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ON THE MECHANISM OF CARBON MONOXIDE OXIDATION

Part I Determination of the Stoichiometric Number of the Rate-determining Step on Platinum Catalyst by Means of Carbon-14 Tracer

By

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Abstract

The reaction, $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, catalyzed by platinum was investigated kinetically at *ca.* 125 mmHg total pressure and at temperatures between 300°C and 474°C by the use of carbon-14 as a tracer. The stoichiometric number of the rate-determining step of the reaction and the relative rates, $v_{a,+}/V_+$ and $v_{b,+}/V_+$, were determined, where V_+ is the forward unidirectional rate of the reaction and $v_{a,+}$ or $v_{b,+}$ that of a path, *i.e.*, a sequence of steps, *a* or *b*, effecting or not effecting the transfer of carbon-14 from carbon dioxide to carbon monoxide respectively. On the basis of the results obtained, it was concluded that the rate-determining step switches over from $\text{O}_2 \rightarrow 2\text{O}$ (a) to $\text{CO} + \text{O}$ (a) \rightarrow CO_2 with rise of the reaction temperature beyond 400°C.

Introduction

It has been established that the method of the stoichiometric number¹⁾ is very useful for determination of the mechanism of heterogeneous catalysis.²⁻¹¹⁾

The present work is devoted to application of the method for investigation in the catalyzed oxidation of carbon monoxide,



in the presence of platinum catalyst by the use of carbon-14 as a tracer.

According to the theory of steady reaction¹⁾, the stoichiometric number of the rate-determining step, r , is given as

$$\nu(r) = \frac{-\Delta G}{RT \ln(V_+/V_-)}, \quad (2)$$

where $-\Delta G$ is the chemical affinity, V_+ or V_- the unidirectional forward or backward rate of the overall reaction respectively. The V_+ or V_- can be

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measured as the unidirectional transfer rate of an appropriate isotope, provided that the isotopic difference of the rates is ignorable and the exchange of the isotope between reactant and resultant of the reaction (1) takes place exclusively through the rate-determining step, r . In the case where the transfer of the isotope occurs through steps other than r , $\nu(r)$ evaluated according to Eq. (2) may be infinitely large on account of $V_+ = V_-$, as shown by FRUMKIN¹²⁾ and generally discussed by MATSUDA and HORIUTI.¹³⁾

Let, for instance, the overall reaction (1) proceeds through a sequence of steps given in Table 1. If one uses carbon dioxide labelled with carbon-14,

TABLE 1. The stoichiometric number, $\nu(s)$, of step s and its observable value of $\nu(r)$ expected for the case of $s=r$ by means of respective isotopic tracer

| Constituent step | Stoichiometric number | | |
|--|-------------------------|---------------------|----------|
| | theoretical $\nu(s)$ | observable $\nu(r)$ | |
| | | 14C | 18O |
| $C_2 \longrightarrow 2O(a)$ (3, i) | 1 | ∞ | 1 |
| $CO \longrightarrow CO(a)$ (3, ii) | 2 | 2 | ∞ |
| $CO(a)+O(a) \longrightarrow CO_2$ (3, iii) | 2 | 2 | 2 |

an infinitely large value or 2 is expected for the $\nu(r)$ -values for the case where the first step (3, i) or either of the others of Table 1 is rate-determining respectively, because the transfer of carbon-14 from carbon dioxide to carbon monoxide is effected by step (3, ii) and (3, iii), but not by (3, i). The $\nu(r)$ -values expected for respective isotopic tracers inclusive of carbon-14 are summarized in Table 1, which shows that the rate-determining step is determinable on the basis of a set of values of $\nu(r)$ observed by the use of appropriate isotopic tracers more than one. The mechanism of the water gas shift reaction, $CO + H_2O = CO_2 + H_2$, catalyzed by iron oxide has thus been determined successfully by the present authors.⁷⁾

In the present work the stoichiometric number, $\nu(r)$, of rate-determining step of reaction (1) is evaluated as ∞ or 2 at temperatures below or above *ca.* 400°C respectively by the use of carbon-14 as a tracer, and a probable mechanism is proposed.

Method of $\nu(r)$ -Evaluation

The stoichiometric number, $\nu(r)$, is evaluated on the basis of Eq. (2) as follows.

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The chemical affinity, $-\Delta G$, of reaction (1) is expressed assuming the ideal gas law as

$$-\Delta G = RT \ln \left[\frac{(P^{O_2})^2 (P^{O_2})}{(P^{CO_2})^2} \cdot K_p \right], \quad (4)$$

where K_p is the equilibrium constant of the reaction¹⁴⁾ and P 's are the partial pressure of the substance indicated superscript.

The steady rate, V , of reaction (1) is given as

$$V = -\frac{dn^r}{dt} = -\frac{1}{2} \frac{dn^{CO}}{dt} = \frac{1}{2} \frac{dn^{CO_2}}{dt} = V_+ - V_-, \quad (5)$$

where n^{CO} , n^{CO_2} or n^r is the number of moles of carbon monoxide, carbon dioxide or whole of gas respectively in the reaction system and t the time of reaction.

