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## ON THE MECHANISM OF WATER GAS SHIFT REACTION

### PART I: Determination of the Stoichiometric Number of Rate- determining Step by Means of Deuterium as Tracer

By

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#### Abstract

The stoichiometric number of rate-determining step  $\nu(r)$  of catalyzed water gas shift reaction in the presence of iron oxide catalyst has been determined under various conditions by means of deuterium as tracer. The overall reaction was allowed to approach its equilibrium, the reaction rate and the deuterium content in hydrogen in course of the approach being concurrently followed in each run of experiment and  $\nu(r)$  was determined from the result according to an equation derived premising that the observed isotopic transfer occurs solely through the rate-determining step of the overall reaction. The same equation gives the value of  $\nu(r)$  which may be apparently augmented boundlessly, if the isotopic transfer takes place through the constituent steps of the overall reaction other than its rate-determining step. The  $\nu(r)$  thus found was definitely of the order of magnitude of unity, even if the isotopic effect is taken into account. Incorporating the present result with ENOMTO and UGAJIN's result that  $\nu(r)$  is found unity by means of  $^{14}\text{C}$  according to the same equation, it is concluded that the possible mechanism is that of LANCMUIR-HINSHELWOOD mechanism or RIDEAL-ELEY mechanism, if there exists a rate-determining step.

#### Introduction

The present paper is devoted to establish the mechanism of the catalyzed water gas shift reaction



in the presence of iron oxide catalyst by determining the stoichiometric number  $\nu(r)$  of the rate-determining step by means of hydrogen isotope.

FRUMKIN<sup>1)</sup> has pointed out with special reference to a mechanism of hydrogen electrode reaction that  $\nu(r)$  as determined by isotope could be apparently boundlessly augmented in case where the isotopic transfer was effected by a constituent step of the overall reaction other than its rate-determining step. HORIUTI and MATSUDA<sup>2)</sup> have assumed the case where the isotopic transfer

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was effected by constituent steps of the overall reaction other than its rate-determining step and only one of them had affinity  $-\Delta F'$  different from zero. In the special case where the isotopic transfer is effected by a single constituent step,  $-\Delta F'$  was assigned to that step. They have thus shown that  $\nu(r)$  as determined formally by the equation

$$\nu(r) = -\Delta F/RT \ln(V_+/V_-) \quad (2)$$

equals  $\Delta F/\Delta F'$ , which tends to infinity as  $\Delta F'$  approaches zero, where  $-\Delta F$  is the affinity of the overall reaction and  $V_+$  or  $V_-$  is the forward or backward rate of the overall reaction as determined, as seen later, from the observed rate of the isotopic transfer, as if the isotopic transfer were effected solely through the rate-determining step of the overall reaction.

Let for instance the overall reaction (1) be the resultant of the sequence of steps shown in row I in Table 1.

TABLE 1. Stoichiometric number  $\nu$  and its observable value  $\nu(r)$  of the rate-determining step

Sequence	Constituent step <sup>*)</sup>	Stoichiometric number			
		$\nu$	$\nu(r)$		
			D	<sup>14</sup> C	<sup>18</sup> O
I	$\text{H}_2\text{O} \longrightarrow 2\text{H(a)}+\text{O(a)}$	1	1	$\infty$	1
	$\text{CO}+\text{O(a)} \longrightarrow \text{CO}_2$	1	$\infty$	1	1
	$2\text{H(a)} \longrightarrow \text{H}_2$	1	1	$\infty$	$\infty$
II	$\text{H}_2\text{O} \longrightarrow \text{H}_2\text{O(a)}$	1	1	$\infty$	1
	$\text{CO} \longrightarrow \text{CO(a)}$	1	$\infty$	1	1
	$\text{CO(a)}+\text{H}_2\text{O(a)} \longrightarrow \text{CO}_2+\text{H}_2$	1	1	1	1
III	$\text{H}_2\text{O} \longrightarrow \text{H}_2\text{O(a)}$	1	1	$\infty$	1
	$\text{CO}+\text{H}_2\text{O(a)} \longrightarrow \text{CO}_2+\text{H}_2$	1	1	1	1

\*) (a) signifies the adsorbed state of a species to which it is attached.

