Isotopic Study of Water Gas Reaction Catalyzed by Platinum

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By the use of ^{13}C- and ^{18}O-labelled carbon dioxide and D_2 gas, water gas reaction over an evaporated Pt film was studied at temperatures 380—450 °C under constant elimination of water vapor with cold traps. The reaction of CO_2 and H_2 was as rapid as that of CO_2 and D_2, the mixture of H_2 and D_2 changing rapidly into an equilibrium mixture of H_2, HD, and D_2 in the course of the reaction with CO_2. The mixture of $C^{18}O_2$ and CO_2 was also rapidly equilibrated by the reaction with H_2. The exchange reactions of ^{18}O and ^{13}C between CO_2 and CO in the course of the water gas reaction were similarly observed. The theory of the stoichiometric number on the rate-determining step was applied to the results. From the results and the observed rate equation of the water gas reaction, $V=k[CO_2]^{0.6}[H_2]^{0.5}[CO]^{-0.5}$, the reaction was supposed to be caused by the sequence of steps, $CO_2 \rightleftharpoons CO_2(a)$, $H_2 \rightleftharpoons 2H(a)$, $CO_2(a)+H(a) \rightleftharpoons X(a)$, $X(a) \rightleftharpoons CO(a)+OH(a)$, $CO(a) \rightleftharpoons CO$, and $OH(a)+H(a) \rightleftharpoons H_2O$, and to be rate-controlled by the third and fourth steps, where (a) denotes the adsorbed state and X(a) is an intermediate to rule out the direct conversion of $CO_2(a)+H(a)$ into $CO(a)+OH(a)$.

The kinetics of water gas reaction,

$$CO_2 + H_2 = CO + H_2O, \qquad (1)$$

catalyzed by platinum was observed by Prichard and Hinshelwood[1)] and the rate equation was given[2)] as

$$V = kP_1P_2/(1+K_1P_1+K_2P_2)^2, \qquad (2)$$

where P_1 and P_2 are the partial pressures of CO_2 and H_2, respectively, and k, K_1 and K_2 constants. In this experiment the rate was followed by the total pressure change caused by absorption of formed water vapor by sulfuric acid kept in the reaction vessel. This equation was considered[2)] to be a prototype of the so-called Langmuir-Hinshelwood mechanism of catalysis, which assumes the rate of reaction (1) to be determined by a surface reaction of adsorbed CO_2 and adsorbed H_2. However, according to the method of Horiuti *et al.*[3)] of estimating the number $N^{\neq}$ of active centers on a catalyst surface, Eq. (2) gave an enormous value of $N^{\neq}$, *ca.* 10^{32} cm^{-2}.[3)] In a previous work[4)] the kinetics was reexamined by the use of a conventional closed circulation apparatus under constant elimination of water vapor, as in the case of Prichard and Hinshelwood, by cold traps:

$$V = k_pP_1^{0.6}P_2^{0.5}P_3^{-0.5}. \qquad (3)$$

This differs from Eq. (2) especially with regard to the dependence on P_3, *i.e.*, the partial pressure of CO, and gave[4)] the value of $N^{\neq}$ at 7.3×10^{14} cm^{-2}, which is of a reasonable order of magnitude as the number of metal atoms exposed on catalyst surface. As regards such a difference in kinetics, Eq. (3) suggests the possibility that the mechanism of (1) differs from those proposed.[1,5)] We have followed the redistribution of ^{13}C and/or ^{18}O atoms between carbon dioxide and monoxide, and that of deuterium atoms in hydrogen gas in the course of reaction. The results were analyzed in reference to the theory of the stoichiometric number[6,7)] and an appropriate reaction mechanism was proposed.

Experimental

Materials. Pure carbon dioxide (Takachiho Chemical Industrial Co., Ltd.) was purified further by repeated distillation in a vacuum., Pure carbon monoxide (*ibid.*) was purified by being passed through copper gauge heated at *ca.* 300 °C and then a trap cooled by liquid nitrogen. Hydrogen and deuterium gas from cylinders were purified by being passed through heated Pd–Ag thimbles.

Carbon dioxide labelled by ^{13}C (Merck Sharp and Dohme Co., Ltd., Canada) was purified by repeated distillation in a vacuum. Carbon dioxide labelled by ^{18}O (Yeda Research and Development Co., Ltd., Israel) and that supplied by a reaction at *ca.* 300 °C of heavy oxygen gas of *ca.* 90 ^{18}O-atomic percents with active carbon supporting platinum were used. They were purified by distillation in a vacuum. Catalysts were platinum films evaporated on the inner surface of a reaction vessel immersed in an ice water bath and preliminarily sintered in a vacuum at 480 °C for 30 min and then 410 °C for 2 hr.