Provided that the isotopic difference of the rate is ignorable and that carbon-14 atoms are transferred in either direction exclusively through the rate-determining step of reaction 1, the ratio, V_+/V_- , in (Eq. 2) is now given as a function of the transfer rate of carbon-14 from carbon dioxide to carbon monoxide as follows. The transfer rate of carbon-14 from carbon dioxide to carbon monoxide is given as

$$2(Z^{CO_2}V_- - Z^{CO}V_+) = \frac{d(n^{CO}Z^{CO})}{dt} \quad (6. i)$$

or

$$2(Z^{CO_2}V_- - Z^{CO}V_+) = -\frac{d(n^{CO_2}Z^{CO_2})}{dt}, \quad (6. ii)$$

where Z^{CO} or Z^{CO_2} are the atomic fraction of carbon-14 in carbon monoxide or carbon dioxide respectively. Since Z^{CO} and Z^{CO_2} are proportional to the specific β -ray counts, C^{CO} and C^{CO_2} , of carbon monoxide and carbon dioxide respectively, Eqs. (6, i) and (6, ii) yield

$$2(C^{CO_2}V_- - C^{CO}V_+) = \frac{d(n^{CO}C^{CO})}{dt} \quad (7. i)$$

$$= -\frac{d(n^{CO_2}C^{CO_2})}{dt}. \quad (7. ii)$$

Solving the equality of the third and the fifth members of Eqs. (5) and (7, i) with respect to V_+ and V_- , it follows that

$$\frac{V_+}{V_-} = 1 - (C^{CO_2} - C^{CO}) \frac{d \ln n^{CO_2}}{dC^{CO_2}}. \quad (8)$$

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Substituting $-ΔG$ and V_+/V_- from Eqs. (4) and (8) into Eq. (2), and taking into account that n^{CO} is proportional to P^{CO} we have

$$\nu(r) = \frac{RT \ln [(P^{CO})^2 (P^{O_2}) K_p / (P^{CO_2})^2]}{RT \ln [1 - (C^{CO_2} - C^{CO}) d \ln P^{CO} / dC^{CO}]} \quad (9)$$

On the other hand, the equality of the fourth and the fifth members of Eqs. (5) and (7,ii) gives another expression for V_+/V_- as

$$\frac{V_+}{V_-} = \frac{1}{1 - (C^{CO} - C^{CO_2}) d \ln P^{CO_2} / dC^{CO_2}}, \quad (10)$$

from which we have

$$\nu(r) = \frac{RT \ln [(P^{CO_2})^2 / (P^{CO})^2 (P^{O_2}) K_p]}{RT \ln [1 - (C^{CO} - C^{CO_2}) d \ln P^{CO_2} / dC^{CO_2}]} \quad (11)$$

The C^{CO} in Eq. (11) is eliminated according to the mass balance of carbon-14,

$$P_0^{CO_2} C_0^{CO_2} = P^{CO} C^{CO} + P^{CO_2} C^{CO_2} \quad (12)$$

Thus, Eq. (11) is rewritten as

$$\nu(r) = \frac{RT \ln \left[\frac{(P^{CO_2})^2}{(P^{CO})^2 (P^{O_2})} \frac{1}{K_p} \right]}{RT \ln \left[1 - \frac{1}{P^{CO}} \left\{ C_0^{CO_2} P_0^{CO_2} - C^{CO_2} (P^{CO} + P^{CO_2}) \right\} \frac{d \ln P^{CO_2}}{dC^{CO_2}} \right]}, \quad (13)$$

where suffix 0 denotes the values at $t=0$.

Experimental

Apparatus Figure 1 shows a diagram of the reaction system all made of glass with *ca.* 6 liters capacity. The system consists of a circulating pump, CP, mercury manometer, M, flow meter, FM, reaction vessel, R, sampling tube, Si, and vessels, V_1 and V_2 . V_1 and V_2 provides an appropriate volume so that the fluctuation caused by operation of circulating pump is negligible. The flow meter consists of a constricted tube and a differential oil manometer, and was calibrated by the use of oxygen gas and a soap film flow meter. The catalyst was mounted in R by means of packed glass wool and splinters. Each of Si's has a breakable joint and fused to the circulating system in parallel with each other through two constrictions as shown in Fig. 1. The whole reaction system was kept around 55°C during the experiment in order to prevent the adsorption of reacting gas on the glass wool.

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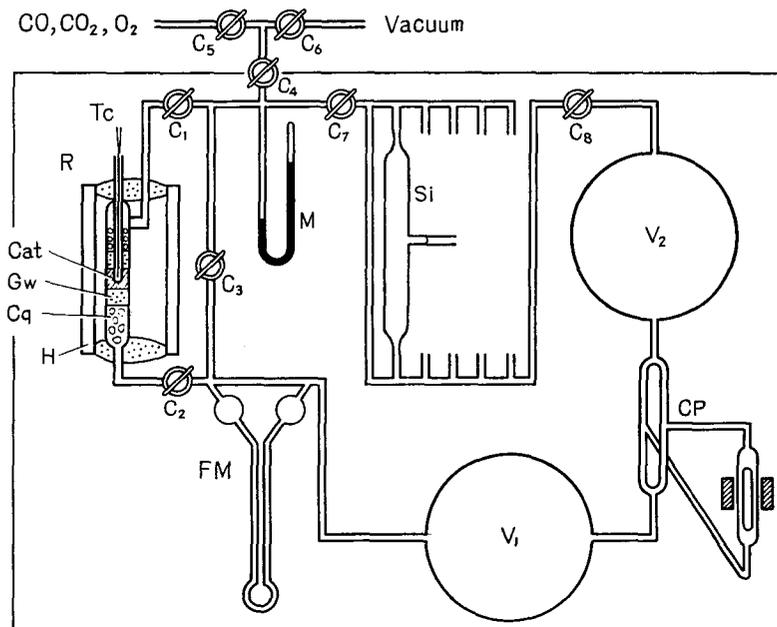