The stoichiometric number  $\nu$ 's of the respective steps are shown in column  $\nu(r)$  in the Table. Columns under  $\nu(r)$  show its value as calculated by (2) with use of the isotope mentioned at the top of the appropriate column for the overall rate determined by the "constituent step" in the relevant row;  $\infty$  denotes the value of  $\nu(r)$  apparently augmented as mentioned above. The Table shows for instance that if one uses <sup>14</sup>C as the tracer  $\nu(r)=1$  only in the case where the second step of sequence I determines the rate but  $\infty$  otherwise.

The  $\nu(r)$  of reaction (1) has now been determined by ENOMOTO and UGAJIN<sup>4)</sup>

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to be unity by means of  $^{14}\text{C}$  as tracer in equilibrium. The  $\nu(r)$  determined by deuterium as tracer must now be  $\infty$ , insofar as sequence I is operative. II and III in the Table are the sequences of so-called LANGMUIR-HINSHELWOOD mechanism and RIDEAL-ELEY mechanism. Another sequence of type III is that where the parts of  $\text{H}_2\text{O}$  and  $\text{CO}$  are interchanged. If the reaction follows the sequence II or III, the  $\nu(r)$  is unity as determined by deuterium consistently with the above value by  $^{14}\text{C}$ , respectively in the case, where the last step of II or III is rate-determining.

The present determination provides thus the criterion for the sequence of steps, which is hitherto in most of cases intuitively selected.

### §1 Theoretical

Consider that mixture of carbon monoxide, heavy water vapor, carbon dioxide and hydrogen is circulated over iron oxide catalyst and both the partial pressure of water and transfer rate of deuterium atom from water to hydrogen are followed until the equilibrium of the water gas shift reaction is attained.

The stoichiometric number is determined from the observation according to (2) as follows. The affinity  $-\Delta F$  of reaction (1) is expressed in terms of partial pressures of carbon monoxide  $P^{\text{CO}}$ , water vapor  $P^{\text{H}_2\text{O}}$ , carbon dioxide  $P^{\text{CO}_2}$  and hydrogen  $P^{\text{H}_2}$ , and the equilibrium constant  $K_p$ , assuming the ideal gas law for these gases as

$$-\Delta F = RT \ln (P^{\text{CO}} P^{\text{H}_2\text{O}} / P^{\text{CO}_2} P^{\text{H}_2}) K_p . \quad (3)$$

The overall reaction rate  $V$  of reaction (1) is written as

$$V = V_+ - V_- = -dn^{\text{H}_2\text{O}}/dt \quad (4)$$

where  $n^{\text{H}_2\text{O}}$  is the number of moles of water containing deuterium. The transfer rate of deuterium atom from water to hydrogen is given on the other hand by

$$-d(n^{\text{H}_2\text{O}} Z^{\text{H}_2\text{O}})/dt = Z^{\text{H}_2\text{O}} V_+ - Z^{\text{H}_2} V_- \quad (5)$$

ignoring the isotopic effect on the rate for the sake of  $\nu(r)$ -determination by order of magnitude under the premise that the transfer of deuterium occurs solely through the rate-determining step of the overall reaction, where  $Z^{\text{H}_2\text{O}}$  or  $Z^{\text{H}_2}$  is the atomic fraction of deuterium in water or that of hydrogen. Combining (4) and (5), we have

$$V_+ / V_- = 1 + (1 - Z^{\text{H}_2} / Z^{\text{H}_2\text{O}}) d \log n^{\text{H}_2\text{O}} / d \log Z^{\text{H}_2\text{O}} \quad (6. a)$$

or

$$V_+ / V_- = 1 + (1 - Z^{\text{H}_2} / Z^{\text{H}_2\text{O}}) d \log P^{\text{H}_2\text{O}} / d \log Z^{\text{H}_2\text{O}} , \quad (6. b)$$

inasmuch as  $n^{\text{H}_2\text{O}}$  is proportional to  $P^{\text{H}_2\text{O}}$ . Substituting  $\Delta F$  and  $V_+/V_-$  respectively from (3) and (6. b) into (2), we have

$$\nu(r) = \frac{\log(P^{\text{CO}}P^{\text{H}_2\text{O}}/P^{\text{CO}_2}P^{\text{H}_2})K_p}{\log\{1 + (1 - Z^{\text{H}_2}/Z^{\text{H}_2\text{O}})d \log P^{\text{H}_2\text{O}}/d \log Z^{\text{H}_2\text{O}}\}}, \quad (7)$$

which gives  $\nu(r)$  in terms of observable quantities in course of progress of the water gas shift reaction.