Procedure and Results. The apparatus was similar to that used in a previous work,[4)] *viz.*, a conventional closed circulation system equipped with a mercury manometer and two dry ice traps on both sides of the reaction vessel. The whole apparatus was made of Pyrex glass.

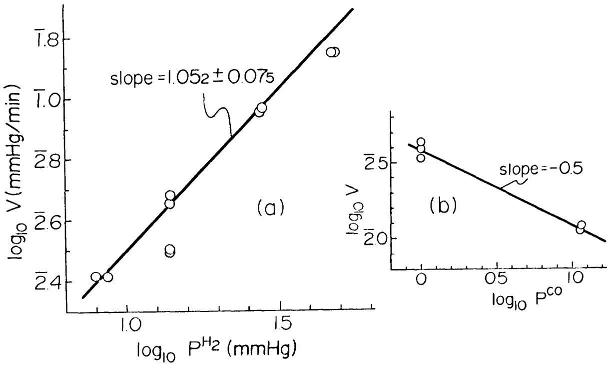


Fig. 1. Pressure dependence of the reaction rate.
(a), $\log_{10} V$ (mmHg/min) *vs.* $\log_{10} P_2$ (H_2, mmHg) at 410 °C: P_1 (CO_2) $= P_2$, P_3 (CO) $= 1.0 \pm 0.04$ mmHg.
(b), $\log_{10} V$ *vs.* $\log_{10} P_3$ at 410 °C: $P_1 = P_2 = 14.9 \pm 0.1$ mmHg.

1. Rate Equation: Rate Eq. (3) was confirmed by two series of experiments with a 1 : 1 mixture of CO_2 and H_2. The results of the first series are shown in Fig. 1(a) where the rate was observed at $P_3 = 1$ mmHg. The rate is proportional to $P_2^{1.1}$ in conformity with Eq. (3). In the second series the dependence of the rate on P_3 was examined by addition of 10 mmHg CO to a 1 : 1 mixture of CO_2 and H_2.

The results are shown in Fig. 1(b) which also confirms Eq. (3).

2. *Kinetic Isotope Effect with Respect to Hydrogen and H_2–D_2 Equilibration*: By the use of a 1 : 1 mixture of CO_2 and H_2 or D_2, it was found that the isotope effect on the rate was absent at temperatures 386—459 °C (Fig. 2).

In the course of reaction of a mixture of 18.2 mmHg CO_2, 18.2 mmHg H_2, and 10.8 mmHg D_2 at 410 °C, the equilibration reaction $H_2+D_2=2HD$ was completed in the first 6 minutes, whereas as little as 0.3 mmHg of the total pressure decrease had proceeded in reaction (1).

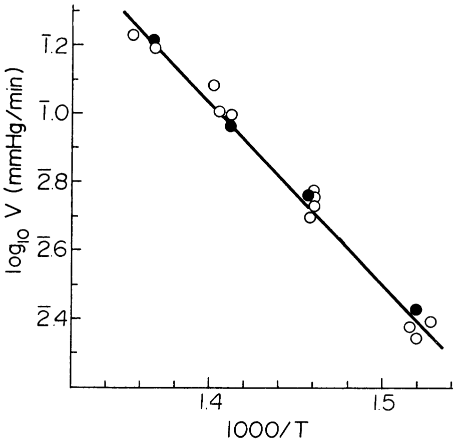


Fig. 2. Kinetic isotope effect of hydrogen: ●, reaction of CO_2 and D_2 at P_1 $(CO_2)=P_2$ $(D_2)=$ 13.90±0.08 mmHg, P_3 (CO)=1.0±0.04 mmHg; ○, reaction of CO_2 and H_2 at $P_1=P_2$ $(H_2)=13.89\pm0.11$ mmHg, $P_3=1.0\pm$ 0.04 mmHg.

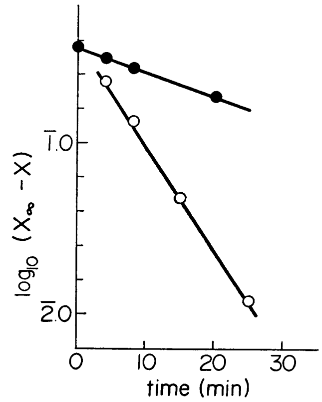


Fig. 3. The equilibration, $C^{18}O_2+CO_2=2CO^{18}O$, at 410 °C:
○, in the presence of Pt at $P_1(CO_2)=21.5\pm1$ mmHg, $P_2(H_2)=24\pm1$ mmHg, $P_3(CO)=3.5\pm0.2$ mmHg; ●, in the absence of catalyst at $P_1=19.3$ mmHg, $P_2=$ 19.1 mmHg, $P_3=5.5$ mmHg.

