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APPLICATION OF THE THEORY OF STOICHIOMETRIC NUMBER DETERMINATION OF THE RATE-DETERMINING STEP: THE MECHANISM OF WATER-GAS SHIFT REACTION CATALYZED BY PLATINUM

By

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Abstract

The mechanism of water-gas shift reaction, $CO+H_2O=CO_2+H_2$, catalyzed by evaporated platinum films was investigated by means of tracers of ^{13}C and ^{18}O over the temperature from 410 to 450°C on the basis of the theory of stoichiometric number determination of the rate-determining step. The stoichiometric number ν_r of the rate-determining step was determined to be unity by tracing the transfer of carbon atoms between CO and CO_2 by ^{13}C, *i.e.* the rate-determining step consists in any constituent step of transfer of carbon atoms. The transfer of oxygen atoms among CO, H_2O and CO_2 traced by ^{18}O, which was observed simultaneously with the former, showed that the ratio of the total forward rate of transfer of oxygen atoms from CO to CO_2 and H_2O to its reverse total rate is close to unity, which enables us to exclude several steps of the constituent steps of transfer of carbon atoms from being rate-determining. Assuming that the reaction follows the sequence of steps, $CO \overset{1}{\rightleftarrows} CO(a)$, $H_2O \overset{2}{\rightleftarrows} H(a)+OH(a)$, $CO(a)+OH(a) \overset{3}{\rightleftarrows} X(a)$, $X(a) \overset{4}{\rightleftarrows} CO_2(a)+H(a)$, $CO_2(a) \overset{5}{\rightleftarrows} CO_2$ and $2H(a) \overset{6}{\rightleftarrows} H_2$, it is concluded from the above results that step 4 or 5 is rate-determining, where (a) denotes the adsorbed state and X(a) is an intermediate; with reference to the rate equation of the reverse reaction previously observed, step 4 is inferred to be rate-determining. Other mechanisms are discussed, and inferred to be less plausible than the above mechanism.

§ 1. Introduction

The investigations of isotopic exchanges accompanied by an overall reaction and of their interrelation with the latter are utilized to clarify the reaction mechanism. HORIUTI has introduced the concept of stoichiometric numbers ν_s's of elementary reactions[1] (termed steps in what follows) and

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developed the method for determining the stoichiometric number ν_r of the rate-determining step by observing a relevant isotopic exchange simultaneously with the overall reaction[2,3]. This method has been applied to various heterogeneous catalysis by many researchers[3,4].

The present author previously investigated the kinetics and mechanism of water-gas shift reaction[5,6],

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

catalyzed by evaporated platinum films under the particular experimental conditions where the reaction proceeds reversely by eliminating water vapor produced from CO_2 and H_2 with cold traps (-78°C). The results are summarized as follows.

i) The rate equation observed is

$$-V = k_p (P^{H_2})^{0.5} (P^{CO_2})^{0.6} (P^{CO})^{-0.5}, \qquad (2)$$

where $-V$ is the net rate of the reverse reaction of (1), k_p the rate constant and P^i ($i = H_2$, CO_2 and CO) partial pressure of species i, over a range of partial pressures of $P^{H_2} = 6 \sim 100$, $P^{CO_2} = 6 \sim 100$ and $P^{CO} = 1 \sim 20$ mmHg, at a reaction temperature of 410°C. The activation energy, $E_p = RT^2 \, d\ln k_p/dT$ was found to be 24.6 ± 1.1 kcal/mole over a temperature range from 382 to 465°C.

ii) The exchanges of ^{13}C and ^{18}O between CO and CO_2 were observed simultaneously with the overall reaction at 410 and 450°C. The ratio V_{+c}/V_{-c} of the unidirectional rate of transfer of carbon atoms from CO_2 to CO to that from CO to CO_2 was not in accordance with the ratio V_{+O}/V_{-O} of the unidirectional rate of transfer of oxygen atoms from CO_2 to CO to the reverse one; V_{+c}/V_{-c} was calculated at around 10 but V_{+O}/V_{-O} was 5~6 which was evaluated on the assumption that oxygen atoms are transferred from CO to H_2O exclusively through CO_2. This difference implies that part of oxygen atoms transferred from CO to H_2O does not pass through CO_2.

iii) The exchange of deuterium between H_2 and H_2O was observed simultaneously with the overall reaction at 450°C. The ratio V_{+H}/V_{-H} of the unidirectional rate of transfer of hydrogen atoms from H_2 to H_2O to the reverse one was found to be larger than 30. The H_2–D_2 equilibration observed simultaneously with the overall reaction occurred very rapidly compared with the latter.

The following reaction scheme*) was proposed on the basis of the

*) The reaction scheme of reaction (1) similar to (3) was proposed to the cases catalyzed by ZnO[7] and by iron oxide[8].

above results:

$$\begin{array}{l} CO \overset{1}{\longleftrightarrow} CO(a) \\ H_2O \overset{2}{\longleftrightarrow} OH(a) \\ \qquad\quad H(a) \end{array} \Bigg\} \overset{3}{\longleftrightarrow} X(a) \overset{4}{\longleftrightarrow} \begin{array}{l} CO_2(a) \overset{5}{\longleftrightarrow} CO_2 \\ H(a) \end{array} \Bigg\} \overset{6}{\longleftrightarrow} H_2 \qquad (3)$$

where (a) denotes the adsorbed state and X(a) is an intermediate. Steps 1 and 5 were presupposed to be in partial equilibria as referred to the rate equation (2) and step 6 is inferred to be also in partial equilibrium from rapid H_2–D_2 equilibration. Steps 3 and 4 were inferred to be apart from in partial equilibria from the results described in ii) and step 2 also apart from in partial equilibrium from slow exchange of deuterium as described in iii).

In the above experiments, however, the mechanism of reaction (1) was not sufficiently established since ν_r could not be determined and the transfer of oxygen atoms among CO, CO_2 and H_2O was not elucidated because of constant elimination of water vapor with cold traps. The present investigation was conducted by means of tracers of ^{13}C and ^{18}O under the conditions where water vapor was circulated with CO, CO_2 and H_2 without its elimination, with precautions taken against contamination of the catalyst by grease and mercury vapor. The method for determining the stoichiometric number ν_r of the rate-determining step is applied to the transfer of carbon atoms between CO and CO_2 traced by ^{13}C and ν_r is determined to be unity. The transfer of oxygen atoms among CO, CO_2 and H_2O traced by ^{18}O is analyzed by the method extended to isotopic exchange among three species[9]. Isotopic difference of rate is ignored throughout the present work.