## § 2 Experimental

**Apparatus:** The apparatus used consists, as shown in Fig. 1, of a circulating system (circumscribed by dotted line) through which the reacting gas was

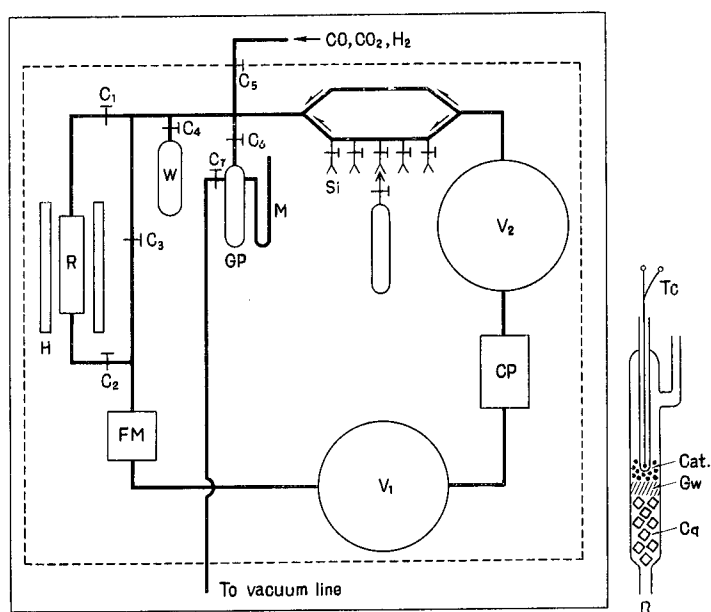


Fig. 1. Circulating system for measuring  $\nu(r)$ .

R: reactor	Cq: cracked quartz
H: heater	FM: Flow meter
C <sub>1</sub> -C <sub>7</sub> : stopcocks	CP: magnetic circulating pump
W: reservoir of heavy water	V <sub>1</sub> , V <sub>2</sub> : glass bulb
GP: gas pipette	Tc: Thermocouple
M: manometer	Cat: catalyst
Si's: sampling tube	Gw: glass wool

circulated over iron oxide catalyst in reactor R; the circulating system was of about 5.5 liters volume and kept about at 50°C for preventing condensation or adsorption of components of reacting gas on the glass wall. The glass

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bulbs  $V_1$  and  $V_2$  provide the circulating system with the above appropriate volume and work as buffer against the pulsation caused by the operation of circulating pump CP. The temperature of the reactor was maintained constant within  $2^\circ\text{C}$  by means of the thermocouple placed at the center of catalyst and thermoregulator.

**Gases:** CO was prepared by dehydration of formic acid and purified by passing it through liquid nitrogen trap.  $\text{CO}_2$  was formed by decomposition of sodium bicarbonate by sulfuric acid and purified by vacuum distillation.  $\text{H}_2$  prepared by electrolysis of water was passed through the Cu-wire kept at  $350^\circ\text{C}$ , silica gel, liquid nitrogen trap and a palladium thimble kept at  $380^\circ\text{C}$ .

Heavy water of 99.65%  $\text{D}_2\text{O}$  provided by SYOWA DENKO Co., Ltd. was used without further purification.

**Catalyst:** Catalyst (i) was supplied by SYOWA DENKO Co., Ltd. and (ii) by MITSUBISHI KASEI Co., Ltd. The catalyst (i) or (ii) was sized 10–14 mesh or 8–10 mesh and R was charged with about 1.5 or 1.0 gr of it. The either catalyst was treated several times with equimolar mixture of carbon dioxide and hydrogen of 80 mmHg total pressure for fifty hours at about  $520^\circ\text{C}$  and finally with equimolar mixture of carbon monoxide and heavy water vapor of the same total pressure for 10 hours at  $520^\circ\text{C}$ , by which the activity of the catalyst attained a steady value.

**Experimental procedure:** The catalyst was evacuated to  $10^{-6}$  mmHg at the reaction temperature for twenty hours after the above treatment and the runs were conducted for the determination of  $\nu(r)$  as follows.