3. *Equilibration of Oxygen Isotope in CO_2 Gas*: Equilibration $C^{18}O_2+CO_2=2CO^{18}O$ was observed by addition of 8 mmHg ^{18}O-labelled CO_2 (79.8% $C^{18}O_2$, 19.0% $CO^{18}O$, and 1.2% CO_2) to a mixture of 25.0 mmHg H_2, 14.5 mmHg CO_2, and 3.3 mmHg CO. The result is shown in Fig. 3 where X is the mole fraction of $CO^{18}O$ in carbon dioxide and X_∞ the equilibrium value of X. The rate V_e of the equilibration was evaluated by the equation

$$N\mathrm{d}X/\mathrm{d}t = V_e(X_\infty - X), \tag{4}$$

where N is the number of carbon dioxide molecules in the reaction system. This equation, being correct in the absence of reaction (1), is applicable to the present case where the decrease of P_1 was as small as 0.6 mmHg and the atomic fraction of ^{18}O in carbon dioxide was kept constant at 0.358± 0.001. Equilibration took place without catalyst as seen in Fig. 3 and was enhanced by the platinum catalyst by as much as 3.6×10^{17} molecules/s; the rate is far greater than that of reaction (1) which was estimated at 2.8×10^{15} molecules/s just before the introduction of ^{18}O-labelled CO_2.

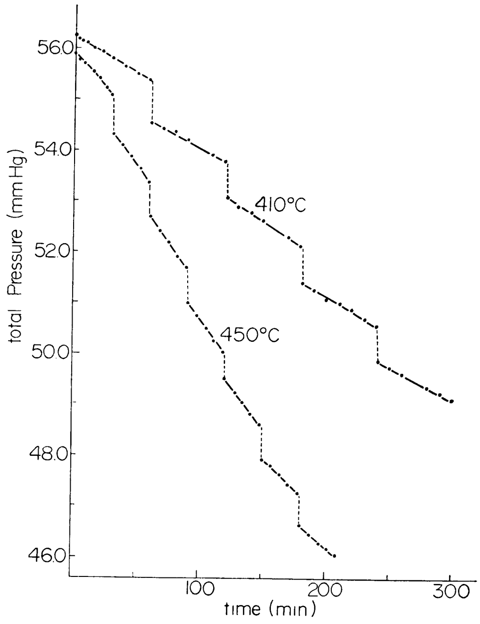


Fig. 4. Time courses of the reaction at 410 °C (runs V.6) and 450 °C (V.8).

4. *Exchanges of ^{18}O and ^{13}C between CO_2 and CO*: In order to see the effect of trapped water on the exchange reactions, several runs of reaction of a 1 : 1 mixture of normal CO_2 and H_2 were conducted at 410 °C and the formed water vapor amounting to *ca.* 9 mmHg was trapped. The exchange reaction was then observed with a mixture of 15 mmHg CO, 21 mmHg H_2, and 21 mmHg labelled CO_2. Typical time courses of the total pressure at 410 and 450 °C are shown in Fig. 4, where steep decreases of the total pressure were caused by samplings of the reacting gas. Sampled gas was analyzed mass spectrometrically for the atomic fractions of ^{18}O, (Z_1 and Z_3), and those of ^{13}C, (Y_1 and Y_3), in CO_2 and CO, respectively. In Fig. 5 Z_1 and Z_3 were plotted

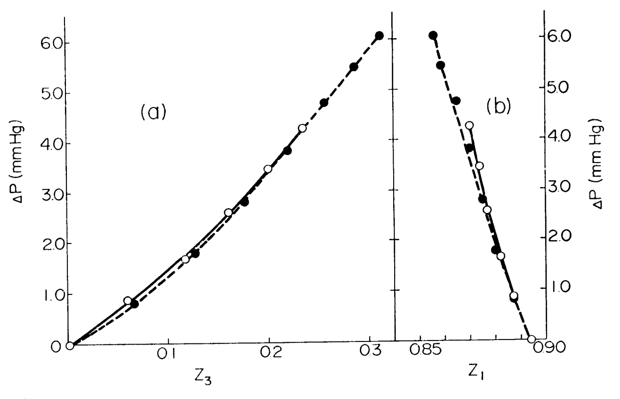


Fig. 5. Exchange reaction of ^{18}O between CO_2 and CO. (a), ΔP(mmHg) *vs.* Z_3 and (b), ΔP *vs.* Z_1: ○, 410 °C (runs V.6); ●, 450 °C (V.8).