§ 2. Experimental

Materials: Platinum wire for preparing evaporated films was of 0.4 mm diameter and of 99.9% purity. ^{13}C-labelled CO and CO_2 (obtained from Merck Sharp and Dohme Ltd., Canada) were of *ca.* 90 and 55 atomic percent of ^{13}C, respectively. ^{18}O-labelled CO and CO_2 (YEDA, Research and Development Co., Israel) were of *ca.* 90 atomic percent of ^{18}O. Pure carbon dioxide (Takachiho Chemical Industrial Co., Japan) was purified by repeated distillation *in vacuo*. Pure carbon monoxide (*ibid.*) was purified by passing through copper gauze heated at *ca.* 300°C and subsequently through a trap cooled by liquid nitrogen. Hydrogen from cylinders was purified by passing through a heated Pd–Ag thimble. Pure water was prepared by careful distillation in air and then *in vacuo*.

Apparatus: Two kinds of glass reaction systems were used. Reaction system *A* shown schematically in Fig. 1 (a) consisted of a reaction vessel, a circulation pump, a reservoir of water vapor and sampling vessels. The reaction vessel was equipped with six constrictions and eight breakable joints as shown in Fig. 1(a), for repeating the runs of the reaction without exposing the catalyst to the air. Reaction system *B* was an improvement upon *A* as shown in Fig. 1 (b), breakable joints being replaced by metal valves. The reaction systems were set in an air bath kept at *ca.* 80°C to prevent the condensation of water vapor. The reaction vessel was of the same type to that used previously[5,6]. A reservoir of water vapor shown in Fig. 1 (c) was equipped with two breakable joints and a constriction, with which the contents were sealed. A sampling vessel shown in Fig. 1 (a) consisted of two parts, *a* and *b*, of *ca.* 1.5 and 6 mℓ capacity, respectively, both of which was connected each other with a constriction.

Reaction system *A* was connected to a vacuum line and a vacuum

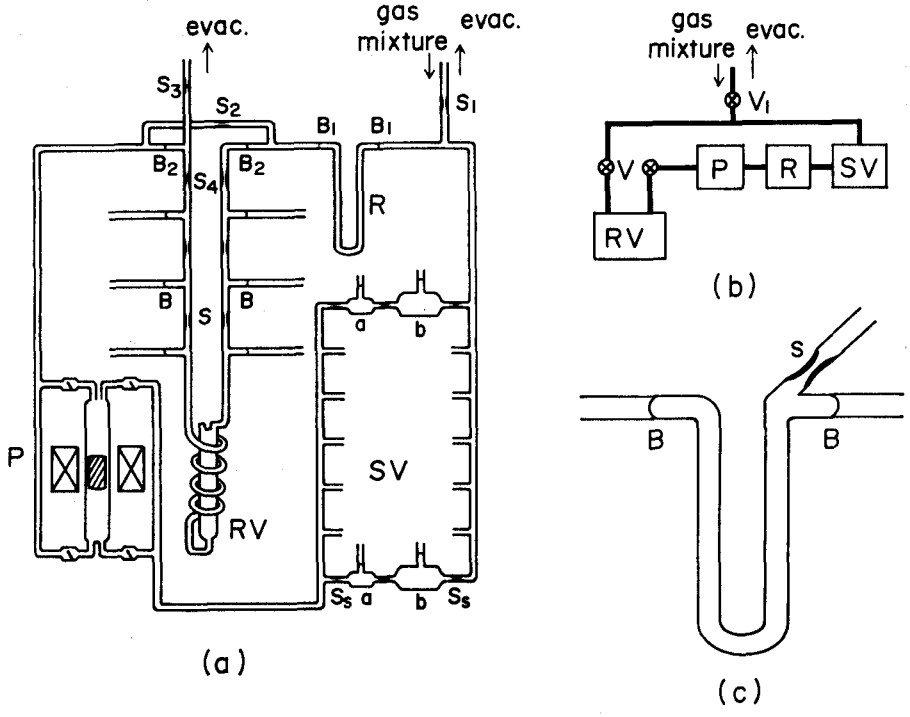

Fig. 1. Apparatus. (a), Schematic drawing of reaction system *A*. (b), Block diagram of reaction system *B*. (c), A reservoir of water vapor. RV, Reaction vessel; SV, Sampling vessels; P, Circulation pump; R, Reservoir of water vapor; S's, Constrictions; B's, Breakable joints; V's, Metal valves.

system for preparing and introducing a gas mixture *via* respective traps cooled at −78°C for preventing the catalyst from contamination by grease and mercury vapor. The vacuum line could be evacuated to 4×10^{-7} mmHg as measured by ionization gauge. The vacuum system, being connected to another vacuum line, consisted of a gas buret, a mercury manometer and gas reservoirs. Reaction system *B* was also connected to the above vacuum line and system *via* a trap cooled at −78°C.

Procedure: Three evaporated platinum films were used as catalyst (termed catalyst I, II and III, respectively), and were prepared as described in a previous work[5]. Experimental procedure using reaction system *A* is as follows. After the catalyst was prepared, mixture of CO, CO_2 and H_2 was introduced into the reaction system except the reaction vessel through constriction S_1, the amount and the composition of the mixture being previously measured. After S_1 was sealed, water vapor was mixed with the above mentioned mixture by opening breakable joints B_1's and circulated in the system keeping it off from the reaction vessel; water vapor was preliminarily introduced into the reservoir through a constriction *via* traps containing Au foil for removing mercury vapor after its amount was measured by a gas buret. Constrictions S_2 and S_3 were now sealed and the reaction was initiated by opening breakable joints B_2's, followed by circulating the mixture through the reaction vessel. Total pressure of the mixture was about 60 mmHg. The reaction was followed by sampling of the mixture by sealing off sampling vessels one after another at constrictions S_5's. After all the sampling vessels were sealed off, constrictions S_4's were sealed off and then the reaction system was reconstructed. The second run was conducted on the same catalyst, which was treated by evacuation at the reaction temperature, by the same procedure described above.

The experimental procedure using reaction system *B* was simplified as follows. After the catalyst was prepared, a gas mixture of CO, CO_2 and H_2 was introduced into the reaction system through metal valve V_1, the breakable joints of a reservoir of water vapor opened and then the mixture was circulated.