Carbon monoxide, heavy water vapor, carbon dioxide and hydrogen, respectively of about 20 mmHg pressure, were admitted into the circulating system excluding the reactor R with stopcocks  $C_1$  and  $C_2$  closed and  $C_3$  opened and mixed by circulating it for an hour by-passing the reactor, the catalyst bed being kept at the reaction temperature in the mean time.

Water gas shift reaction was started by switching the circuit to the catalyst bed, *i.e.* by opening stopcocks  $C_1$  and  $C_2$  and closing  $C_3$ . The reaction was followed by sampling the gas mixture from time to time into the gas pipette GP and one of sampling tubes  $\text{Si}$ 's simultaneously. GP was immersed in liquid nitrogen, noncondensing gas evacuated, the bath changed to that of alcohol at  $-50^\circ\text{C}$ , the gas evaporated was evacuated through  $C_7$ ,  $C_7$  closed and the bath removed to restore the temperature of gas pipette to  $50^\circ\text{C}$ . The pressure measured by manometer M was identified with the partial pressure of water in the circulating system at the moment of sampling from which the partial pressure of water  $P^{\text{H}_2\text{O}}$  in the supposed absence of sampling was calculated

by multiplying it by ratio of the initial total pressure to the total pressure prevailing at the sampling. The gas sampled in one of Si's was analyzed by a mass spectrometer for the atomic fraction of deuterium in hydrogen. The total pressure was reduced by 2-3% at each sampling into GP and one of Si. The reaction was thus followed until the decrease of  $P^{\text{H}_2\text{O}}$  was imperceptible.

### § 3 Experimental results

The results obtained are shown in Table 2-4. Fig. 2 shows the plot of  $Z^{\text{H}_2}$  observed against reaction time, *i.e.* the time elapsed from the beginning

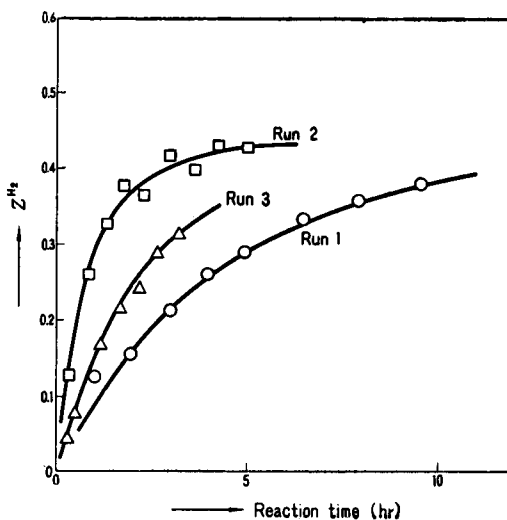


Fig. 2. Atomic fraction of deuterium in hydrogen *vs.* reaction time

of the circulation through the reactor until the sampling. Atomic fraction of deuterium in water  $Z^{\text{H}_2\text{O}}$  was calculated from  $P^{\text{H}_2\text{O}}$  and  $Z^{\text{H}_2}$  as

$$Z^{\text{H}_2\text{O}} = (P_0^{\text{H}_2\text{O}} Z_0^{\text{H}_2\text{O}} - P^{\text{H}_2} Z^{\text{H}_2}) / P^{\text{H}_2\text{O}}, \quad (8)$$

where  $P_0^{\text{H}_2\text{O}}$  and  $Z_0^{\text{H}_2\text{O}}$  denote initial partial pressure of water and initial atomic fraction of deuterium in water and  $P^{\text{H}_2}$  is the initial partial pressure of hydrogen plus  $(P_0^{\text{H}_2\text{O}} - P^{\text{H}_2\text{O}})$ .

Fig. 3 shows the plot of  $P^{\text{H}_2\text{O}}$  against reaction time. From these curves the equilibrium constant  $K_p = P_e^{\text{CO}_2} P_e^{\text{H}_2} / P_e^{\text{CO}} P_e^{\text{H}_2\text{O}}$  was determined as shown in Table 5, where  $P_e^{\text{CO}_2} = P_0^{\text{CO}_2} + (P_0^{\text{H}_2\text{O}} - P_e^{\text{H}_2\text{O}})$  and  $P_e^{\text{CO}} = P_0^{\text{CO}} + (P_e^{\text{H}_2\text{O}} - P_0^{\text{H}_2\text{O}})$ , suffix *e* signifying the final values as read from the curve. The values of  $K_p$  thus obtained agreed with those observed by NEUMANN and KÖHLER<sup>5)</sup> as shown

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TABLE 2. Observed data of run at 520°C.