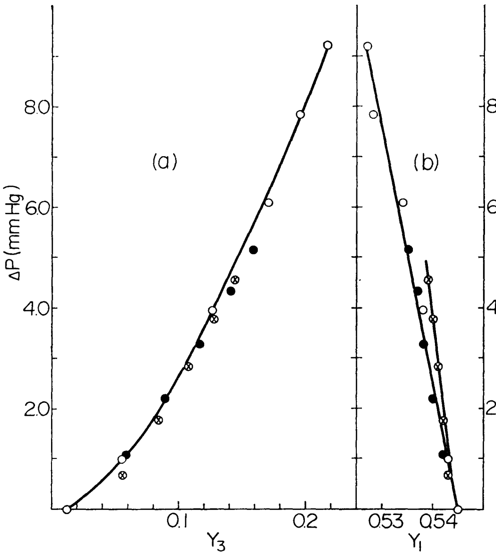


Fig. 6. Exchange reaction of ^{13}C between CO_2 and CO. (a), ΔP (mmHg) *vs.* Y_3 and (b), ΔP *vs.* Y_1: ⊗, 410 °C (V.31); ●, 450 °C (V.32); ○, 450 °C (V.34).

Table 1. Equilibration $^{13}C^{18}O+CO={}^{13}CO+C^{18}O$

Runs	Reaction time (min)	CO (x_1)	^{13}CO (x_2)	$C^{18}O$ (x_3)	$^{13}C^{18}O$ (x_4)	$\frac{x_1x_4}{x_2x_3}$
VI. 7	0	0.985	0.011	0.004	0.000	
(410 °C)	360	0.910	0.042	0.038	0.010	5.7
	660	0.870	0.060	0.055	0.015	4.0
	1030	0.831	0.077	0.073	0.019	2.8
	1330	0.811	0.087	0.082	0.020	2.3
	1750	0.787	0.097	0.094	0.022	1.9
VI. 9	0	0.984	0.011	0.005	0.000	
(450 °C)	180	0.914	0.041	0.035	0.010	6.4
	360	0.865	0.062	0.056	0.017	4.2
	540	0.835	0.074	0.069	0.022	3.6
	720	0.810	0.086	0.080	0.024	2.8
	900	0.791	0.094	0.088	0.027	2.6

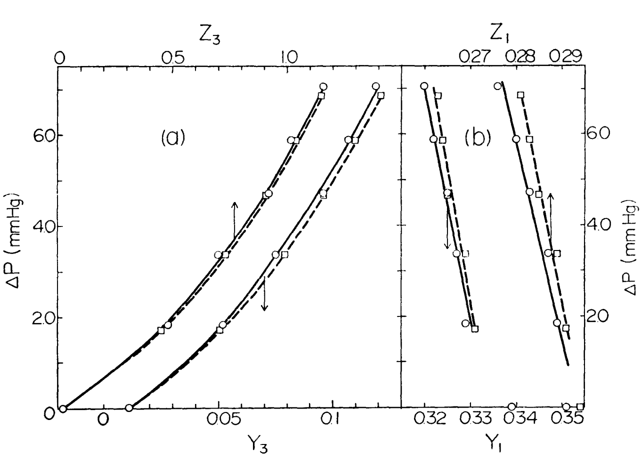


Fig. 7. Simultaneous exchange reactions of ^{13}C and ^{18}O between CO_2 and CO.

(a), ΔP (mmHg) *vs.* Y_3 or Z_3 and (b), ΔP *vs.* Y_1 or Z_1: ○, 410 °C (runs VI.7); □, 450 °C (VI.9).

against ΔP, *i.e.*, the sum of the total pressure decrements caused by the progress of reaction (1) but not by sampling. Figure 6 shows the changes of Y_1 and Y_3 with ΔP.

The exchange of ^{13}C as well as of ^{18}O between CO_2 and CO in the course of reaction (1) were followed simultaneously by the use of a mixture of ^{13}C- and ^{18}O-labelled CO_2. The results are shown in Fig. 7. In this case an equilibration, $CO+{}^{13}C^{18}O={}^{13}CO+C^{18}O$, of isotopes in CO took place additionally (Table 1), which was far slower than the equilibration of isotopes in CO_2 (Table 2).

5. Hydrogen Exchange between D_2 and H_2O: A mixture of 22.0 mmHg CO_2, 15.1 mmHg CO, and 22.1 mmHg D_2 was introduced on the catalyst successively to the runs described above. During reaction (1) which gave rise to 8.7 mmHg of the total pressure decrease, D atomic fraction of D_2 gas changed from 0.991 to 0.974, that is, dilution of D_2 by protium from condensed water was slight.