Sampled gases in part *b* of sampling vessels were analyzed gas chromatographically using an active carbon column of 1 m length at 50°C, to determine the ratio $[CO]/[CO_2]$ of mole fraction of CO to that of CO_2. Mole fractions, [CO], $[CO_2]$, $[H_2]$ and $[H_2O]$ were determined by this ratio and their initial compositions. Isotopic distributions in CO and CO_2 were determined mass spectrographically as follows. The sampled gas in part *a* of a sampling vessel was introduced into mass spectrometer (Hitachi,

Model RMU 6) through a trap cooled with liquid nitrogen; the peaks, m/e = 28 to 31, were resistered at 70 V of the ionization voltage. Carbon dioxide collected in the trap was then introduced into mass spectrometer by raising the temperature of the trap at −78°C after evacuating the residual gases in the trap; the peaks, m/e = 44 to 49, were resistered.

§ 3. Experimental results

3.1 Transfer of carbon and oxygen atoms traced by means of labelled CO_2

The transfer of carbon atoms between CO and CO_2, and that of oxygen atoms among CO, CO_2 and H_2O were observed during reaction (1) by simultaneous use of ^{13}C- and ^{18}O-labelled CO_2, using reaction system *A*. Fig. 2 shows the time courses of reaction (1), [CO] *vs.* time. Catalytic activity of the film seems to slightly decayed by repeating the runs since the time course of the third run conducted at 430°C over catalyst II was

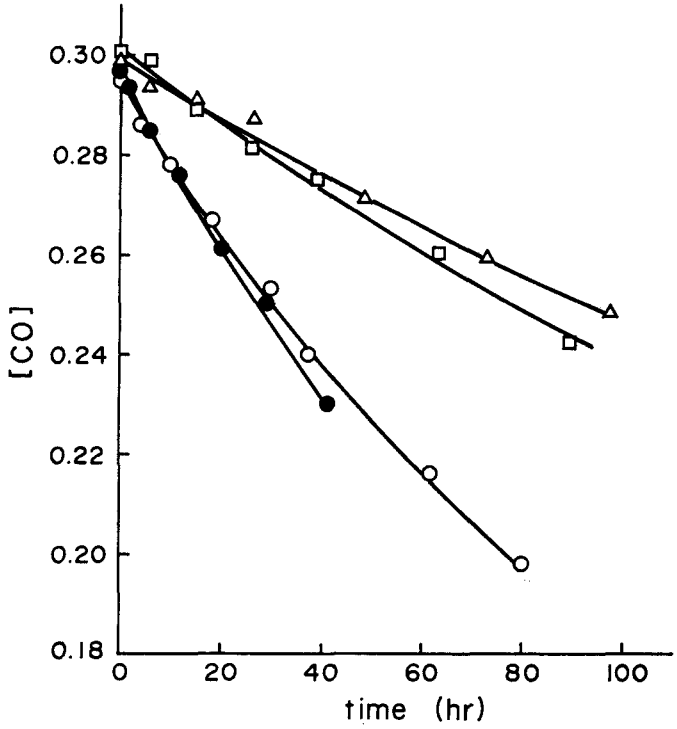

Fig. 2. Time courses of reaction, $CO+H_2O=CO_2+H_2$, [CO] *vs.* time. Over catalyst I: ●, the first run (415°C). Over catalyst II: ○, the first run (450°C); △, the second run (410°C); □, the third run (430°C).

near that of the second run at 410°C rather than that of the first run at 450°C. The activation energy of reaction (1), $RT^2 \mathrm{d}\ln V/\mathrm{d}T$, where V is the net rate of (1), appears to be smaller than 20 kcal/mole as evaluated from the initial inclinations of the first and second runs.

Fig. 3 shows the atomic fractions Y_{CO} and Y_{CO_2} of ^{13}C in CO and CO_2 and those Z_{CO} and Z_{CO_2} of ^{18}O in CO and CO_2, respectively, as a function of [CO] on the run at 451°C over catalyst I and on the first run (450°C) over catalyst II. All the data observed are summarized in Table 1. Y_{CO} is slowly increased and the material balance of ^{13}C holds within experimental error (*ca.*$\pm 1\%$) throughout the whole course of the reaction. Z_{CO_2} decreases rapidly at initial stage of the reaction, whereas Z_{CO} does not increase so fast as compared with the decrease of Z_{CO_2}. The atomic fraction of ^{18}O in H_2O (Z_{H_2O}) calculated from the material balance of ^{18}O are shown by dashed line in Fig. 3. Its values are rapidly increased at the initial stage along with the rapid decrease of Z_{CO_2}. However, this line exceeds

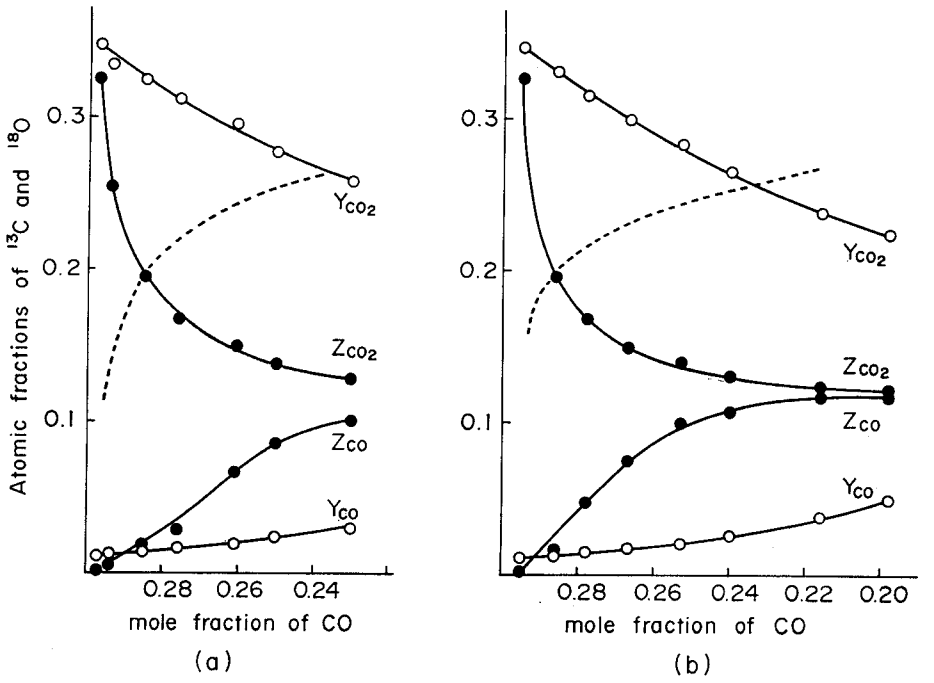

Fig. 3. Transfer of carbon and oxygen atoms observed by means of ^{13}C- and ^{18}O-labelled CO_2. (a), Atomic fractions of ^{13}C and ^{18}O in CO and CO_2 *vs.* mole fraction of CO at 451°C over catalyst I and (b), those at 450°C over catalyst II.