Fig. 1. Schematic diagram of the reaction system.

| | |
|---------------------|----------------------------|
| R: Reactor | V_1, V_2 : Glass bulb |
| H: Electric furnace | $C_1 \sim C_8$: Stopcocks |
| Cat: Catalyst | FM: Flow meter |
| Gw: Glass wool | M: Manometer |
| Cq: Inert material | CP: Circulating pump |
| Tc: Thermocouple | Si: Sampling tube |

Materials Platinum gauze, 1.0 or 10.0 gr, made of 0.1 mm diameter wire was used as a catalyst. After the purification by *aqua regia* and distilled water, the gauze was mounted in the reaction vessel. In advance of measurements, the gauze was exposed repeatedly to a 2 : 1 mixture of carbon monoxide-oxygen for a few hours and evacuated at *ca.* 500°C.

Oxygen was prepared by thermal decomposition of potassium permanganate of GR grade, from Koso Chemical Co. Ltd. The evolved gas was purified by fractional distillation in vacuum; in each distillation the first three fourth of the gas was reserved as a distillate.

Carbon monoxide was prepared by dehydration of formic acid of GR grade from the same company as above and purified by passing it successively through two liquid nitrogen traps.

Radioactive barium carbonate was diluted by normal barium carbonate

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of GR grade and the mixture was decomposed by adding *ca.* 60% aqueous solution of hydroperchlorate.¹⁵⁾ Evolved radioactive carbon dioxide was condensed into a liquid nitrogen trap, and then purified by repetition of fractional distillation in vacuum.

Experimental procedure After further evacuation at a desired reaction temperature for about 20 hours, radioactive carbon dioxide was first introduced into the circulating system with closed stop cocks C_1 and C_2 and open C_3 , under operation of CP. The pressure of radioactive carbon dioxide was measured by mercury manometer. The carbon monoxide-oxygen mixture (2 : 1) was then introduced similarly and mixed with the radioactive carbon dioxide by circulating them for an hour through C_3 . Reaction (1) was started by bringing the circulating gas in contact with the catalyst by opening C_1 and C_2 and closing C_3 . The change of total pressure was followed by mercury manometer, and a part of the reacting gas was sampled from time to time by sealed off Si from the system. The reaction was thus followed until the total pressure comes to a standstill.

Carbon dioxide in a sampled gas was converted to barium carbonate by

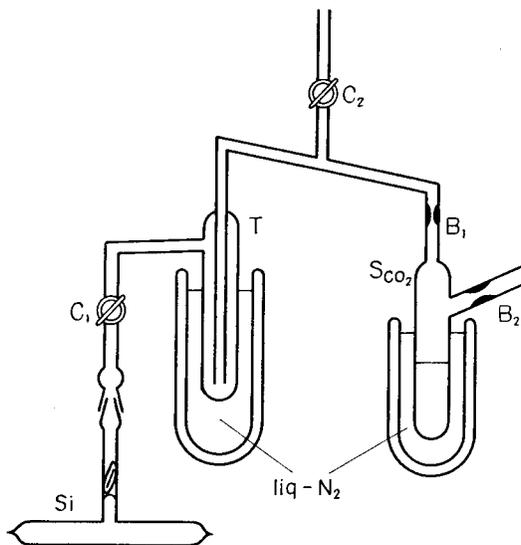


Fig. 2. Apparatus for CO_2 -separation.

| | |
|--|----------------------------|
| Si: Sample vessel | C_1, C_2 : Stopcocks |
| T: Trap | B_1, B_2 : Constrictions |
| S_{CO_2} : CO_2 absorber | |

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the apparatus shown in Fig. 2*) and its β -ray counts was counted by a scintillation counter or a G-M counter.

The temperature of the catalyst was read by the thermocouple, Tc, inserted in the catalyst bed and controlled within $\pm 1^\circ\text{C}$ throughout a course of reaction.

Results

Exchange of carbon-14 between carbon dioxide and carbon monoxide and the change of total pressure were not observed in the absence of catalyst as shown in Table 2 and Fig. 3.

Results of the catalyzed reactions are summarized in Tables 3 to 12.

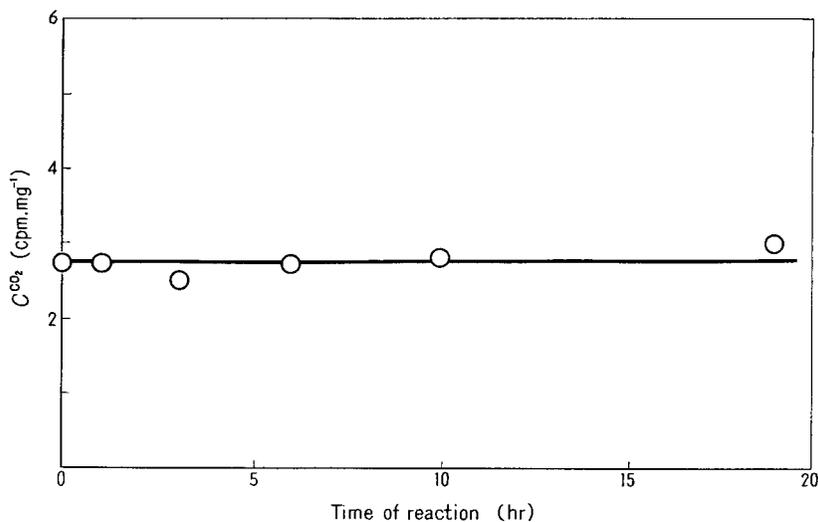


Fig. 3. Specific β -ray count plotted against time of reaction, run without catalyst at 350°C .

