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ON THE MECHANISM OF WATER GAS SHIFT REACTION

Part III: Determination of Stoichiometric Number of Rate-determining Step in the Neighbourhood of Equilibrium of the Reaction

By

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Abstract

The stoichiometric number, $\nu(r)$, of rate-determining step r of catalyzed water gas shift reaction was developed theoretically in terms of quantities observable in use of carbon-14 as a tracer in the neighbourhood of equilibrium of the reaction and, on its basis, the $\nu(r)$ of the reaction in the presence of iron oxide catalyst was determined to be around unity in accordance with the previous results obtained in the state of the reaction remote from equilibrium using deuterium as well as carbon-14 as tracer.

Introduction

It was found in the previous works^{1,2)} that the stoichiometric number, $\nu(r)$, of rate-determining step r of catalyzed water gas shift reaction,



in the presence of iron oxide was unity using deuterium¹⁾ as well as carbon-14²⁾ as tracer in a state of the reaction remote from equilibrium, hence concluded that the rate-determining step was a bimolecular reaction of water and carbon monoxide on the catalyst surface.

The present work is devoted to the determination of the stoichiometric number, $\nu(r)$, of rate-determining step of reaction (1) in the neighbourhood of equilibrium by means of carbon-14 as tracer.

Method of $\nu(r)$ -Evaluation

The determination of $\nu(r)$ is based on the general equation,

$$V = V_+ \left\{ 1 - \exp \left(\frac{\Delta G}{\nu(r)RT} \right) \right\} \quad (2)$$

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derived by HORIUTI³⁾, where V or V_+ is the overall rate or the unidirectional forward rate, respectively, of a steady reaction, $-\Delta G$ its chemical affinity, *i. e.* the excess of the sum of chemical potential of the reactants over that of the products of the reaction, and R and T of usual meanings.

The ΔG in Eq. (2) is expressed for water gas shift reaction in terms of partial pressure of water vapor, $P^{\text{H}_2\text{O}}$, etc. and equilibrium constant K_p of the reaction, assuming the ideal gas law, as

$$-\Delta G = RT \ln \left\{ \frac{P^{\text{CO}} P^{\text{H}_2\text{O}}}{P^{\text{CO}_2} P^{\text{H}_2}} \cdot K_p \right\}. \quad (3)$$

$P^{\text{H}_2\text{O}}$ etc. are given in terms of total pressure P and mole fraction of water vapor, x , as

$$P^{\text{H}_2\text{O}} = P^{\text{CO}} = Fx \quad (4)$$

and

$$P^{\text{H}_2} = P^{\text{CO}_2} = P \left(\frac{1}{2} - x \right). \quad (5)$$

We have from Eqs. (2), (3), (4) and (5)

$$V = V_+ \left[1 - \left\{ \left(\frac{1/2 - x}{x} \right) \left(\frac{x_e}{1/2 - x_e} \right) \right\}^{\frac{2}{\nu(r)}} \right], \quad (6)$$

where x_e is the particular value of x in equilibrium of the reaction.

Writing V of reaction (1) as

$$V = - \frac{dP^{\text{H}_2\text{O}}}{dt} = - \frac{d(Px)}{dt}, \quad (7)$$

we have

$$- \frac{dx}{dt} = \frac{1}{P} V. \quad (8)$$

In the neighbourhood of equilibrium, we have, expanding the term $\left\{ \left(\frac{1/2 - x}{x} \right) \left(\frac{x_e}{1/2 - x_e} \right) \right\}^{\frac{2}{\nu(r)}}$ of the above equation into a power series of $(x - x_e)$ and neglecting terms higher than the second order,

$$- \frac{dx}{dt} = r_1 (x - x_e), \quad (10)$$

where

$$r_1 = \frac{V_{e,1}}{\nu(r) P x_e (1/2 - x_e)} \quad (11)$$

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and $V_{e,1}$ is the particular value of V_+ or V_- of reaction (1), which is balanced with each other in equilibrium.

The value of r_1 is experimentally determined by Eq. (10) or by its integral form

$$\ln \frac{x_0 - x_e}{x - x_e} = r_1 t, \quad (12)$$

where x_0 is the value of x at $t=0$.

The $\nu(r)$ is now evaluated according to Eq. (11) from the value of $V_{e,1}$, which is determined by using carbon-14 as tracer as follows. Carbon-14 contained in carbon dioxide is transferred to carbon monoxide at a rate

$$-P_e^{CO_2} \frac{dC^{CO_2}}{dt} = V_e (C^{CO_2} - C^{CO}), \quad (13)$$

where C^{CO_2} or C^{CO} is the specific β -ray counts of CO_2 or CO respectively and $P_e^{CO_2}$ the particular value of P^{CO_2} in equilibrium of reaction (1); it is admitted as regards Eq. (13) that the isotopic difference of rate is ignorable.

