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KINETICS OF WATER GAS SHIFT REACTION ON EVAPORATED PLATINUM FILM

By

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Abstract

The kinetics of the catalyzed water gas shift reaction $H_2 + CO_2 = H_2O + CO$ in the presence of evaporated platinum film was investigated over a range of partial pressures both of hydrogen and carbon dioxide from about 6 to 100 mmHg and of temperature from 382 to 465°C.

The rate V of the reaction was determined at 413°C as

$$V = k_p (P_{H_2})^{0.5} (P_{CO_2})^{0.6} (P_{CO})^{-0.5},$$

where k_p is a rate constant and P_{H_2} , P_{CO_2} and P_{CO} are partial pressures of hydrogen, carbon dioxide and carbon monoxide respectively. $E_p = RT^2 d \ln k_p / dT$ was found to be 24.6 ± 1.1 Kcal/mole.

The lower limit N_0^* of the number of seats of the critical complex of the rate-determining step was calculated statistical mechanically from the above result according to J. HORIUTI *et al.* at $7.3 \times 10^{14} \text{ cm}^{-2}$. It was concluded from the result that the lattice plane model applied to the metallic catalyst on the one hand and that the transmission coefficient of the rate-determining step was of the order of magnitude of unity on the other hand.

Introduction

The number N^* of seats of critical complex of an elementary reaction amounts 10^{15} cm^{-2} , if they are physically identical with each other and each of them is furnished by one or a set of a few adjacent metal atoms on a lattice plane but smaller in order of magnitude, if provided by one or a few metal atoms of peculiar arrangement as suggested by the active center theory.

It was shown recently that the lower limit N_0^* to N^* of the rate-determining step may be calculated from the observation of the rate as a function of temperature and concentrations of reactants and products irrespective of the mechanism of reaction and that the lower limits of 66 available data amount $10^{15.32 \pm 0.32}$, where 0.32 is the standard deviation¹⁾.

The kinetics of the catalyzed water gas shift reaction $H_2 + CO_2 = H_2O + CO$ in the presence of platinum has been observed by PRICHARD and HINSHEL-

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WOOD²⁾, whose result gives, however, an extravagant value of $N_0^* = 10^{32}$. The present experiment has been conducted with a view to investigating the kinetics of the reaction with sufficient accuracy for the N_0^* -determination.

Experimental

Fig. 1, (a) shows a glass reaction system consisting of reaction vessel V, circulation pump P, trap T cooled by dry ice ethanol mixture and mercury manometer M. The reaction vessel is, as shown in Fig. 1, (b), of 1.5 cm inner diameter, in which 99.9% pure platinum wire of 0.4 mm diameter and 14 cm length was sealed.

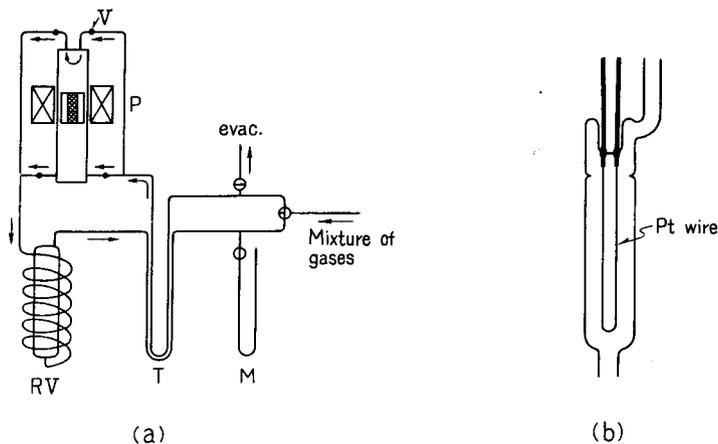


Fig. 1, (a) The reaction system consisting of RV: Reaction vessel, P: Circulation pump, T: Trap cooled by dry ice ethanol mixture, M: Mercury manometer, V: Valve.
(b) Details of RV.

The platinum wire was evaporated on the wall of the reaction vessel as follows. The reaction vessel was evacuated at *ca.* 400°C for about 15 hr and further at *ca.* 500°C for a few hours, while platinum wire was heated electrically by passing a current of 5 A. The reaction vessel was now immersed in ice water and the platinum wire was evaporated by heating it by passing a current of 6.8 A for 90 min. The platinum film thus evaporated was sintered at *ca.* 480°C for 30 min. and kept at *ca.* 410°C for 2 hr until used as catalyst.