Reaction time (hr)	$P_{H_2O}$ mmHg	$P_{CO}$ mmHg	$P_{H_2}$ mmHg	$P_{CO_2}$ mmHg	$Z_{H_2}$	$Z_{H_2O}$	$\left(1 - \frac{Z_{H_2}}{Z_{H_2O}}\right) \frac{d \log P_{H_2O}}{d \log Z_{H_2O}}$
0	21.0	19.3	24.1	23.6	0	0.9965	
1	19.6	17.4	26.0	25.5	0.0953	0.9655	1.52
2	18.0	16.2	27.2	26.7	0.1529	0.9356	0.89
3	17.3	15.5	27.9	27.4	0.2091	0.8774	0.45
4	16.8	15.0	28.4	27.9	0.2634	0.8054	0.24
5	16.4	14.6	28.8	28.3	0.2868	0.7775	0.21
6.5	16.0	14.2	29.1	28.6	0.3304	0.7086	0.09
8	15.8	14.0	29.4	28.9	0.3547	0.6689	0.06
9.5	15.6	13.8	29.5	29.0	0.3780	0.6283	0.02
11.0	15.5	13.7	29.7	29.1			
12	15.4	13.6	29.8	29.2			
13	15.4	13.6	29.8	29.2			
14.5	15.3	13.5	29.9	29.3			
52.5	15.2	13.4	30.0	29.5			

TABLE 3. Observed data of run at 380°C.

Reaction time (min)	$P_{H_2O}$ mmHg	$P_{CO}$ mmHg	$P_{H_2}$ mmHg	$P_{CO_2}$ mmHg	$Z_{H_2}$	$Z_{H_2O}$	$\left(1 - \frac{Z_{H_2}}{Z_{H_2O}}\right) \frac{d \log P_{H_2O}}{d \log Z_{H_2O}}$
0	20.3	21.0	22.2	20.6	0	0.9965	
20	17.3	18.0	25.2	23.6	0.1280	0.9824	5.51
50	13.7	14.4	28.8	27.2	0.2615	0.9264	3.10
80	12.5	13.2	30.0	28.4	0.3281	0.8382	1.38
110	11.9	12.6	30.6	28.9	0.3580	0.7885	0.76
140	10.8	11.4	31.7	30.1	0.3850	0.7382	0.55
180	10.5	11.1	32.0	30.4	0.4000	0.7167	0.40
220	9.1	9.7	33.4	31.8	0.4100	0.7022	0.03
260	9.3	9.9	33.2	31.6	0.4180	0.6889	
300	8.6	9.2	33.9	32.3	0.4225	0.6869	
340	8.3	8.9	34.2	32.6			
560	8.2	8.8	34.3	32.7			
620	8.2	8.8	34.3	32.7			
760	8.2	8.8	34.3	32.7			

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TABLE 4. Observed data of run 3 at 375°C.

Reaction time (min)	$P_{H_2O}$ mmHg	$P_{CO}$ mmHg	$P_{H_2}$ mmHg	$P_{CO_2}$ mmHg	$Z_{H_2}$	$Z_{H_2O}$	$\left(1 - \frac{Z_{H_2}}{Z_{H_2O}}\right) \frac{d \log P_{H_2O}}{d \log Z_{H_2O}}$
0	20.3	21.2	21.8	20.0	0	0.9965	
15	18.1	19.1	23.9	22.1	0.0429	1.0335	
30	17.1	18.0	25.0	23.2	0.0772	1.0421	
50	16.1	17.5	25.5	23.7	—	—	
70	14.8	15.8	27.2	25.4	0.1694	1.0201	
100	14.3	15.3	27.8	25.9	0.2187	0.9920	5.33
130	13.3	14.2	28.8	26.9	0.2406	0.9761	2.89
160	12.3	13.2	29.8	27.9	0.2928	0.9459	1.60
190	11.3	12.2	30.8	29.0	0.3145	0.9302	1.23
250	10.0	11.0	32.0	30.2			
300	8.3	9.3	33.7	31.9			
345	8.6	9.6	33.4	31.6			
465	7.5	8.4	34.6	32.7			
585	7.4	8.3	34.7	32.8			
645	7.4	8.3	34.7	32.8			
705	7.3	8.3	34.7	32.9			
765	7.3	8.3	34.7	32.9			