The rate of transfer, V_e , is assumed to consist of two parts of contribution of reaction (1), $V_{e,1}$, and that, $V_{e,2}$, of exchange reaction



which proceeds simultaneously with but independent of reaction (1), hence

$$V_e = V_{e,1} + V_{e,2}. \quad (15)$$

V_e is directly determined by measuring the initial rate of decrease, $-(dC^{CO_2}/dt)_0$, of C^{CO_2} according to Eq. (13) or by integrating Eq. (13) with regard to the conservation of carbon-14 stated as

$$P_e^{CO_2} C_0^{CO_2} = P_e^{CO} C^{CO} + P_e^{CO_2} C^{CO_2}, \quad (16)$$

where $C_0^{CO_2}$ is the initial value of C^{CO_2} . Eliminating from Eqs. (13) and (16), and integrating we have

$$\ln \left[\left(1 + \frac{P_e^{CO_2}}{P_e^{CO}} \right) \frac{C^{CO_2}}{C_0^{CO_2}} - \frac{P_e^{CO_2}}{P_e^{CO}} \right] = -\frac{V_e t}{P_e^{CO_2}} \left(1 + \frac{P_e^{CO_2}}{P_e^{CO}} \right).$$

The argument of the natural logarithm in the above equation vanishes at $t \rightarrow \infty$, hence

$$\frac{P_e^{CO_2}}{P_e^{CO}} = \frac{C_\infty^{CO_2}}{(C_0^{CO_2} - C_\infty^{CO_2})},$$

where $C_\infty^{CO_2}$ is the value of C^{CO_2} at $t \rightarrow \infty$. Elimination of $P_e^{CO_2}/P_e^{CO}$ from the above two equations gives

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$$V_e = \frac{P_e^{CO_2}}{t} \frac{C_0^{CO_2} - C_\infty^{CO_2}}{C_0^{CO_2}} \ln \frac{C_0^{CO_2} - C_\infty^{CO_2}}{C^{CO_2} - C_\infty^{CO_2}}. \quad (17)$$

$V_{e,2}$ is determined, on the other hand, according to the equation,

$$-P_e^{CO_2} \left(\frac{dC^{CO_2}}{dt} \right)_2 = V_{e,2} (C^{CO_2} - C^{CO}), \quad (18)$$

similar to Eq. (13), by determining the rate of decrease of through exchange reaction (14), $-\left(\frac{dC^{CO_2}}{dt}\right)_2$, or by integrating Eq. (18) with reference to Eq. (16), provided that the carbon-14 transfer due to exchange reaction (14) proceed at the same rate in the absence of water vapor and hydrogen as in their presence.

Let k be the ratio of $V_{e,2}$ to V_e , *i. e.*

$$k \equiv V_{e,2}/V_e \quad (19. a)$$

We have thus from (Eq. 15)

$$V_{e,1} = (1-k)V_e \quad (19. b)$$

The $\nu(r)$ is expressed in terms of observable quantities, by eliminating, $V_{e,1}$ and V_e from Eqs. (11), (17) and (19.b) with reference to the relation $P_e^{CO_2} = P(\frac{1}{2} - x_e)$ in accordance with Eq. (5), as

$$\nu(r) = (1-k)\nu(r)' \quad (20. a)$$

$$\nu(r)' = \frac{C_0^{CO_2} - C_\infty^{CO_2}}{x_e C_0^{CO_2}} \cdot \frac{\ln \{(C_0^{CO_2} - C_\infty^{CO_2}) / (C^{CO_2} - C_\infty^{CO_2})\}}{r_1 t}. \quad (20. b)$$

Experimental Results and Discussion

The apparatus for the observation is the same as that in the previous work. Two series of experiments at 375°C and 380°C were conducted by following the partial pressure of water vapor and that of β -ray counts of carbon dioxide labelled with carbon-14. No change of catalytic activity was found before and after the exchange reaction. Sampled carbon dioxide was absorbed in aqueous solution of $Ba(OH)_2$ and the β -ray count of the precipitated $BaCO_3$ was measured similarly as in the previous work.²⁾