Pure carbon dioxide from TAKACHIHO Chemical Industrial Co., Tokyo was purified by repeated distillation in vacuo and hydrogen from cylinder was purified by passing it through a heated Pd-Ag alloy thimble.

The reaction was initiated by introducing a mixture of hydrogen and carbon

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dioxide and circulating it through the reaction vessel and trap T by means of circulation pump P. The reaction was followed by observing the decrease of total pressure with manometer M along with condensation of water produced. M was read by a traveling microscope with an accuracy of ± 0.02 mmHg. The reaction temperature was kept constant within $\pm 0.5^\circ\text{C}$ by means of an electric furnace around the reaction vessel controlled by a thermoregulator.

The rate V of the reaction was determined as the inclination of the total pressure against time at the point, where the total pressure decreased by 1 mmHg after the initial charge of the reaction mixture except in case of series III described below; it took at least five minutes for the total pressure to decrease by 1 mmHg. The latter condition of rate measurement was preferred for the sake of its definiteness, since it was found that the rate depended significantly on the partial pressure of carbon monoxide. The partial pressures of hydrogen and carbon dioxide were determined by subtracting the observed decrease of the total pressure from the initial partial pressure of the respective gas.

Four series of experiments have thus been conducted as follows.

I. Several runs of the reaction were successively conducted at 413°C and the initial total pressure of 30 mmHg of 1 : 1 mixture of hydrogen and carbon dioxide without any treatment of the catalyst except evacuation between runs. The rate of each run was observed reproducibly within fluctuation of $\pm 10\%$, without any perceptible decay of catalytic activity. The resultant gas was analyzed by means of a mass spectrometer; no species but hydrogen,

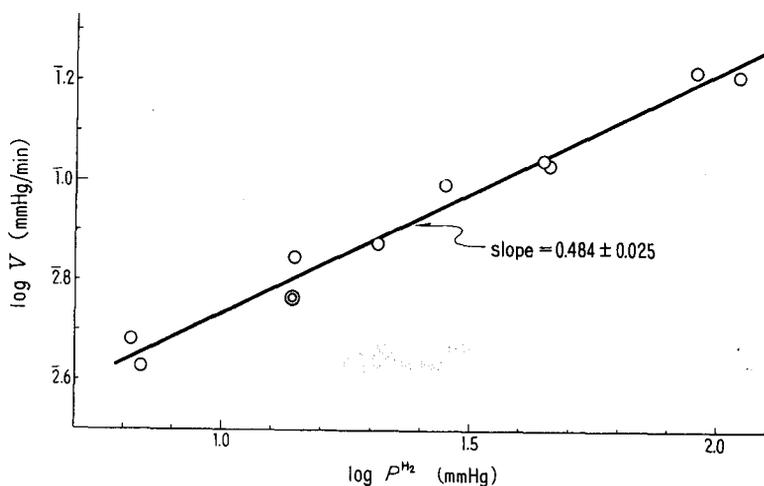


Fig. 2. $\log V$ (mmHg/min) vs. $\log P^{\text{H}_2}$ (mmHg) at 413°C : $P^{\text{CO}_2} = 13.75 \pm 0.14$ mmHg, $P^{\text{CO}} = 1.0 \pm 0.04$ mmHg.

carbon dioxide and carbon monoxide was thus found in the resultant gas. Water was neither detected*).

II. The pressure dependences of the rate V on partial pressures of hydrogen and carbon dioxide were now investigated at 413°C by varying either of initial partial pressures of hydrogen and carbon dioxide keeping the other constant. The result was, as shown in Fig. 2 and Fig. 3, that the rate was