*) Twenty ml of barium hydroxide solution was introduced into S_{CO_2} through the constriction B_2 in a atmosphere of oxygen, and then B_2 was sealed off. The S_{CO_2} was immersed into liquid nitrogen bath and then S_1 was adjoined to the apparatus joint. The whole system of Fig. 2 was then evacuated to a pressure less than 10^{-5} mmHg through C_1 , C_2 and liquid nitrogen trap T . Stopcocks C_1 was closed and breakable joint of S_1 was opened, and then C_1 was gradually opened. Carbon dioxide condensed in T was now transferred into S_{CO_2} by closing C_1 and C_2 and warming up T to room temperature. The B_1 was now sealed off and S_{CO_2} was kept at room temperature for about 24 hours to allow barium hydroxide to absorb carbon dioxide separated. Barium carbonate formed in S_{CO_2} was then filtrated, washed by water, dried at 100°C for about 3 hours, spread in a dish by using ethylalcohol and its β -ray was counted.

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TABLE 2. Observed data of blank run, 350°C
 $P_0^{\text{CO}} = 35.1$ mmHg, $P_0^{\text{O}_2} = 22.3$ mmHg, $P_0^{\text{CO}_2} = 54.6$ mmHg

| time of reaction hr | total pressure mmHg | C^{CO_2} cpm(mg-BaCO ₃) ⁻¹ |
|------------------------|------------------------|---|
| 0 | 112.0 | 2.7 |
| 1 | 112.0 | 2.7 |
| 2.3 | 112.0 | |
| 3 | 112.0 | 2.5 |
| 4.5 | 112.0 | |
| 6 | 112.0 | 2.7 |
| 10 | 112.0 | 2.8 |
| 19 | 112.0 | 3.0 |

TABLE 3. Observed data of run 1, 352°C.

| time of reaction min | total pressure mmHg | P^{CO} mmHg | P^{O_2} mmHg | P^{CO_2} mmHg | C^{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(\tau)$ |
|-------------------------|------------------------|-------------------------|--------------------------|---------------------------|---|-------------|
| 0 | 154.0 | 80.7 | 39.9 | 33.5 | 7.4 | |
| 20 | 149.5 | 71.7 | 35.4 | 42.5 | | |
| 30 | 147.5 | 67.7 | 33.4 | 46.5 | 4.5 | 75.2 |
| 70 | 142.5 | 57.7 | 28.4 | 56.5 | | |
| 90 | 140.3 | 53.3 | 16.2 | 60.9 | | |
| 105 | 138.6 | 49.9 | 24.5 | 64.3 | 3.1 | 77.4 |
| 145 | 135.8 | 44.3 | 21.7 | 69.9 | | |
| 180 | 132.3 | 37.3 | 18.2 | 76.9 | | |
| 250 | 128.1 | 28.9 | 14.0 | 85.3 | | |
| 300 | 125.5 | 23.7 | 11.4 | 90.5 | 2.3 | 180.4 |

The partial pressures, P^{CO} etc., of CO etc. at any time of reaction was evaluated from the observed total pressure decrease $P_0^T - P^T$, and the following relations.

$$P^{\text{CO}} = P_0^{\text{CO}} - 2(P_0^T - P^T),$$

$$P^{\text{O}_2} = P_0^{\text{O}_2} - (P_0^T - P^T),$$

$$P^{\text{CO}_2} = P_0^{\text{CO}_2} + 2(P_0^T - P^T),$$

where P_0^{CO} etc. are the initial values of P^{CO} etc. respectively.

Observed time dependences of P^T and specific β -ray count of carbon dioxide, C^{CO_2} , are exemplified in Fig. 4 with respect to run 1.

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TABLE 4. Observed data of run 2, 352°C.

| time of reaction min | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|-------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 125.5 | 49.7 | 25.1 | 50.7 | 7.4 | |
| 30 | 123.0 | 44.7 | 22.6 | 55.7 | | |
| 45 | 122.0 | 42.7 | 21.6 | 57.7 | 6.2 | 96.4 |
| 90 | 119.0 | 37.1 | 18.8 | 63.3 | | |
| 120 | 118.0 | 34.7 | 17.6 | 65.7 | 5.2 | 68.1 |
| 180 | 115.0 | 29.3 | 14.9 | 71.1 | | |
| 270 | 113.0 | 24.7 | 12.6 | 75.7 | 4.5 | 73.1 |
| 390 | 110.0 | 18.7 | 9.6 | 81.7 | | |
| 480 | 108.1 | 14.9 | 7.7 | 85.5 | | |
| 600 | 105.8 | 10.0 | 5.4 | 90.1 | 3.9 | 104.0 |
| 660 | 104.8 | 8.3 | 4.4 | 92.1 | | |
| 840 | 102.8 | 4.3 | 2.4 | 96.1 | 3.8 | 83.1 |

TABLE 5. Observed data of run 3, 352°C.