The results obtained are shown in Figs. 1 to 6. From Fig. 1 or 2 the equilibrium partial pressure of water vapor, P^{H_2O} , was determined to be 7.03 or 8.30 mmHg respectively. Linear relation was obtained between $\log_{10} |P^{H_2O} - P_e^{H_2O}|$ and the time of reaction as shown in Fig. 3 or 4, from which the value of r_1 was determined according to Eq. (12) to be 0.276 or 0.338 hr⁻¹

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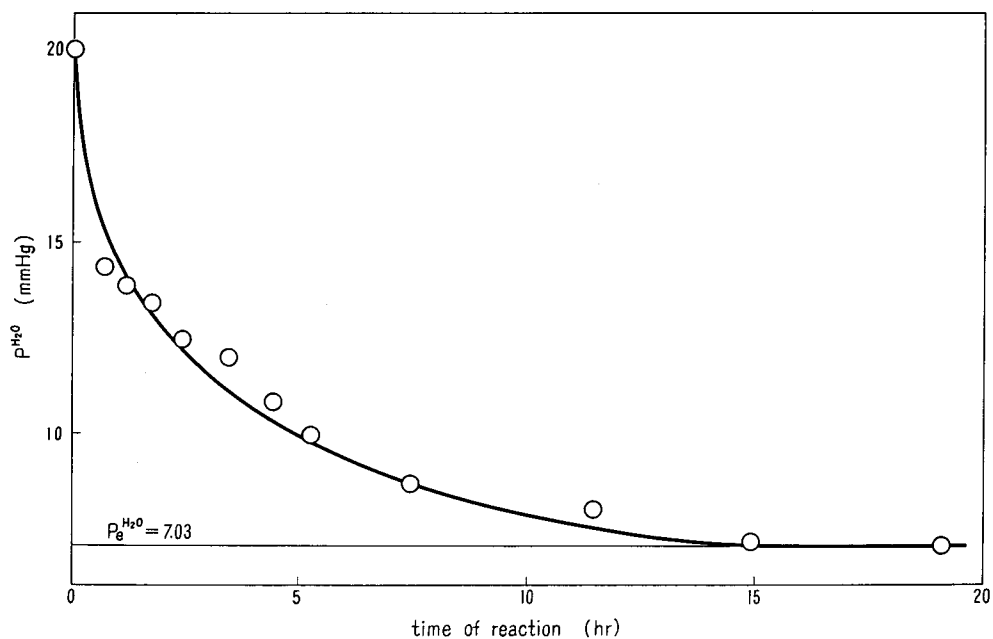


Fig. 1. Variation of P_{H_2O} with time of reaction; series 1 at 375°C.

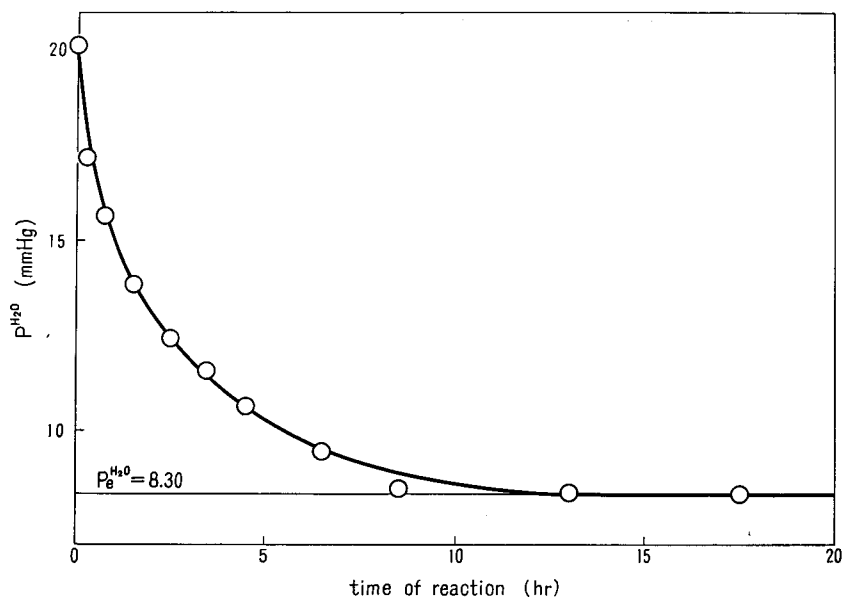


Fig. 2. Variation of P_{H_2O} with time of reaction; series 2 at 380°C.