TABLE 1. Observed data by means of labelled CO_2

Reaction temperature (°C)	Reaction time (hr)	[CO]	[CO_2]	[H_2]	[H_2O]	Y_{CO}	Y_{CO_2}	Z_{CO}	Z_{CO_2}
Over catalyst I									
	0	0.297	0.226	0.220	0.257	0.011_3	0.348	0.002_2	0.325
	2.0	0.294	0.229	0.223	0.254	0.012_5	0.335	0.005_3	0.253
	6.0	0.285	0.238	0.232	0.245	0.013_9	0.325	0.018_9	0.195
451 ± 1	12.0	0.276	0.247	0.241	0.236	0.015_9	0.312	0.027_7	0.167
	20.0	0.261	0.262	0.256	0.221	0.018_8	0.295	0.066_8	0.149
	29.0	0.250	0.273	0.267	0.210	0.023_4	0.277	0.085_7	0.137
	41.0	0.230	0.293	0.287	0.190	0.029_5	0.258	0.100_5	0.127
Over catalyst II									
	0	0.295	0.225	0.226	0.254	0.011_7	0.347	0.002_0	0.326
	4.0	0.286	0.234	0.235	0.245	0.012_4	0.331	0.017_5	0.196
	10.0	0.278	0.242	0.243	0.237	0.014_6	0.315	0.047_3	0.168
450 ± 2	18.3	0.267	0.253	0.254	0.226	0.017_6	0.297	0.074_9	0.149
(first run)	26.0	0.253	0.267	0.268	0.212	0.020_9	0.283	0.099_6	0.140
	37.3	0.240	0.280	0.281	0.199	0.026_0	0.265	0.107_9	0.131
	61.3	0.216	0.304	0.305	0.175	0.038_0	0.238	0.117_4	0.124
	85.0	0.198	0.322	0.323	0.157	0.049_9	0.224	0.117_9	0.122
	0	0.299	0.225	0.224	0.252	0.011_5	0.349	0.002_2	0.326
	6.0	0.294	0.230	0.229	0.247	0.011_6	0.339	0.004_7	0.237
	15.2	0.291	0.233	0.232	0.244	0.012_3	0.334	0.015_3	0.202
410 ± 1	26.7	0.287	0.237	0.236	0.240	0.013_5	0.319	0.033_3	0.173
(second run)	48.9	0.271	0.253	0.252	0.224	0.015_6	0.302	0.064_7	0.153
	73.0	0.259	0.265	0.264	0.212	0.018_7	0.286	0.088_5	0.141
	97.5	0.248	0.276	0.275	0.201	0.022_1	0.267	0.103_7	0.132
	0	0.301	0.225	0.230	0.244	0.011_6	0.348	0.002_4	0.325
	6.0	0.299	0.227	0.232	0.242	0.011_7	0.342	0.004_8	0.253
	15.0	0.289	0.237	0.242	0.232	0.012_5	0.335	0.016_3	0.201
430 ± 2	26.0	0.281	0.245	0.250	0.224	0.013_2	0.325	0.034_9	0.177
(third run)	39.0	0.275	0.251	0.256	0.218	0.013_7	0.313	0.051_8	0.161
	63.4	0.260	0.266	0.271	0.203	0.017_2	0.294	0.083_3	0.144
	89.5	0.242	0.284	0.289	0.185	0.020_9	0.277	0.101_2	0.134

Z_{H_2O} expected from the simple exchange of ^{18}O, which suggests that ^{18}O atoms are transferred to some species other than CO, CO_2 and H_2O; it

TABLE 2. Redistribution of ^{13}C and ^{18}O in CO_2 during the reaction, $CO+H_2O=CO_2+H_2$, over catalyst II

Reaction temperature	Reaction time (hr)	Mole fraction of						Y_{CO_2}	Z_{CO_2}
		CO_2	$^{13}CO_2$	$CO^{18}O$	$^{13}CO^{18}O$	$C^{18}O_2$	$^{13}C^{18}O_2$		
450°C	0	0.322	0.336	0.025	0.008	0.306	0.003	0.347	0.326
		(0.297	0.158	0.278	0.152	0.069	0.037)		
	4.0	0.409	0.245	0.220	0.079	0.040	0.007	0.331	0.196
		(0.431	0.214	0.210	0.105	0.026	0.013)		
	10.0	0.473	0.221	0.193	0.086	0.020	0.008	0.315	0.168
		(0.474	0.218	0.192	0.088	0.019	0.009)		
	18.3	0.509	0.215	0.179	0.076	0.016	0.006	0.297	0.149
		(0.509	0.215	0.178	0.075	0.016	0.007)		
410°C	0	0.322	0.338	0.021	0.007	0.308	0.004	0.349	0.326
		(0.296	0.159	0.286	0.153	0.069	0.037)		
	6.0	0.353	0.290	0.195	0.046	0.113	0.003	0.339	0.237
		(0.385	0.197	0.239	0.123	0.037	0.019)		
	15.2	0.402	0.244	0.222	0.083	0.042	0.007	0.334	0.202
		(0.424	0.213	0.215	0.108	0.027	0.014)		
	26.7	0.462	0.223	0.197	0.087	0.022	0.009	0.319	0.173
		(0.466	0.218	0.195	0.091	0.020	0.010)		
	48.9	0.501	0.217	0.181	0.078	0.016	0.007	0.302	0.153
		(0.501	0.217	0.181	0.078	0.016	0.007)		

Values in parentheses are those in equilibrium at the observed values of Y_{CO_2} and Z_{CO_2}.

may be reasonable to consider that ^{18}O atoms are transferred to residual water adsorbed on glass and OH group or oxygen atoms on glass. Moreover, it was observed that in the absence of the catalyst Z_{CO_2} decreases rapidly but Z_{CO}, Y_{CO} and Y_{CO_2} are not changed and Z_{H_2O} goes up to over Z_{CO_2} similarly to the case in the presence of the catalyst.

The redistribution of ^{13}C and ^{18}O in CO_2 observed simultaneously with the transfers of ^{13}C and ^{18}O is shown in Table 2, which shows that the equilibrium distributions were attained in course of the observation; this redistribution was also observed even in the absence of the catalyst.

In the following chapter, the transfer of carbon atoms between CO and CO_2, and the transfer of oxygen atoms from CO to CO_2 and H_2O and its reverse one are discussed on the basis of the theory of the stoichiometric number determination of the rate-determining step; the transfer of oxygen

atoms from CO_2 to the others, the transfer from H_2O to the others and the redistribution of ^{13}C and ^{18}O in CO_2 are not here referred to since the occurrence of the transfer of oxygen atoms between CO_2 and H_2O and of the redistribution goes on in the absence of the catalyst.