| time of reaction hr | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 139.0 | 55.2 | 30.1 | 53.7 | 7.4 | |
| 0.45 | 134.0 | 45.2 | 25.1 | 63.7 | | |
| 1 | 131.5 | 40.2 | 22.6 | 68.7 | | |
| 1.75 | 129.5 | 36.2 | 20.6 | 72.7 | 5.1 | 63.3 |
| 3 | 127.0 | 31.2 | 18.1 | 77.7 | | |
| 5.25 | 123.3 | 23.8 | 14.4 | 85.1 | 4.3 | 71.8 |
| 9 | 120.0 | 16.2 | 11.1 | 91.7 | 4.0 | 84.3 |
| 12 | 118.0 | 13.2 | 9.1 | 95.7 | | |
| 15.08 | 116.7 | 10.6 | 7.8 | 98.3 | | |
| 18.5 | 116.0 | 9.2 | 7.1 | 99.7 | 3.3 | 78.9 |

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TABLE 6. Observed data of run 4, 410°C.

| time of reaction hr | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 152.7 | 60.3 | 31.2 | 61.3 | 234 | |
| 1.5 | 150.2 | 55.3 | 28.7 | 66.3 | | |
| 2.5 | 158.6 | 52.1 | 27.1 | 69.5 | | |
| 3.5 | 146.8 | 58.5 | 25.3 | 73.1 | 184 | 32.4 |
| 4.5 | 144.7 | 44.3 | 23.2 | 77.3 | | |
| 5.25 | 143.5 | 41.9 | 22.0 | 79.7 | | |
| 6 | 142.0 | 38.9 | 30.5 | 82.7 | | |
| 7 | 140.3 | 35.5 | 18.8 | 86.1 | | |
| 8 | 138.5 | 31.9 | 17.0 | 89.7 | 152 | 23.6 |
| 9.5 | 137.1 | 29.1 | 15.6 | 92.5 | | |
| 12 | 133.9 | 22.7 | 12.4 | 98.9 | | |
| 13 | 132.9 | 20.7 | 11.4 | 100.9 | 137 | 18.9 |
| 15.75 | 130.3 | 14.9 | 8.5 | 106.7 | | |
| 32.5 | 124.2 | 3.3 | 2.7 | 118.3 | 119 | 39.1 |

TABLE 7. Observed data of run 5, 450°C

| time of reaction hr | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 132.9 | 50.9 | 26.9 | 55.1 | 230.5 | |
| 0.42 | 127.3 | 39.7 | 21.3 | 66.3 | 184 | 38.1 |
| 1 | 123.3 | 91.7 | 17.3 | 74.3 | 168 | 28.8 |
| 1.83 | 121.5 | 28.1 | 15.5 | 77.9 | | |
| 3 | 119.1 | 23.3 | 13.1 | 82.7 | 142 | 47.5 |
| 6.08 | 115.6 | 16.3 | 9.6 | 89.7 | 131 | 66.7 |
| 10.17 | 112.5 | 10.1 | 6.5 | 95.1 | | |
| 11 | 111.8 | 8.7 | 5.8 | 97.3 | | |
| 12.25 | 111.1 | 7.3 | 5.1 | 98.7 | 122 | 125.6 |
| 14 | 110.3 | 5.7 | 4.3 | 100.3 | | |
| 18 | 109.4 | 3.9 | 3.4 | 102.1 | | |

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TABLE 8. Observed data of run 6, 450°C.

| time of reaction hr | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 128.3 | 52.0 | 25.3 | 51.0 | 234 | |
| 1 | 124.8 | 45.0 | 21.8 | 58.0 | 204 | 33.9 |
| 2.5 | 121.4 | 38.2 | 18.4 | 64.8 | 174.6 | 38.7 |
| 3 | 120.3 | 36.0 | 17.3 | 67.0 | | |
| 4 | 118.0 | 31.4 | 15.0 | 71.6 | | |
| 4.5 | 117.0 | 29.4 | 14.0 | 73.6 | 155.1 | 16.4 |
| 5.5 | 115.5 | 25.4 | 12.0 | 77.6 | | |
| 7 | 113.0 | 21.4 | 10.0 | 81.6 | 140.8 | 30.0 |
| 9 | 110.9 | 17.2 | 7.9 | 85.8 | | |
| 12 | 108.5 | 12.4 | 5.5 | 90.6 | 125.7 | 39.2 |
| 14 | 107.8 | 11.0 | 4.8 | 92.0 | | |

TABLE 9. Observed data of run 7, 457°C.

| time of reaction hr | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 162.4 | 71.4 | 17.6 | 73.4 | 51.75 | |
| 1 | 160.7 | 67.6 | 15.9 | 76.8 | 48.87 | 7.6 |
| 2.5 | 158.1 | 62.8 | 13.3 | 82.6 | 45.95 | 7.6 |
| 4 | 157.1 | 60.8 | 12.3 | 84.0 | | |
| 4.9 | 155.8 | 58.2 | 11.0 | 86.6 | | |
| 7 | 154.3 | 55.2 | 9.5 | 89.6 | 40.81 | 6.5 |
| 10.5 | 152.0 | 50.6 | 7.2 | 94.2 | | |
| 14 | 150.2 | 47.0 | 5.4 | 97.8 | | |
| 16 | 149.0 | 44.0 | 4.2 | 100.2 | 37.63 | 7.6 |
| 19.5 | 148.3 | 43.2 | 3.5 | 101.6 | | |
| 25.5 | 146.6 | 39.8 | 1.8 | 105.0 | | |

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TABLE 10. Observed data of run 8, 462°C.