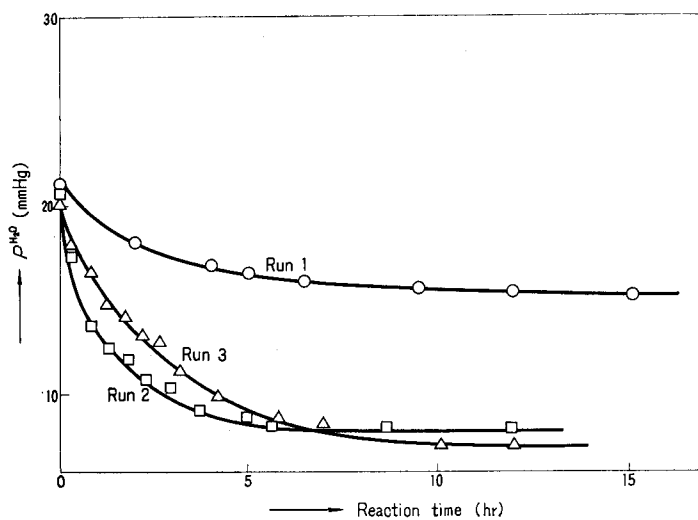


Fig. 3. Partial pressure of water vs. reaction time.

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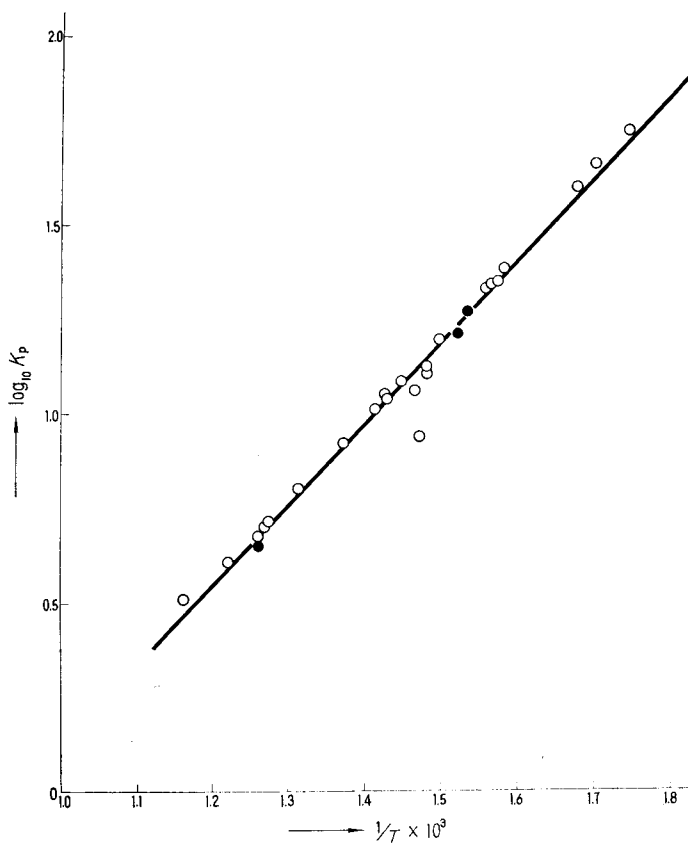


Fig. 4.  $\log K_P$  vs.  $10^3/T$ .

● : Present result  
○ : NEUMANN and KÖHLER

in Fig. 4.

Fig. 5 shows the plot of  $\log_{10} P^{H_2O}$  against  $Z^{H_2O}$  from which the values of  $(1 - Z^{H_2}/Z^{H_2O}) d \log P^{H_2O} / d \log Z^{H_2O}$  in (7) is worked out as shown in Table 2-4.

Fig. 6 shows the value of  $\nu(r)$  as calculated from the experimental data by (7) at different values of  $-\Delta F$ , from which it is concluded with certainty that  $\nu(r)$  is order of magnitude of unity.