3.2 Transfer of carbon and oxygen atoms traced by means of labelled CO

The transfer of carbon and oxygen atoms were observed by simultaneous use of ^{13}CO and $C^{18}O$ during reaction (1) over catalyst III, using reaction system *B*. The atomic fractions, Y_{CO}, Y_{CO_2}, Z_{CO} and Z_{CO_2}, are shown as a function of [CO] in Fig. 4 and their numerical values are summarized in Table 3. Z_{CO} is rapidly decreased as compared with Y_{CO} whereas Z_{CO_2} is not increased so fast, which indicates that ^{18}O atoms are

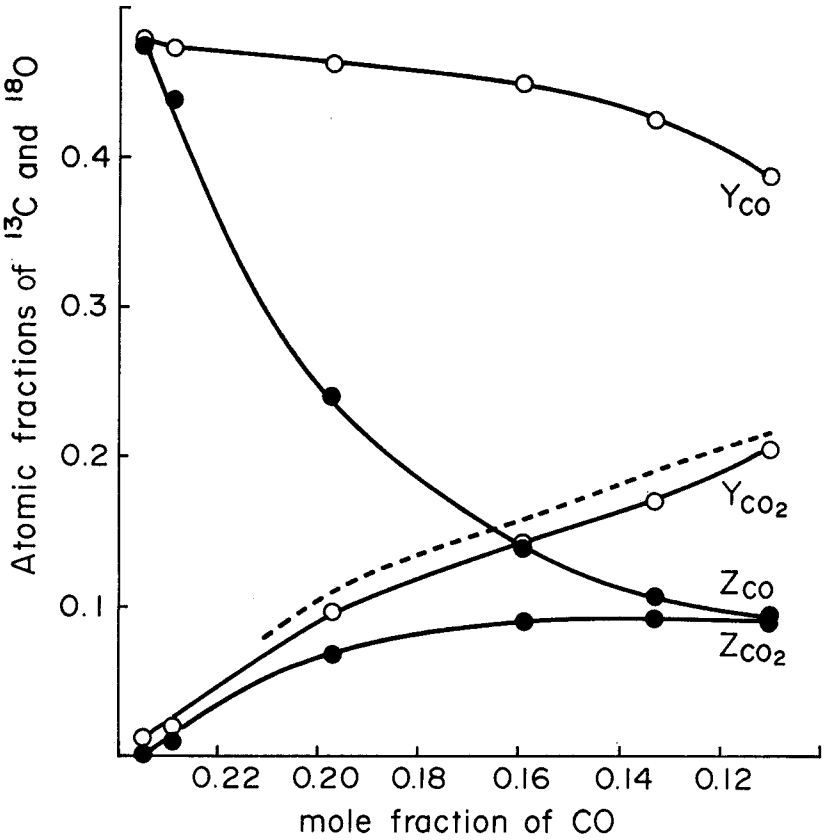

Fig. 4. Transfer of carbon and oxygen atoms observed by means of ^{13}CO and $C^{18}O$ at 410°C over catalyst III, atomic fractions of ^{13}C and ^{18}O in CO and CO_2 *vs.* mole fraction of CO.

TABLE 3. Observed data by means of labelled CO at 410°C over catalyst III

Reaction time (hr)	[CO]	[CO_2]	[H_2]	[H_2O]	Y_{CO}	Y_{CO_2}	Z_{CO}	Z_{CO_2}
0	0.235	0.218	0.227	0.320	0.476	0.011	0.475	0.002
2.1	0.229	0.224	0.233	0.314	0.473	0.020	0.439	0.010
20.0	0.197	0.256	0.265	0.282	0.463	0.096	0.240	0.068
43.1	0.159	0.294	0.303	0.244	0.449	0.139	0.138	0.090
67.0	0.133	0.320	0.329	0.218	0.428	0.170	0.106	0.092
109.0	0.110	0.343	0.352	0.195	0.387	0.204	0.093	0.089

TABLE 4. Redistribution of ^{13}C and ^{18}O in CO during the reaction, $CO+H_2O=CO_2+H_2$, at 410°C over catalyst III

Reaction time (hr)	Mole fraction of				Y_{CO}	Z_{CO}
	CO	^{13}CO	$C^{18}O$	$^{13}C^{18}O$		
0	0.057	0.468	0.467	0.008	0.476	0.475
	(0.275	0.250	0.249	0.226)		
1.1	0.116	0.435	0.411	0.037	0.473	0.448
	(0.291	0.261	0.236	0.212)		
2.1	0.142	0.419	0.384	0.055	0.473	0.439
	(0.296	0.265	0.231	0.208)		
20.0	0.408	0.352	0.129	0.111	0.463	0.240
	(0.408	0.352	0.129	0.111)		

Values in parentheses are those in equilibrium at the observed values of Y_{CO} and Z_{CO}.

transferred mainly from CO to H_2O. Z_{H_2O} calculated from the material balance of ^{18}O is increased beyond Z_{CO} similarly to Z_{CO_2} as described in the preceding section. The redistribution of ^{13}C and ^{18}O in CO is shown in Table 4, which shows that the equilibrium distributions were attained at early stage of the observation.

§ 4. Discussion

4.1 Application of the theory of the stoichiometric number determination of the rate-determining step

We now discuss the unidirectional rates of transfer of carbon atoms between CO and CO_2, and those of oxygen atoms among CO, CO_2 and

H_2O on the basis of the theory of the stoichiometric number of the rate-determining step. It is assumed that transfer of both atoms occurs by the following scheme, which consists of not all but a part of the constituent steps of reaction (1):

$$\left.\begin{array}{l} CO \overset{I}{\longrightarrow} X_c \\ H_2O \overset{II}{\longrightarrow} X_d \end{array}\right\} \overset{b}{\longrightarrow} X_b \overset{III}{\longrightarrow} CO_2, \qquad (5)$$

where X_b, X_c and X_d are intermediates adsorbed on the catalyst which comprise carbon and/or oxygen atoms. Molecules and intermediates not comprising carbon nor oxygen atoms are not expressed. Oxygen atoms are assumed to be transferred from CO to X_c, from H_2O to X_d or from X_b to CO_2 by respective consecutive steps (termed path I, II or III, respectively). Intermediate X_c is assumed to react with X_d through step b to result in intermediate X_b. Carbon atoms are assumed to be transferred exclusively through path I, step b and path III.