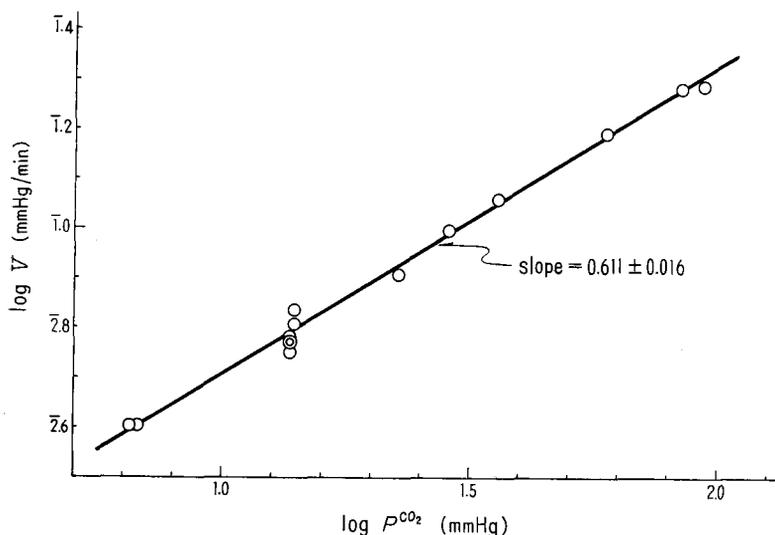


Fig. 3. $\log V$ (mmHg/min) vs. $\log P^{\text{CO}_2}$ (mmHg) at 413°C : $P^{\text{H}_2} = 13.80 \pm 0.12$ mmHg, $P^{\text{CO}} = 1.0 \pm 0.04$ mmHg.

proportional to the 0.5th power of partial pressure P^{H_2} of hydrogen and the 0.6th power of partial pressure P^{CO_2} of carbon dioxide, *i.e.*,

$$V \propto (P^{\text{H}_2})^{0.5} (P^{\text{CO}_2})^{0.6} \quad (1)$$

so that in case, where $P^{\text{H}_2} = P^{\text{CO}_2}$, the rate is proportional to $(P^{\text{H}_2})^{1.1}$.

III. The dependence of V on partial pressure P^{CO} of carbon monoxide was now determined by following $V/(P^{\text{H}_2})^{1.1}$ with increase of P^{CO} identified with the decrease of the total pressure along with the progress of reaction as shown in Fig. 4. The results shown in Fig. 2, 3 and 4 are summarized as

$$V = k_p (P^{\text{H}_2})^{0.5} (P^{\text{CO}_2})^{0.6} (P^{\text{CO}})^{-0.5}, \quad (2)$$

where k_p is the rate constant.

IV. The $E_p = RT^2 d \ln k_p / dT$ was determined by conducting the experi-

*) Vapor pressure of ice at dry ice temperature (-78°C) is 0.00056 mmHg.

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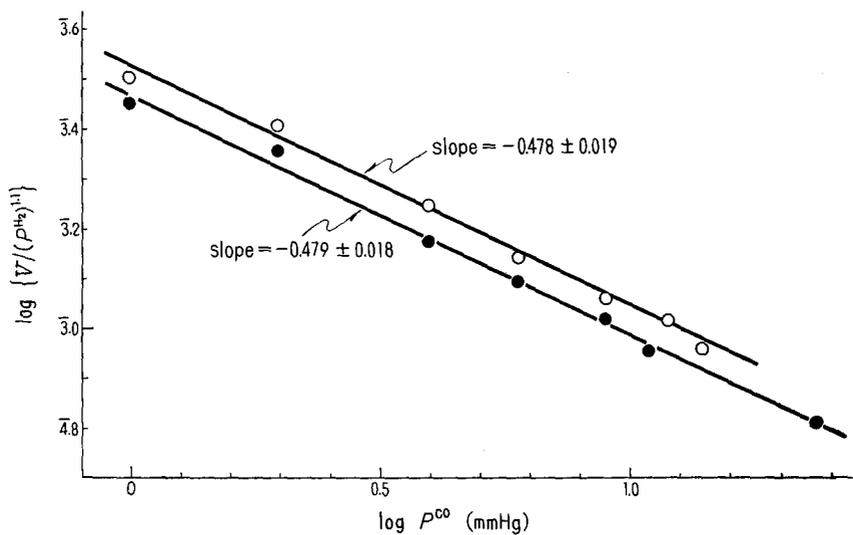


Fig. 4. $\log \{V/(P^{H_2})^{1.1}\}$ vs. $\log P^{CO}$ (mmHg) at 413°C : \circ , first run; \bullet , second run. Initial values of $P^{H_2} = P^{CO_2}$ are 42.30 mmHg for the first run and 32.10 mmHg for the second run.