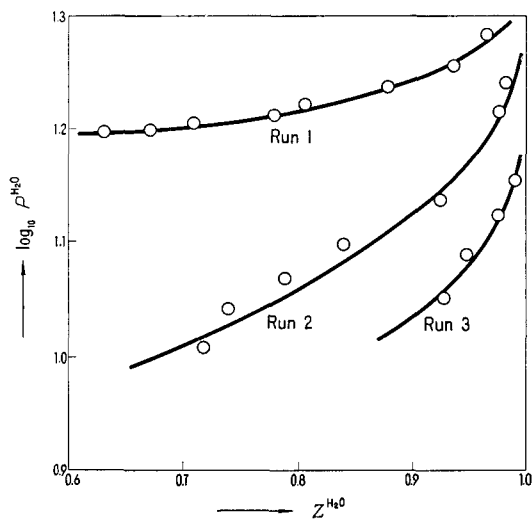
Run 1 was conducted by catalyst (i) and runs 2 and 3 by catalyst (ii).

The total pressure of the reacting gas decreases through a run by a few ten percent. This decrease does not affect  $\nu(r)$ -value as seen from (7), provided that the pressure decrease affects  $d \log P^{H_2O} / dt$  and  $d \log Z^{H_2O} / dt$  by the same

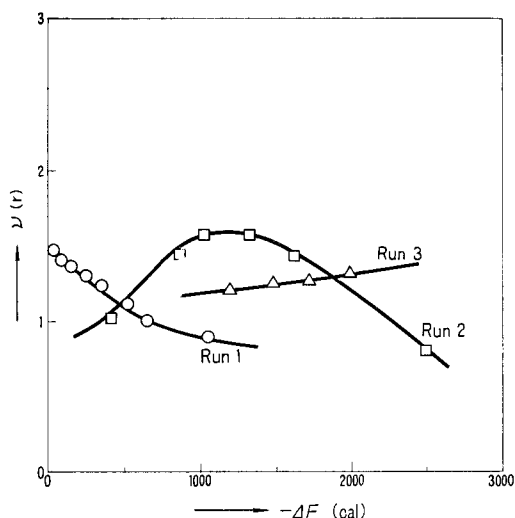
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TABLE 5. Equilibrium constant

No. of run	Catalyst	Reaction temperature °C	Gases	Partial pressure mmHg		$K_p$
				initial	final	
1	(i)	520	H <sub>2</sub> O	21.0	15.2	4.35
			CO	19.3	13.4	
			CO <sub>2</sub>	23.6	29.5	
			H <sub>2</sub>	24.1	30.0	
2	(ii)	380	H <sub>2</sub> O	20.3	8.2	15.37
			CO	21.0	8.9	
			CO <sub>2</sub>	22.2	34.3	
			H <sub>2</sub>	20.6	32.7	
3	(ii)	375	H <sub>2</sub> O	20.3	7.3	18.84
			CO	21.2	8.3	
			CO <sub>2</sub>	21.8	34.7	
			H <sub>2</sub>	20.0	32.9	

Fig. 5.  $\log P^{\text{H}_2\text{O}}$  vs.  $Z^{\text{H}_2\text{O}}$ . $P^{\text{H}_2\text{O}}$ : partial pressure of water $Z^{\text{H}_2\text{O}}$ : atomic fraction of deuterium in water

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**Fig. 6.** Observed values of  $\nu(r)$  vs. affinity  $-\Delta F$ .

factor, which should approximately the case insofar as the isotopic transfer is effected solely through the rate-determining step of the overall reaction. The difference between the factors, if any, could hardly affect the order of magnitude of  $\nu(r)$  as seen from (7) and the values of  $(1 - Z^{\text{H}_2}/Z^{\text{H}_2\text{O}})d \ln P^{\text{H}_2\text{O}}/d \ln Z^{\text{H}_2\text{O}}$  given in Tables 2-4.

#### § 4 Conclusion

We see that the experimental results do not fit in with the sequence I in Table 1, insofar as there exists a rate-determining step. It follows that either there exists no rate-determining step, or a sequence other than I is operative. If sequence II or III is operative and a rate-determining step should exist it must be the last step of sequence II or III.

#### Acknowledgement

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