Discussion

Application of the Theory of Stoichiometric Number. The theory of stoichiometric number[6,7] assumes that all the reaction routes[8] of reaction (1) and accompanying exchanges of ^{13}C and ^{18}O are single. The stoichiometric number $\nu(s)$ of step s is the number of acts of step s necessary to complete one act of the overall reaction, *i.e.*, (1). The forward or the backward unidirectional rate of exchange is defined by the formation rate, V_{+c} or V_{-c}, of ^{13}CO or CO_2, respectively, in the reaction between pure $^{13}CO_2$ and CO, *viz.*, a particular case with $Y_1=1$ and $Y_3=0$. According to mass balance of carbon atoms irrespective of isotopic difference, it follows that

$$V = -dP_1/dt = dP_3/dt = V_{+c}-V_{-c}, \tag{5}$$

and the mass balance of ^{13}C gives

$$-d(Y_1P_1)/dt = Y_1V_{+c}-Y_3V_{-c} = d(Y_3P_3)/dt. \tag{6}$$

Solving these equations with respect to V_{+c} and V_{-c}, we have

$$V_{+c}/V_{-c} = 1 + (Y_1-Y_3)(dP_1/dY_1)/P_1 \tag{7a}$$

or

$$V_{+c}/V_{-c} = 1/[1-(Y_1-Y_3)(dP_3/dY_3)/P_3]. \tag{7b}$$

When step r in the single route of the exchange reaction is so slow as to be rate-determining for reaction (1), V_{+c} or V_{-c} might be equal to the forward or backward unidirectional rate, V_+ or V_-, of reaction (1), respectively. The stoichiometric number $\nu(r)$ of step r is then given by[6]

$$\nu(r) = -\Delta G/[RT\ln(V_+/V_-)], \tag{8}$$

where $-\Delta G$ is the affinity of reaction (1) given by

$$-\Delta G = RT\ln(K_pP_1P_2/P_3P_4). \tag{9}$$

K_p is the equilibrium constant of reaction (1) and P_4 the partial pressure of water. On the other hand, when the exchange reaction takes place without step r, V_{+c} and V_{-c} may be far larger than V_+ and V_-, and the value of V_{+c}/V_{-c} might be close to unity. Accordingly, ν_{ex} defined by

$$\nu_{ex} = -\Delta G/[RT\ln(V_{+c}/V_{-c})].$$

becomes infinitely large in this case.[9]

For the exchange of ^{18}O, similar equations are derived as

$$V = \mathrm{d}P_3/\mathrm{d}t = V_{+\mathrm{o}} - V_{-\mathrm{o}} \tag{10}$$

and

$$\mathrm{d}(Z_3P_3)/\mathrm{d}t = Z_1V_{+\mathrm{o}} - Z_3V_{-\mathrm{o}}, \tag{11}$$

where it is noteworthy that the exchange of ^{18}O between carbon monoxide and water was assumed not to take place at all. It follows from Eqs. (10) and (11) that

$$V_{+\mathrm{o}}/V_{-\mathrm{o}} = 1/[1-(Z_1-Z_3)(\mathrm{d}P_3/\mathrm{d}Z_3)/P_3]. \tag{12}$$

To evaluate the ratios of $V_{+\mathrm{C}}/V_{-\mathrm{C}}$ and $V_{+\mathrm{O}}/V_{-\mathrm{O}}$, the terms $\mathrm{d}P_1/\mathrm{d}Y_1$, $\mathrm{d}P_3/\mathrm{d}Y_3$, and $\mathrm{d}P_3/\mathrm{d}Z_3$ in Eqs. (7a), (7b), and (12) were approximated by $-\mathrm{d}\Delta P/\mathrm{d}Y_1$, $\mathrm{d}\Delta P/\mathrm{d}Y_3$, and $\mathrm{d}\Delta P/\mathrm{d}Z_3$, respectively, which can be determined by Figs. 5, 6, and 7. The values of $V_{+\mathrm{O}}/V_{-\mathrm{O}}$ given in Figs. 8 and 9 considerably fluctuate due to the large errors of estimation of terms, $\mathrm{d}P_3/\mathrm{d}Z_3$ *etc.*

