointed out from the result obtained that the consecutive reaction mechanism of the chemisorption is justified.

(4) The existence of ferrosoferric oxide as one of the chemisorption products has been indicated.

(5) From the above-mentioned important facts and considerations, it has been suggested that the chemisorption in question consists of the following four reactions (1), (2), (3), and (4), and that reaction (5) is the apparent reaction in this system.

(1) $Fe+CO_2=FeO+CO$, (2) $3FeO+CO_2=Fe_3O_4+CO$,
(3) $3Fe+4CO_2=Fe_3O_4+CO$, (4) $2CO=C+CO_2$,
(5) $3Fe+2CO_2=Fe_3O_4+2C$.

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

This paper is presented to the Committee of Catalysis of the Japan Society for the Promotion of Scientific Research.

The Laboratory of Physical Chemistry,
Kyoto Imperial University.

(Received June 24, 1939.)