Transfer of carbon atoms between CO and CO_2

Let us denote the forward and backward unidirectional rates of transfer of carbon atoms traced by ^{13}C by V_{+c} and V_{-c}, respectively, the unique rate-determining step being step b or one of the steps of path I or III. We have then[3],

$$V_{+c}/V_{-c} = v_{+r}/v_{-r}, \qquad (6)$$

where v_{+r} and v_{-r} are the forward and backward unidirectional rates of the rate-determining step. The net rate V of reaction (1) and rate of decrease or increase of ^{13}C atoms in CO_2 or CO are expressed, respectively, as

$$V = V_{+c} - V_{-c} = -\mathrm{d}N_{CO}/\mathrm{d}t \qquad (7)$$

and

$$-\mathrm{d}(N_{CO}Y_{CO})/\mathrm{d}t = Y_{CO}V_{+c} - Y_{CO_2}V_{-c} = \mathrm{d}(N_{CO_2}Y_{CO_2})/\mathrm{d}t, \qquad (8)$$

where $N_i (i = CO \text{ or } CO_2)$ is the number of molecules i in the system. We have from Eqs. (7) and (8)

$$\begin{aligned} V_{+c}/V_{-c} &= 1 + (Y_{CO} - Y_{CO_2})\,\mathrm{d}\ln N_{CO}/\mathrm{d}Y_{CO} \\ &= 1 + (Y_{CO} - Y_{CO_2})\,\mathrm{d}\ln [CO]/\mathrm{d}Y_{CO} \end{aligned} \qquad (9.1)$$

or

$$V_{-c}/V_{+c} = 1 + (Y_{CO_2} - Y_{CO})\,\mathrm{d}\ln [CO_2]/\mathrm{d}Y_{CO_2}. \qquad (9.2)$$

The stoichiometric number ν_r of the rate-determining step is determined by[3]

$$\nu_r = -\Delta G/RT \ln (V_{+c}/V_{-c}), \tag{10}$$

where $-\Delta G$ is Gibbs free energy decrease of reaction (1), which is approximated by

$$-\Delta G = RT \ln \left\{K[\mathrm{CO}]\,[\mathrm{H_2O}]/[\mathrm{CO_2}]\,[\mathrm{H_2}]\right\}, \tag{11}$$

where K is equilibrium constant of reaction (1)*).

In Fig. 5(a), $-\Delta G/2.3RT$ is plotted against $\log (V_{+c}/V_{-c})$, both of which

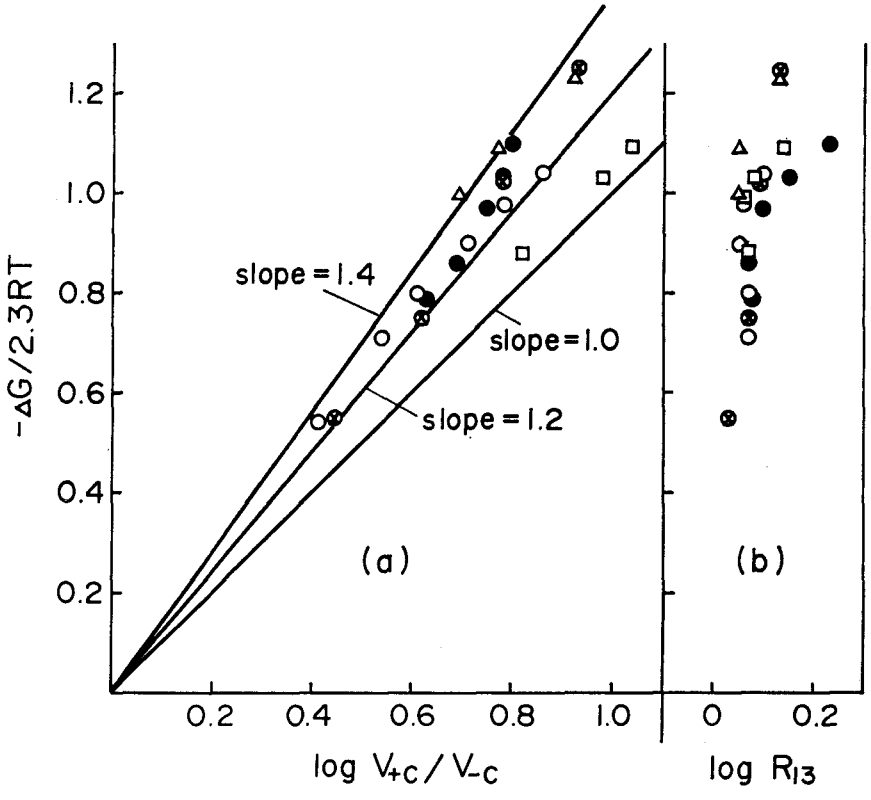

Fig. 5. Determination of the stoichiometric number of the rate-determining step. (a), $-\Delta G/2.3\,RT$ *vs.* $\log V_{+c}/V_{-c}$ traced by ^{13}C : (b), $-\Delta G/2.3\,RT$ *vs.* $\log R_{13}$ traced by ^{18}O.
Over catalyst I : ●, the first run (451°C).
Over catalyst II : ○, the first run (450°C); △, the second run (410°C); □, the third run (430°C).
Over catalyst III : ⊗, the first run (410°C).

*) Equilibrium constant K was calculated from the data by KANEKO and OKI[10] as $\log K = 0.93$ at 450 and 451°C, 1.02 at 430°C and 1.11 at 410°C.

are evaluated from the data shown in Tables 1 and 3, by Eqs. (9.1) and (11). According to Eq. (10) we see from the figure that ν_r observed is close to unity (but scattered between 1.1~1.3).

Transfer of oxygen atoms among CO, CO_2 and H_2O

The present author[9] has previously discussed isotopic exchange among three species on the basis of a scheme similar to (5). This method is now applied to the transfer of oxygen atoms. The net rate V of reaction (1) and rates of decrease or increase of ^{18}O atoms in CO, H_2O and CO_2 are expressed as

$$V=(V_{12}+V_{13})-(V_{21}+V_{31}) \tag{12.1}$$

$$=(V_{21}+V_{23})-(V_{12}+V_{32}) \tag{12.2}$$

$$=\left\{(V_{13}+V_{23})-(V_{31}+V_{32})\right\}/2 \tag{12.3}$$

$$-\mathrm{d}(N_{CO}Z_{CO})/\mathrm{d}t=(V_{12}+V_{13})Z_{CO}-V_{21}Z_{H_2O}-V_{31}Z_{CO_2} \tag{13.1}$$

$$-\mathrm{d}(N_{H_2O}Z_{H_2O})/\mathrm{d}t=(V_{21}+V_{23})Z_{H_2O}-V_{12}Z_{CO}-V_{32}Z_{CO_2} \tag{13.2}$$

$$2\mathrm{d}(N_{CO_2}Z_{CO_2})/\mathrm{d}t=V_{13}Z_{CO}+V_{23}Z_{H_2O}-(V_{31}+V_{32})Z_{CO_2}, \tag{13.3}$$

where V_{ij} ($i,j=1,2$ and 3) is the unidirectional rate of transfer of oxygen atoms from M_i to M_j (where M_1, M_2 and M_3 are CO, H_2O and CO_2, respectively), which is specified by the rate of increase of ^{18}O atoms in M_j under the conditions that the atomic fraction of ^{18}O in M_i is unity and those of the other two are zero.