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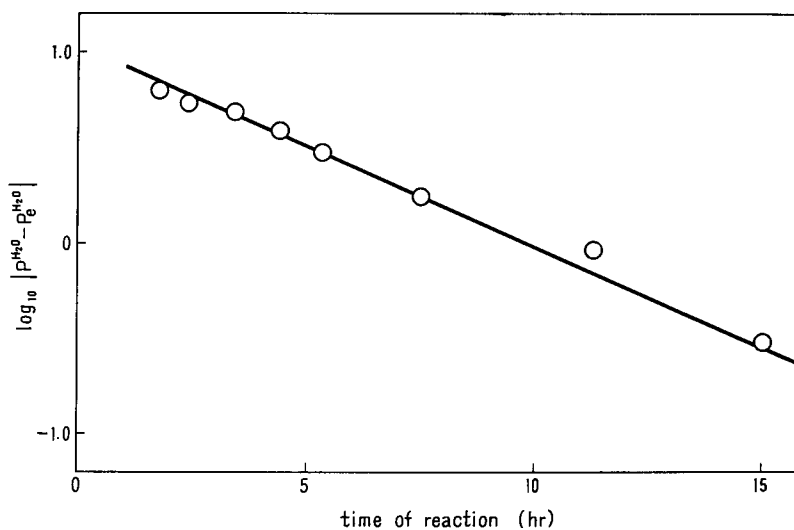


Fig. 3. $\log_{10} |P^{\text{H}_2\text{O}} - P_e^{\text{H}_2\text{O}}|$ vs. time of reaction;
series 1 at 375°C.

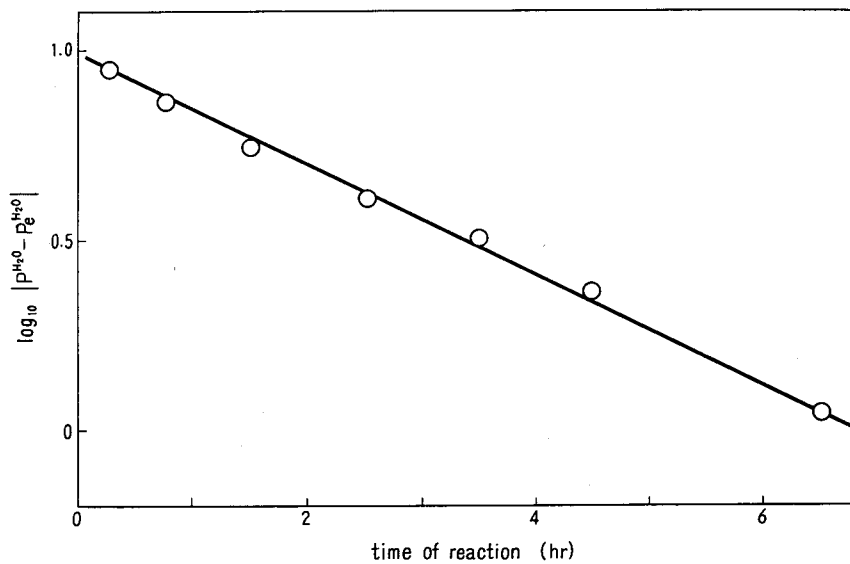


Fig. 4. $\log_{10} |P^{\text{H}_2\text{O}} - P_e^{\text{H}_2\text{O}}|$ vs. time of reaction;
series 2 at 380°C.

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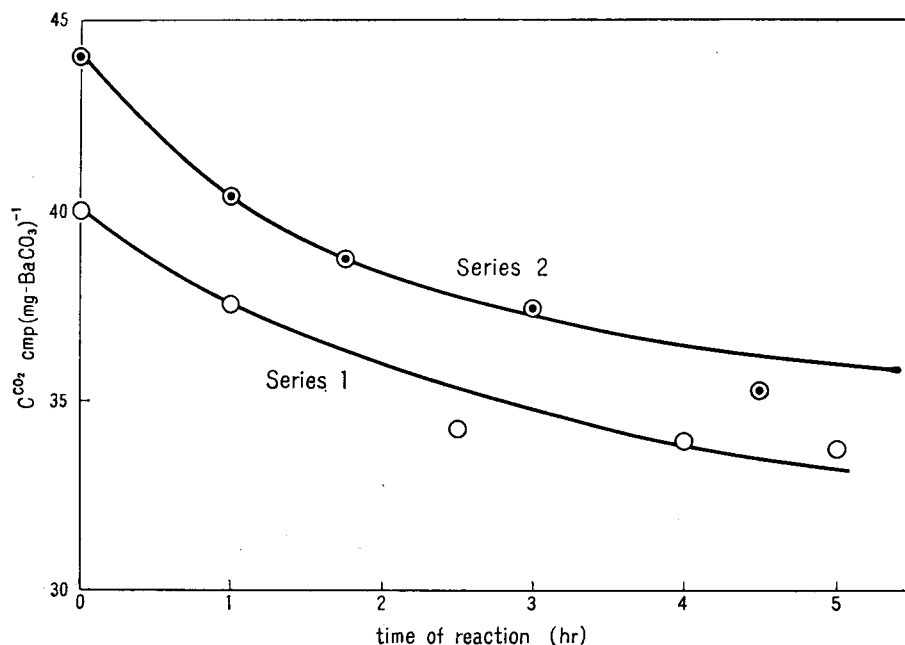