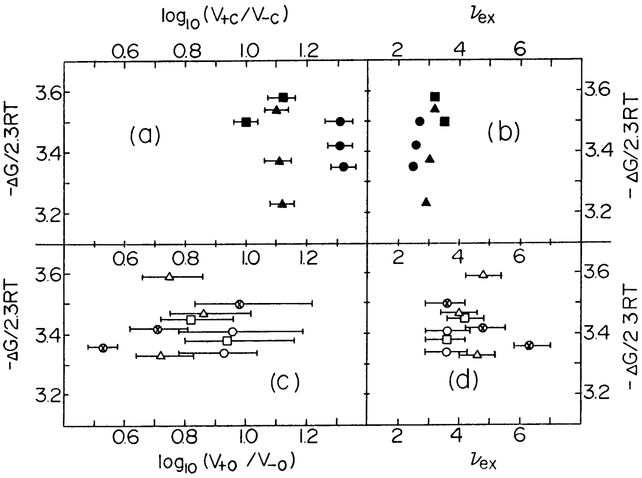


Fig. 8. $\log_{10}(V_{+\mathrm{C}}/V_{-\mathrm{C}})$, $\log_{10}(V_{+\mathrm{O}}/V_{-\mathrm{O}})$ and ν_{ex} *vs.* $-\Delta G/2.3RT$.
(a), $\log_{10}(V_{+\mathrm{C}}/V_{-\mathrm{C}})$ *vs.* $-\Delta G/2.3\,RT$. $V_{+\mathrm{C}}/V_{-\mathrm{C}}$ was evaluated according to Eq. (7a). ●, 410 °C (runs V.31); ■, 450 °C (V.32); ▲, 450 °C (V.34)
(b), ν_{ex} (calculated from the data (a)) *vs.* $-\Delta G/2.3RT$.
(c), $\log_{10}(V_{+\mathrm{O}}/V_{-\mathrm{O}})$ *vs.* $-\Delta G/2.3RT$: ○, 410 °C (V.6); ⊗, 450 °C (V.8); □, 410 °C (V.29); △, 450 °C (V.35).
(d), ν_{ex} (calculated from the data (c)) *vs.* $-\Delta G/2.3RT$.

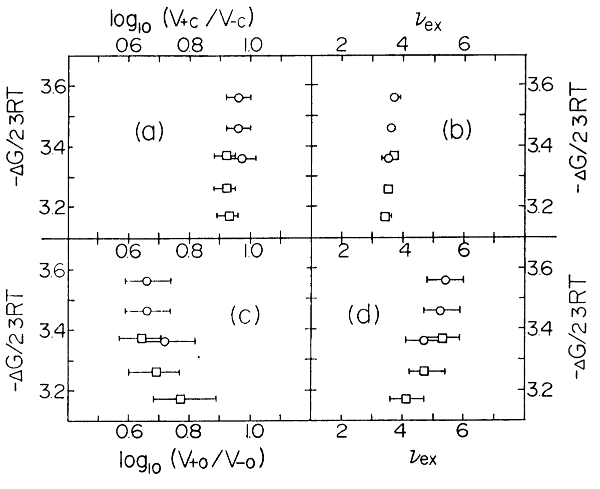


Fig. 9. $\log_{10}(V_{+\mathrm{C}}/V_{-\mathrm{C}})$, $\log_{10}(V_{+\mathrm{O}}/V_{-\mathrm{O}})$ and ν_{ex} *vs.* $-\Delta G/2.3RT$: ○, 410 °C (runs VI.7); □, 450 °C (VI.9).
(a), $\log_{10}(V_{+\mathrm{C}}/V_{-\mathrm{C}})$ *vs.* $-\Delta G/2.3RT$. $V_{+\mathrm{C}}/V_{-\mathrm{C}}$ was evaluated according to Eq. (7a).
(b), ν_{ex} (calculated from data (a)) *vs.* $-\Delta G/2.3RT$.
(c), $\log_{10}(V_{+\mathrm{O}}/V_{-\mathrm{O}})$ *vs.* $-\Delta G/2.3RT$.
(d), ν_{ex} (calculated from the data (c)) *vs.* $-\Delta G/2.3RT$.

Applying the present method of analysis to the experimental result of hydrogen exchange between D_2 and H_2O, the ratio of the forward unidirectional rate $V_{+\mathrm{H}}$ of this exchange to the reverse one, $V_{-\mathrm{H}}$, was estimated to be *ca.* 32.

Adsorption of Gaseous Components. The steps of adsorption of CO_2 and H_2 and desorption of CO and H_2O are discussed first in connection with the mechanism of reaction (1).

A large number of studies on hydrogen adsorption on platinum[10)] confirm a rapid and reversible chemisorption to form adsorbed hydrogen atoms. The present results of rapid equilibration of deuterium in hydrogen gas and the fact that V was proportional to $P_2^{0.5}$ suggest that chemisorption of hydrogen is so rapid as to be nearly in equilibrium and reaction (1) is rate-determined by a surface reaction of an adsorbed hydrogen atom.