As oxygen atoms were transferred between CO_2 and H_2O also in the absence of the catalyst, both the rate of increase (or decrease) of ^{18}O atoms in CO_2 and that in H_2O are undetermined but that in CO gives information upon the unidirectional rates of the constituent steps as follows. We have from Eqs. (12.1) and (13.1)

$$R_1=(V_{12}+V_{13})/(V_{21}+V_{31})$$

$$=1+(Z_{CO}-Z_{CO_2})(\mathrm{d}N_{CO}/\mathrm{d}t)/\left\{N_{CO}\,\mathrm{d}Z_{CO}/\mathrm{d}t+(Z_{CO_2}-Z_{H_2O})V_{21}\right\}, \tag{14}$$

where R_1 is the ratio of the total forward rate of oxygen atoms transferred from M_1 (*viz.*, CO) to the other two to its reverse total rate. Under the experimental conditions shown in Table 1 or Table 3, *i.e.* $\mathrm{d}N_{CO}/\mathrm{d}t<0$, $\mathrm{d}Z_{CO}/\mathrm{d}t>0$ and $Z_{CO}<Z_{CO_2}\geqq Z_{H_2O}$, or $\mathrm{d}N_{CO}/\mathrm{d}t<0$, $\mathrm{d}Z_{CO}/\mathrm{d}t<0$ and $Z_{CO}>Z_{H_2O}>Z_{CO_2}$, Eq. (14) assumes the form,

$$R_1 \leqq 1+(Z_{CO}-Z_{CO_2})\,d\ln N_{CO}/dZ_{CO} = 1+(Z_{CO}-Z_{CO_2})\,d\ln [CO]/dZ_{CO}\,. \tag{15}$$

The second member R_{13} of the above relation gives the upper limit of R_1, which can be evaluated from the last member of (15) with the experimental data shown in Tables 1 and 3, its values being plotted against $-\Delta G/2.3RT$ in Fig. 5(b). We see from the figure that R_{13} is close to unity. According to the previous discussion[9] R_1 gives v_{+r}/v_{-r} of the rate-determining step in case where one of the steps of path I or step b is rate-determining or is close to unity in the other cases*). It is clear from Fig. 5(b) that R_1 does not give v_{+r}/v_{-r}, so that R_1 is concluded to be close to unity.

The rate-determining step

It was concluded from the observation of the transfer of carbon atoms traced by ^{13}C that ν_r was close to unity. This indicates that the rate-determining step consists in step b or one of the steps of path I or III and its stoichiometric number is unity. The transfer of oxygen atoms as traced by ^{18}O, *i.e.* $R \approx 1$, on the other hand, shows that the rate-determining step consists in neither step b nor the steps of path I, but leads to the conclusion that the rate-determining step consists in one of the steps of path III with its stoichiometric number unity.

4.2 Discussion of scheme (3)

We now discuss reaction scheme (3) on the basis of the present results incorporated with the previous ones[5,6]. The present results shown in the preceding section lead to the conclusion that step 4 or 5 of scheme (3) is rate-determining. We now infer which of step 4 or 5 is rate-determining from the rate equation (2).

*) The rate ratio R_1 ($\equiv(V_{12}+V_{13})/(V_{21}+V_{31})$) was expressed in terms of the forward and backward unidirectional rates of the atoms (*i.e.* oxygen atoms in the present discussion) transferred by step b, path I, II and III, which were denoted by V_{+i} and V_{-i} ($i=b$, 1, 2 and 3, respectively). It was shown that R_1 is reduced to simple forms, *i.e.* rate ratios, as shown below in the presence of the rate-determining step.

rate-determing step	one of the steps of			step b
	path I	path II	path III	
R_1	V_{+1}/V_{-1}	1	1	V_{+b}/V_{-b}

This table shows that R_1 equals v_{+r}/v_{-r} in case where step b or one of the steps of path I is rate-determining or is close to unity in the other cases.

Suppose that step 5 is rate-determining and under the previous experimental conditions (where partial pressure of water vapor was *ca.* 6×10^{-4} mmHg) the net rate $-V$ is approximated by v_{-5} of the backward unidirectional rate of step 5 expressed, according to the absolute rate theory developed by HORIUTI[3], as*)

$$-V=(kT/h)\,N^{\mp(5)}\theta^{\mp(5)}(0)\,q^{\mp(5)}C^{CO_2}/Q^{CO_2}, \qquad (16)$$

where kT/h is of usual meaning, $N^{\mp(5)}$ the number of the site $\sigma^{\mp(5)}$ for the critical system $\mp(5)$ of step 5, $\theta^{\mp(5)}(0)$ the probability that the site $\sigma^{\mp(5)}$ is unoccupied, $q^{\mp(5)}$ the Boltzmann factor of the reversible work required to bring a critical system $\mp(5)$ from its standard state onto a definite $\sigma^{\mp(5)}$, preliminarily evacuated, to form a critical system $\mp(5)$ there, Q^{CO_2} the partition function of a single CO_2 in unit volume and C^{CO_2} its concentration. Let us consider whether the rate equation (2) can be reproduced from Eq. (16) or not. The amount of CO_2(a) does not presumably vary along with varying C^{CO_2} because of the rate-determining step of step 5, so that $\theta^{\mp(5)}(0)$ and $q^{\mp(5)}$ may not vary along with varying C^{CO_2} so much as the reaction order with respect to CO_2 is reduced to the observed value 0.6. The reaction order with respect to H_2 found to be 0.5 cannot be drawn from Eq. (16) unless the attractive interaction of the critical system $\mp(5)$ with adsorbed hydrogen atoms is assumed.