| time of reaction hr | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 154.2 | 67.9 | 17.1 | 69.3 | 59.42 | |
| 1 | 152.1 | 63.7 | 15.0 | 73.5 | 56.05 | 8.9 |
| 2 | 150.7 | 60.9 | 13.6 | 76.3 | | |
| 3 | 149.8 | 59.1 | 12.7 | 78.1 | 52.69 | 12.5 |
| 4 | 148.8 | 57.1 | 11.7 | 80.1 | | |
| 5 | 147.8 | 55.1 | 10.7 | 82.1 | | |
| 7.75 | 145.8 | 51.1 | 8.7 | 86.1 | 49.00 | 9.4 |
| 14.25 | 142.6 | 44.7 | 5.5 | 92.5 | | |
| 17 | 140.9 | 41.3 | 3.8 | 95.9 | | |
| 19 | 140.3 | 40.1 | 3.2 | 97.1 | 42.26 | 10.3 |
| 25.5 | 138.0 | 35.5 | 0.9 | 101.7 | | |

TABLE 11. Observed data of run 9, 474°C.

| time of reaction hr | total pressure mmHg | P_{CO} mmHg | P_{O_2} mmHg | P_{CO_2} mmHg | C_{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 142.7 | 44.7 | 23.8 | 74.2 | 31.75 | |
| 0.5 | 141.5 | 42.3 | 22.6 | 76.6 | | |
| 1.5 | 140.5 | 40.3 | 21.6 | 78.6 | 29.92 | 10.5 |
| 3.5 | 138.5 | 36.3 | 19.6 | 82.6 | | |
| 5.5 | 137.5 | 34.3 | 18.6 | 84.6 | 27.49 | 7.5 |
| 8.5 | 135.9 | 31.1 | 17.0 | 87.8 | | |
| 13.5 | 133.1 | 25.5 | 14.2 | 93.4 | 25.26 | 8.6 |
| 19.5 | 131.2 | 21.7 | 12.3 | 97.2 | | |
| 26.5 | 129.5 | 18.3 | 10.6 | 100.6 | 23.59 | 7.6 |
| 31.5 | 127.7 | 14.9 | 8.9 | 104.0 | | |

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TABLE 12. Observed data of run 10, 300°C

| time of reaction hr | total paessure mmHg | P^{CO} mmHg | P^{O_2} mmHg | P^{CO_2} mmHg | C^{CO_2} cpm(mg-BaCO ₃) ⁻¹ | $\nu(r)$ |
|------------------------|------------------------|------------------|-------------------|--------------------|--|----------|
| 0 | 124.8 | 49.4 | 25.5 | 49.8 | 124 | |
| 1.25 | 122.7 | 45.2 | 23.4 | 54.0 | 112 | 72.7 |
| 2.5 | 121.7 | 43.2 | 22.4 | 56.0 | | |
| 3.5 | 121.3 | 42.4 | 22.0 | 56.8 | | |
| 4.5 | 120.8 | 41.4 | 21.5 | 57.8 | | |
| 10 | 119.9 | 39.6 | 20.6 | 59.6 | 96 | 111.0 |
| 21.5 | 118.8 | 37.4 | 19.5 | 61.8 | | |
| 29 | 118.4 | 36.6 | 19.1 | 62.6 | 89 | 138.4 |
| 46.5 | 117.7 | 35.2 | 18.4 | 64.0 | | |

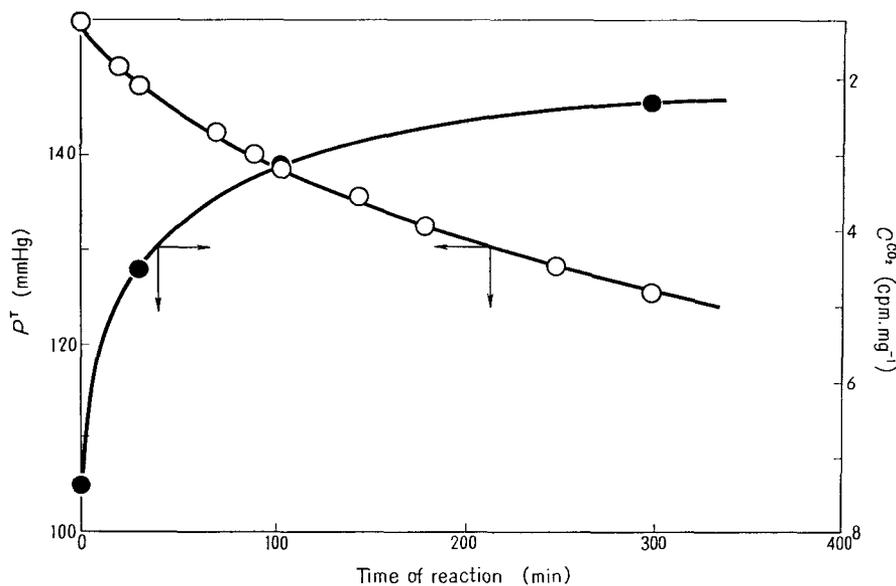


Fig. 4. Total pressure or specific β -ray count plotted against time of reaction, run 1 at 352°C.