Carbon dioxide has been reported[10)] to be hardly chemisorbed on platinum, but one of the authors (M.M.) observed[11)] that adsorption of CO_2 on platinum film was perceptibly enhanced by the presence of equimolar hydrogen gas at temperatures above room temperature.

Adsorption of CO on platinum was found to take place reversibly and as rapidly as hydrogen[12)] and, furthermore, it may be so strong as to retard reaction (1) by occupying active sites on platinum surface according to the fact that V was proportional to $P_3^{-0.5}$.

In the case where CO_2 adsorption is dissociative to form adsorbed CO, ^{13}C or ^{18}O might be exchanged between CO_2 and CO much faster than in reaction (1) on account of the rapid and reversible adsorption of CO_2 and CO and, accordingly, the ratios $V_{+\mathrm{O}}/V_{-\mathrm{O}}$ and $V_{+\mathrm{C}}/V_{-\mathrm{C}}$ might be close to unity against the observed results. The dissociative adsorption of CO_2 to form adsorbed CO is, thus, ruled out. The fact that the randomization of ^{18}O in CO_2 took place in the absence of platinum catalyst (Fig. 3) suggests that CO_2 adsorbed on glass surface may interact with OH groups to give an intermediate of oxygen exchange such as bicarbonate ion. However, such an intermediate is not considered to be effective for reaction (1) and isotope exchange between CO_2 and CO, since the decomposition of bicarbonate ion to CO is not plausible, and these reactions were far slower than the randomization of ^{18}O in CO_2 (Table 2).

The value of $V_{+\mathrm{H}}/V_{-\mathrm{H}}$ estimated to be *ca.* 32 indicates that the step of H_2O desorption is practically irreversible in the course of reaction (1) carried out with cold traps. The adsorbed state of H_2O may be dissociative to result in the observed though slight hydrogen exchange.

Reaction Scheme and Relative Rates of Constituent Steps. According to the above discussions the water gas reaction consists of three rapid and reversible adsorption steps,

$$CO_2 \overset{1}{\longleftrightarrow} CO_2(a), \tag{13·1}$$

$$H_2 \overset{2}{\longleftrightarrow} 2H(a), \tag{13·2}$$

Table 2. Redistribution of ^{13}C and ^{18}O in CO_2

Runs	Reaction time (min)	Mole fraction of CO_2	$^{13}CO_2$	^{18}COO	$^{13}C^{18}OO$	$C^{18}O_2$	$^{13}C^{18}O_2$	Y_1	Z_1
VI. 7 (410 °C)	0	0.321	0.325	0.115	0.012	0.225	0.002	0.339	0.291
		(0.332	0.170	0.273	0.140	0.056	0.029)		
	360	0.339	0.167	0.275	0.135	0.057	0.027	0.329	0.289
		(0.339	0.166	0.276	0.135	0.056	0.027)		
VI. 8 (450 °C)	0	0.319	0.324	0.115	0.012	0.227	0.003	0.339	0.293
		(0.330	0.169	0.274	0.140	0.057	0.029)		
	180	0.336	0.167	0.276	0.136	0.057	0.028	0.331	0.291
		(0.336	0.166	0.276	0.136	0.057	0.028)		

Values in parentheses are those in equilibrium at the observed values of Y_1 and Z_1 of CO_2.

and

$$CO \overset{3}{\longleftrightarrow} CO(a), \tag{13·3}$$

and desorption of H_2O as

$$OH(a) + H(a) \overset{4}{\longleftrightarrow} H_2O, \tag{13·4}$$

which may be practically irreversible on account of constant condensation of H_2O vapor. $CO_2(a)$ is now assumed, as the simplest case, to be directly converted into CO(a) by the step

$$CO_2(a) + H(a) \overset{5'}{\longleftrightarrow} CO(a) + OH(a). \tag{13·5'}$$

The relative rates of the above steps and the propriety of step 5′ are now discussed by applying the theory of the stoichiometric number[6)] on the results of the present experiments.

The ratio V_+/V_- with respect to reaction (1) is given by

$$V_+/V_- = \prod_s (v_{+s}/v_{-s}), \ (s=1, 2, 3, 4 \text{ and } 5') \tag{14}$$

where v_{+s} and v_{-s}, respectively, are the forward and the backward unidirectional rates of constituent steps s's. Similarly we have

$$V_{+c}/V_{-c} = \prod_s (v_{+s}/v_{-s}), \ (s=1, 3 \text{ and } 5') \tag{15}$$

for the ^{13}C-exchange between CO_2 and CO. If ^{18}O-exchange between CO and H_2O were negligible as compared with that between CO_2 and CO, the latter exchange consists of steps 1, 3, and 5′ and it follows that

$$V_{+O}/V_{-O} = V_{+c}/V_{-c}. \tag{16}$$

However, the results given in Figs. 8 and 9 are not the case, hence ^{18}O-exchange between CO and H_2O is not negligible.