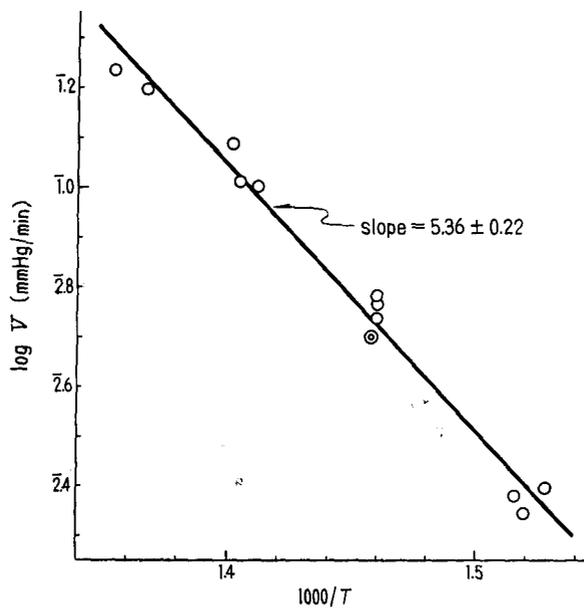


Fig. 5. ARRHENIUS plots of the reaction rate: $P^{H_2} = P^{CO_2} = 13.89 \pm 0.11$ mmHg, $P^{CO} = 1.0 \pm 0.04$ mmHg.

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ments similar to those in series I at different temperatures from 382 to 465°C*) at the initial total pressure of 30 mmHg with 1 : 1 mixture of hydrogen and carbon dioxide. Fig. 5 shows the result from which E_p is determined to be 24.6 ± 1.1 Kcal/mole.

The surface area of the catalyst was determined to be 45 ± 10 cm², on the basis of its geometric area and the roughness factor identified with that 1.2 of a platinum film similarly evaporated and sintered; the geometric area and the monolayer capacity of krypton at liquid nitrogen temperature of the latter film were determined from which the roughness factor was calculated. Fig. 6

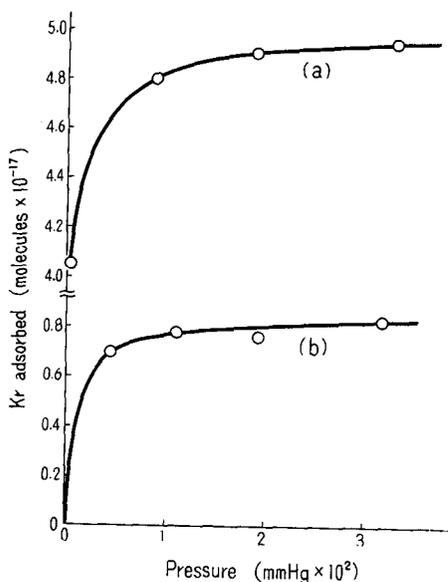


Fig. 6. Isotherm of krypton adsorption on Pt-film at -196°C : (a), before sinter; (b), after sinter at ca. 480°C for 30 min. and at ca. 410°C for 2 hr. The geometric area of Pt-film is 120 cm².

shows the isotherms of krypton on the latter film observed before and after the sintering, which reduced the roughness factor of the film from 7.9 to 1.2**).

*) The quantity of gas contained in the reaction system at a constant pressure depends negligibly on reaction temperature, since the volume of the reaction vessel is small as compared with the volume of the rest of the system kept at room temperature.

***) The monolayer capacity of adsorbed krypton was determined by the point-B method, assuming the cross-sectional area of an adsorbed krypton molecule to be 19.4 \AA^2 ³⁾.

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Calculation of the number N_0^*

It has been shown by J. HORIUTI *et al.*¹⁾ that the lower limit N_0^* cm⁻² to the number N^* cm⁻² of the seat σ^* of critical complex of the rate-determining step is determined by the equation

$$\log N_0^* = \log v_+ + E_+^*/2.3RT - \log kTe/h + \sum_{\delta^g} \nu_{\delta^g} (\log Q^{\delta^g}/N^{\delta^g} + T \partial \log Q^{\delta^g}/\partial T), \quad (3)$$

where v_+ is the forward unidirectional rate of the rate-determining step per unit area, RT or RT/h of usual meaning, N^{δ^g} the concentration of reactant or product δ^g in gas, Q^{δ^g} the partition function of a single δ^g in unit volume, $E_+^* = RT^2 (\partial \ln v_+ / \partial T)_N$ and $\nu_{\delta^g} = (\partial \ln v_+ / \partial \ln N^{\delta^g})_{T, N(\neq N^{\delta^g})}$, suffix N or $N(\neq N^{\delta^g})$ indicating every concentration or every but N^{δ^g} being kept respectively constant.