In Fig. 5 C^{CO} and C^{CO_2} of run 1 are plotted against $\log P^{CO_2}$ from which $d \log P^{CO_2} / dC^{CO_2}$ in Eq. (13) was determined accurately by using prism.¹⁶⁾

Figure 6 shows plots of $\nu(r)$ -values calculated by Eq. (13) vs. the chemical affinity, $-\Delta G$, for various runs of reaction. The $\nu(r)$ -values evaluated by Eq. (9) with respect to run 9 and 10, which were conducted at 474°C and 300°C

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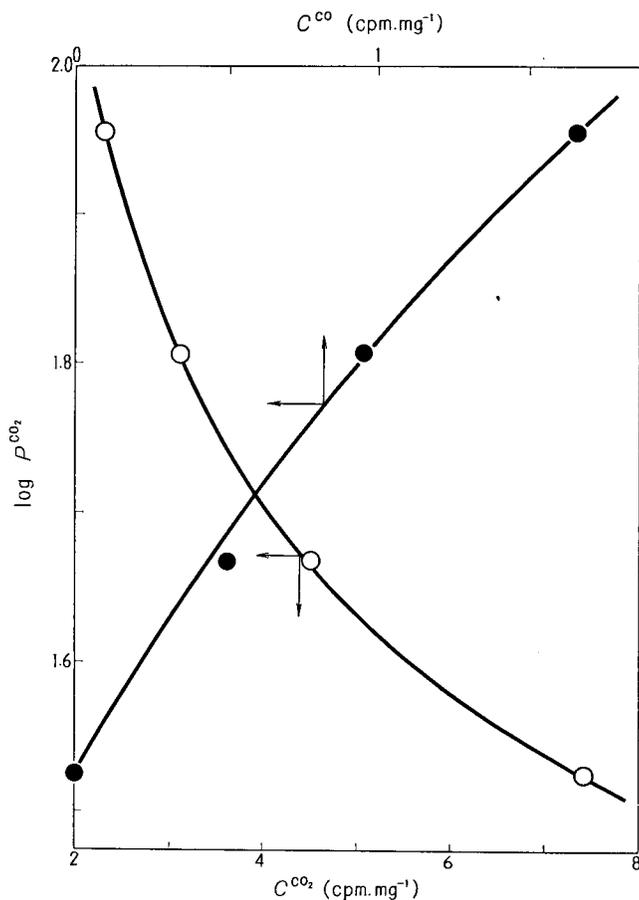


Fig. 5. Logarithm P^{CO_2} against C^{CO} or C^{CO_2} , run 1 at 352°C.

respectively, are shown in Fig. 7 in comparison with those evaluated by Eq. (13). This figure shows that the $\nu(r)$ -value by Eq. (9) is in good agreement with that by Eq. (13) for run 9 but not for run 10.

Figure 8 shows that the value of $\nu(r)$ is very large at *ca.* 300°C and rapidly decreased to a value less than ten with rise of reaction temperature. The length of vertical lines on each plot shows the magnitude of the experimental error.

Discussion

The fact in Fig. 8 that the stoichiometric number, $\nu(r)$, steeply decreases

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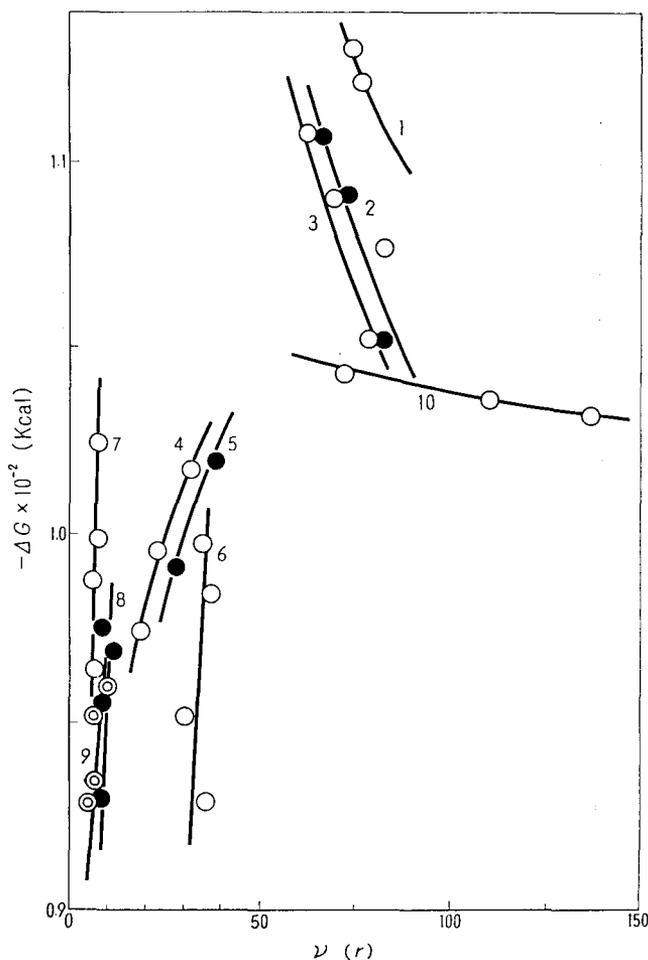


Fig. 6. Observed values for $\nu(r)$ in each runs as a function of chemical affinity.

from around a hundred to ten or less with rise of reaction temperature indicates the change of the rate-determining step from a step in the path *a*, independent on the exchange of carbon-14 to the other in the path *b*, effecting the exchange. Fluctuation the results in Fig. 8 is mainly caused by extraordinarily large value of K_p in Eq. (13), which is several tens power of ten at the present experimental condition. Thus, the values of C^{CO_2} , P^{CO_2} , $d \ln P^{CO_2} / dC^{CO_2}$ etc. should be measured with extremely high accuracy far beyond the present one as seen from Eq. (13) in order to obtain $\nu(r)$ -value within a fluctuation of ± 10 . The $\nu(r)$ values of above two rate-determining steps will be determined as follows by direct comparison of the