Supposing that step 4 is rate-determining alternatively, the net rate $-V$ is approximated by v_{-4} of the backward unidirectional rate of step 4 and expressed, taking into account the partial equilibria of steps 5 and 6, as**)

$$-V=(kT/h)\,N^{\mp(4)}\theta^{\mp(4)}(0)\,q^{\mp(4)}C^{CO_2}(C^{H_2})^{1/2}/Q^{CO_2}(Q^{H_2})^{1/2}, \qquad (17)$$

where superscript $\mp(4)$ signifies the critical system of step (4). The amount of CO_2(a) may be increased along with increasing C^{CO_2} through step 5 in

*) According to the absolute rate theory developed by HORIUTI[3], the forward and backward unidirectional rates of step s, v_{+s} and v_{-s}, are expressed as

$$v_{+s}=(kT/h)p^{\mp(s)}/p^{I(s)} \text{ and } v_{-s}=(kT/h)p^{\mp(s)}/p^{F(s)}, \qquad \text{(i), (ii)}$$

respectively, where p^i is the Boltzmann factor of the chemical potential μ^i, superscripts $\mp(s)$, $I(s)$ and $F(s)$ signifying the critical system, the initial and final systems of step s, respectively. $p^{\mp(s)}$ is expressed in case of a heterogeneous elementary reaction as $p^{\mp(s)}=N^{\mp(s)}\theta^{\mp(s)}(0)q^{\mp(s)}$ and p^δ of a dilute gas δ as $p^\delta=Q^\delta/C^\delta$, *i.e.* $p^{F(5)}=p^{CO_2}=Q^{CO_2}/C^{CO_2}$ in the above discussion, hence we have Eq. (16).

**) Eq. (17) is derived from the equations shown in the above footnote: $p^{F(4)}$ in Eq. (ii) is expressed, taking into account the partial equilibria of steps 5 and 6, as

$$p^{F(4)}=p^{CO_2(a)}p^{H(a)}=p^{CO_2}(p^{H_2})^{1/2}=(Q^{CO_2}/C^{CO_2})(Q^{H_2}/C^{H_2})^{1/2}$$

and $p^{\mp(4)}=N^{\mp(4)}\theta^{\mp(4)}(0)q^{\mp(4)}$, hence we have Eq. (17). (Cf. Ref. 3)

partial equilibrium. Taking into account the repulsive interaction of the critical system $\neq(4)$ with $CO_2(a)$, $q^{*(4)}$ may be decreased along with increasing C^{CO_2} to reduce the reaction order with respect to CO_2 from the first order to 0.6 in accordance with the observation. It is hence plausible that step 4 is rate-determining than step 5 is.

4.3 Reaction schemes other than (3)

We first discuss a simple reaction scheme, *i.e.*

$$\begin{array}{l} CO \overset{1}{\longleftrightarrow} CO(a) \left| \begin{array}{l} \overset{5a}{\longleftrightarrow} CO_2 \\ \end{array} \right. \\ H_2O \overset{2a}{\longleftrightarrow} \left\{ \begin{array}{l} O(a) \\ 2H(a) \end{array} \right. \left| \begin{array}{l} \\ \overset{6}{\longleftrightarrow} H_2 \end{array} \right. \end{array} \qquad (18.\,a)$$

on the basis of the results shown in section 4.1. The result of the transfer of carbon atoms traced by ^{13}C shows that step 1 or 5a is rate-determining. According to the previous discussion[9], the rate ratio R_1 gives v_{+r}/v_{-r} in the case where step 1 or 5a is rate-determining or is close to unity in the other cases*). The result of the transfer of oxygen atoms traced by ^{18}O, *i.e.* $R_1 \approx 1$, is not compatible with the former result, so that scheme (18.a) is ruled out.

We next discuss the following two reaction schemes, *i.e.*

$$\begin{array}{l} CO \overset{1}{\longleftrightarrow} CO(a) \left| \begin{array}{l} \overset{3b}{\longleftrightarrow} CO_2(a) \overset{5}{\longleftrightarrow} CO_2 \\ \end{array} \right. \\ H_2O \overset{2b}{\longleftrightarrow} \left\{ \begin{array}{l} O(a) \\ 2H(a) \end{array} \right. \left| \begin{array}{l} \\ \overset{6}{\longleftarrow\!\!\!\!\!\!\longrightarrow} H_2 \end{array} \right. \end{array} \qquad (18.\,b)$$

and

$$\begin{array}{l} CO \overset{1}{\longleftrightarrow} CO(a) \left| \begin{array}{l} \overset{3c}{\longleftrightarrow} \left\{ \begin{array}{l} CO_2(a) \\ H(a) \end{array} \right. \overset{5}{\longleftrightarrow} CO_2 \\ \end{array} \right. \\ H_2O \overset{2}{\longleftrightarrow} \left\{ \begin{array}{l} OH(a) \\ H(a) \cdots\cdots\cdots\cdots\cdots\cdots \end{array} \right. \left| \begin{array}{l} \\ \overset{6}{\longleftrightarrow} H_2 \end{array} \right. \end{array} \qquad (18.\,c)$$

The results shown in section 4.1 leads to the conclusion that step 5 is rate-determining in the cases of both schemes. Assuming that step 5 of scheme (18.b) or (18.c) is rate-determining, the rate equation (2) may not be drawn from the backward unidirectional rate of step 5, as discussed in the preceding section. Therefore, it is inferred that schemes (18.b) and (18.c) are less plausible than scheme (3).

*) The table shown in footnote on p. 97 holds in the case of scheme (18.a) except for the column of path III.

§ 5. Conclution

The theory of the stoichiometric number determination of the rate-determining step gives the criteria to determine whether any reaction scheme is reliable or not and which step of an adopted reaction scheme is rate-determining. So far we discussed, on the basis of the theory, the transfer of carbon atoms between CO and CO_2, and that of oxygen atoms among CO, H_2O and CO_2, which are accompanied by reaction (1). The former leads to the conclusion that the rate-determining step consists in any constituent step of the transfer of carbon atoms and its stoichiometric number is unity. From the latter we see that the ratio, $R_1 \equiv (V_{12}+V_{13})/(V_{21}+V_{31})$, of the total forward rate of transfer of oxygen atoms from CO to CO_2 and H_2O to its reverse total rate is close to unity, which implies that the rate-determining step is neither step *b* nor any steps of path I in scheme (5). It follows that one of the steps of path III in scheme (5) is rate-determining, and in consequence step 4 or 5 in scheme (3) is rate-determining. It is plausible that step 4 is rate-determining as referred to the rate equation (2) observed under the conditions where reaction (1) proceeds reversely. Other schemes, *e.g.* schemes (18), are less plausible than scheme (3). It is hence plausibly concluded that reaction (1) consists of the sequence of steps of scheme (3) with rate controlled by step (4).

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