The forward unidirectional rate V_+ of the overall reaction is the quotient v_+ of the rate-determining step over its stoichiometric number¹⁾, which is assumed to be unity. The V_+ is now identified with V given by Eq. (2) on account of the observed absence of water. The activation energy E_+^* is expressed as

$$E_+^* = RT^2 \left(\frac{\partial \ln V}{\partial T} \right)_N = RT^2 \left(\frac{\partial \ln V}{\partial T} \right)_P - RT^2 \sum_{\delta^g} \left(\frac{\partial \ln V}{\partial \ln N^{\delta^g}} \right)_{(T, N \neq N^{\delta^g})} \left(\frac{\partial \ln N^{\delta^g}}{\partial T} \right)_P, \quad (4)$$

where suffix P signifies the partial pressure of every gaseous component being

TABLE 1. Experimental data

| | |
|--|--|
| Activation energy E_+^* | $(24.6 \pm 1.1 \text{ Kcal/mole}) + 0.6 RT$ |
| Order of reaction | |
| ν_{H_2} | 0.484 ± 0.025 |
| ν_{CO_2} | 0.611 ± 0.016 |
| ν_{CO} | -0.478 ± 0.013 |
| Surface area of catalyst | $45 \pm 10 \text{ cm}^2$ *) |
| Capacity of the reaction system | $(7.73 \pm 0.07) \times 10^{18}$ molecules at 1 mmHg |
| Reaction rate V at $P_{\text{H}_2} = P_{\text{CO}_2} = 13.84 \pm 0.08$ mmHg, $P_{\text{CO}} = 1.0 \pm 0.04$ mmHg and $413 \pm 1^\circ\text{C}$. | $(5.9 \pm 0.6) \times 10^{-2}$ mmHg/min**) |

*) The error $\pm 10 \text{ cm}^2$ is estimated from the accuracy of the basic measurement.

**) This value is the average of V read from Fig. 2, 3 and 5.

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TABLE 2. Calculation of N_0^*

| | |
|---|--------------------|
| $\log V$ (molecules \cdot sec $^{-1}\cdot$ cm $^{-2}$) | 14.23 \pm 0.11 |
| $E_{\ddagger}^*/2.3 RT$ | 8.10 \pm 0.35 |
| $-\log (kT_e/h)$ | -13.59 \pm 0.001 |
| $\nu_{H_2} \{ \log Q^{H_2}/N^{H_2} + (5/2)/2.3 \}$ | 4.54 \pm 0.24 |
| $\nu_{CO_2} \{ \log Q^{CO_2}/N^{CO_2} + (5/2)/2.3 \}$ | 8.30 \pm 0.25 |
| $\nu_{CO} \{ \log Q^{CO}/N^{CO} + (5/2)/2.3 \}$ | - 6.72 \pm 0.18 |
| $\log N_0^*$ (cm $^{-2}$) | 14.86 \pm 0.53 |

kept constant. In the above equation $RT^2 (\partial \ln V / \partial T)_P$ is E_P observed in series IV, $\nu_\theta = (\partial \ln V / \partial \ln N^{\nu_\theta})_{T, N(\neq N^{\nu_\theta})}$ is identical with the relevant exponent in Eq. (2) and $(\partial \ln N^{\nu_\theta} / \partial T)_P$ is $-1/T$, hence

$$E_{\ddagger}^* = E_P + 0.6 RT.$$

The N_0^* is determined by Eq. (3), from ν_θ and E_{\ddagger}^* obtained above as shown in Table 1 with their mean errors. Table 2 shows the value of N_0^* and each term of Eq. (3) with their mean errors.

Conclusive Remarks

The above result shows that the lower limit $\log N_0^*$ to $\log N^*$ is almost in coincidence with value the $\log N^* = 15$ as required by the lattice plane model of metallic adsorbent. It follows that $\log N^*$ in the present experiment was actually almost 15 in accordance with the lattice plane model and that the transmission coefficient of the rate-determining step is of the order of magnitude of unity¹⁾.

Acknowledgement

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