Fig. 5. Variation of C^{CO_2} with time of reaction.

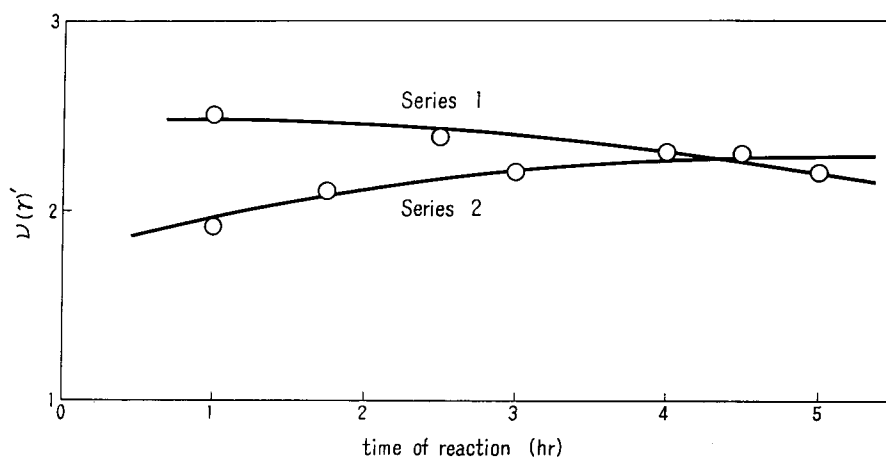


Fig. 6. Values of $\nu(r)'$ determined along with the progress of reaction.

for series 1 or 2 respectively. The value of $C_0^{\text{CO}_2}$ was 39.9 or 44.0 cpm $(\text{mg-BaCO}_3)^{-1}$ for series 1 or 2 respectively, from which and the values of $P_e^{\text{CO}_2}$ and P_e^{CO} , the value of $C_\infty^{\text{CO}_2}$ was calculated at 30.8 or 34.5 cpm $(\text{mg-BaCO}_3)^{-1}$ for series 1 or 2 respectively equating C^{CO} and C^{CO_2} in Eq. (16)

with $C_{\infty}^{\text{CO}_2}$. This value of $C_{\infty}^{\text{CO}_2}$ coincides with its value determined according to Eq. (17) to be its value which provides best linear relation between $\log_{10}(C^{\text{CO}_2} - C_{\infty}^{\text{CO}_2})$ and t . The value of $\nu(r)'$ calculated by Eq. (20.b) from these results is nearly 2 as shown in Fig. 6.

The k is estimated from the comparison of the previous results²⁾ with the present one as follows. The initial rate of decrease of C^{CO_2} was observed previously with regard to reaction (14) at $P_e^{\text{CO}_2} = P_e^{\text{CO}} = 20$ mmHg and 385°C and 405°C in the absence of water vapor and hydrogen. The initial rate of decrease of C^{CO_2} was now found with regard to reaction (1) at *ca.* $P_e^{\text{CO}_2} = 30$ mmHg, $P_e^{\text{CO}} = 10$ mmHg and the same value of $C_e^{\text{CO}_2}$ to be three times as large as the rate previously observed with reaction (14) as mentioned above both at the temperatures. It follows from Eqs. (13), (18) and (19.a) that

$$k = \frac{V_{e,2}}{V_e} = \frac{30}{20} \frac{1}{3} = \frac{1}{2},$$

assuming that $(dC^{\text{CO}_2}/dt)_2$ remains the same, it $P_e^{\text{CO}_2}$ be raised from 20 to 30 mmHg in line with the present condition of reaction (1).

It follows from Eq. (20.a) and the above equation that $\nu(r)$ lies around unity in accordance with the previous result in the state of reaction (1) remote from equilibrium.

Closer investigation is regard on $V_{e,2}$ and the effect of adsorption of water vapor and hydrogen on $V_{e,2}$ for a quantitative determination of $\nu(r)$, which is left to further works.

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