It follows from Eqs. (14) and (15) that

$$V_+/V_- = (V_{+c}/V_{-c})(v_{+2}/v_{-2})(v_{+4}/v_{-4}),$$

where

$$v_{+2}/v_{-2} \cong 1$$

on account of step 2 being nearly in equilibrium. Each act of the present five steps results in one act of reaction (1), *viz.*, $\nu(r)$ of Eq. (8) is unity, whatever the rate-determining step is. We have thus

$$-\Delta G/2.3RT = \log_{10}[(V_{+c}/V_{-c})(v_{+4}/v_{-4})] \tag{17}$$

The value of $\log_{10}(V_{+C}/V_{-C})$ varied from 0.9 to 1.3 for $-\Delta G/2.3RT$=3.2—3.6 as shown in Figs. 8 and 9 and, accordingly, it follows from Eq. (17) that

$$v_{+4}/v_{-4} \cong 10^2. \tag{18}$$

This shows the practical irreversibility of step 4 and, consequently, that the irreversible transfer of ^{18}O from CO to H_2O affects the ^{18}O-exchange between CO_2 and CO.

The propriety of step 5′ is now investigated. From Eq. (15) it follows that

$$V_{+c}/V_{-c} = v_{+5'}/v_{-5'},$$

taking account of the equilibria of steps 1 and 3, *viz.*,

$$v_{+1}/v_{-1} \cong 1 \cong v_{+3}/v_{-3}. \tag{20}$$

In reference to the steady state condition of reaction (1)

$$V = v_{+1} - v_{-1} = v_{+5'} - v_{-5'},$$

and the value 8 to 20 of V_{+C}/V_{-C}, it follows from Eqs. (19) and (20) that

$$v_{-1} \gg v_{+5'},$$

which indicates that the ^{18}O-exchange between CO and H_2O is negligibly slower than that between CO and CO_2. Consequently, Eq. (16) might contradict the observed result. The next simplest set of steps to fit the experimental results in place of step 5′ is

$$CO_2(a) + H(a) \overset{5}{\longleftrightarrow} X(a) \tag{13·5}$$

and

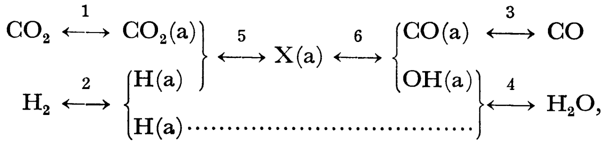
$$X(a) \overset{6}{\longleftrightarrow} CO(a) + OH(a), \tag{13·6}$$

where X(a) is an intermediate like formate ion in its composition. In this case the effect of the ^{18}O-exchange between CO and H_2O on the rate of that between CO and CO_2 depends on how far reaction (1) is rate-controlled by steps 5 and 6. Taking account of X(a) decomposing into CO(a)+OH(a) by a rate of v_{+6} and into $CO_2(a)$+H(a) by v_{-5}, ^{18}O transfer from CO(a) to H_2O might affect the ^{18}O-exchange between CO_2 and CO in a case where v_{+6} is not negligibly smaller than v_{-5}. Furthermore, taking account of the steady state condition

$$V = v_{+5} - v_{-5} = v_{+6} - v_{-6},$$

step 6 is concluded to be the slowest in conformity with the observed slow randomization of ^{18}O and ^{13}C in CO gas (Table 1).

The simplest scheme applicable to reaction (1) catalyzed by platinum is thus concluded to be



where steps 1, 2, and 3 are so fast as to be nearly in equilibria, step 4 is practically irreversible, and the reaction is rate-controlled by step 5 and a slower step 6.

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8) "Reaction route" of reaction (1) implies a linearly independent combination of constituent steps giving (1) as an overall reaction. For instance, the number of routes of the simple hydrogen electrode reaction, $2H^+ + 2e = H_2$, is single if it consists of steps $H^+ + e \rightleftharpoons H(a)$ and $2H(a) \rightleftharpoons H_2$, whereas two when another independent step, $H^+ + H(a) + e \rightleftharpoons H_2$, takes place additionally (*cf.* Ref. 6). H^+, e, and H(a) are proton in liquid phase, free electron in electrode metal and hydrogen atom adsorbed on electrode surface, respectively.

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