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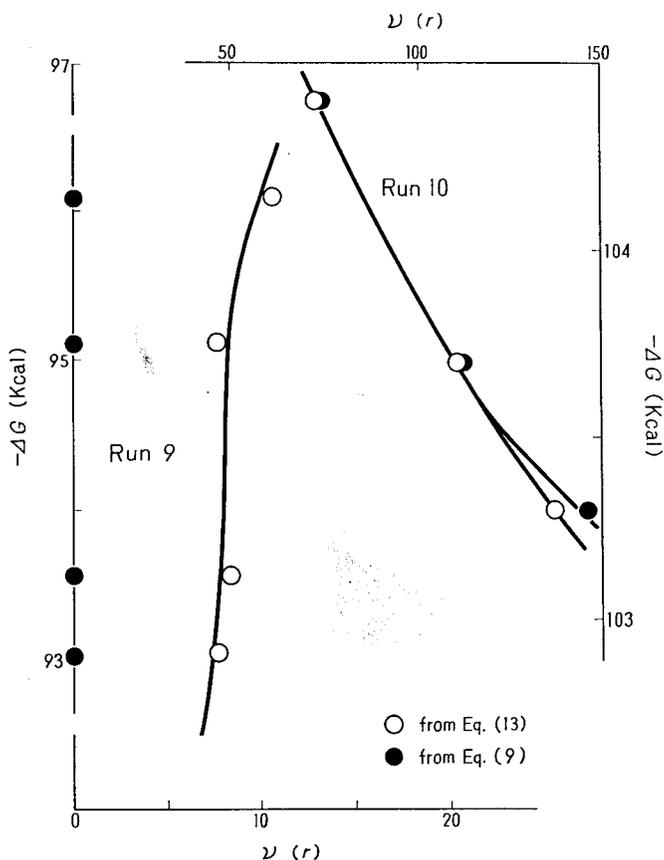


Fig. 7. Observed values for $\nu(r)$ in run 9 or 10 as a function of chemical affinity.

forward unidirectional rate of the path a or b with that of reaction (1) without the use of Eq. (2),

Provided that reaction (1) proceeds steadily along with a single route²¹⁾ of reaction¹⁾ inclusive of path a , it follows that

$$V = \frac{1}{\nu(a)}(v_{a,+} - v_{a,-}),$$

where $v_{a,+}$ or $v_{a,-}$ is the forward or backward unidirectional rate of path a respectively and $\nu(a)$ the stoichiometric number of path a , *i. e.*, 2 in the present case. In the case where the rate of reaction (1) is determined by path a , we have $V_+ \cong \frac{v_{a,+}}{\nu(a)}$ ²¹⁾ and, hence,

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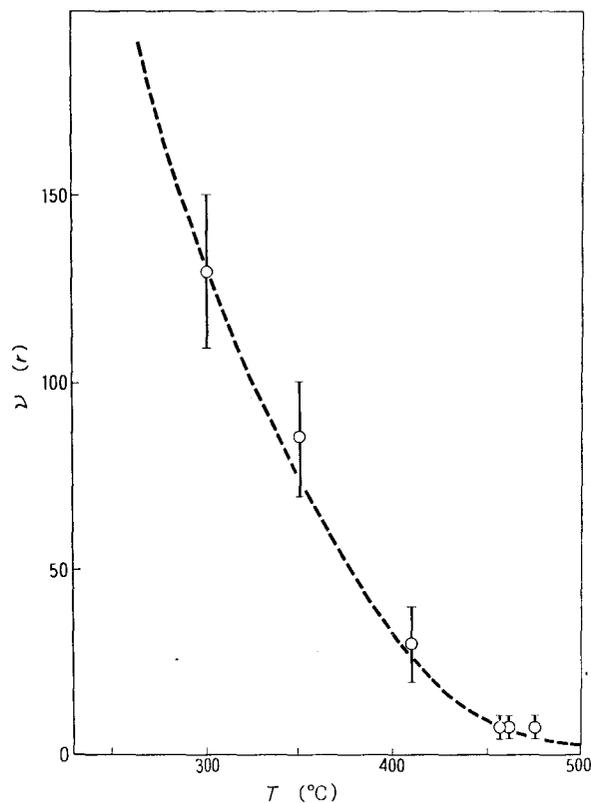


Fig. 8. Variation of $\nu(r)$ with temperature of reaction.

$$\nu(a) \cong v_{a,+}/V_+ \quad (14)$$

On the other hand, in the case where path a is not rate-determining but is in partial equilibrium, it follows that

$$V_+ \ll v_{a,+} \cong v_{a,-},$$

and thus $\nu(a)$ much higher than 2 may be obtained by Eq. (14) in this case. Equation (5) leads by neglect of V_- as compared with V_+ that

$$V_+ = -\frac{V_0}{RT} \frac{dP^r}{dt}, \quad (15)$$

where V_0 is the volume of the reaction system. The $v_{a,+}$ is determined by the equation,

$$v_{a,+} = -\frac{P^{\text{CO}_2} V_0}{RT} \frac{1}{C^{\text{CO}_2} - C^{\text{CO}}} \frac{dC^{\text{CO}_2}}{dt} \quad (16)$$

which is derived by the elimination of dn^{CO_2}/dt from the rate expression for the exchange of carbon-14,

$$-\frac{d(n^{\text{CO}_2}C^{\text{CO}_2})}{dt} = C^{\text{CO}_2}v_{a,-} - C^{\text{CO}_2}v_{a,+} \quad (17. i)$$

and the steady state condition of reaction (1) that

$$V = \frac{1}{2} \frac{dn^{\text{CO}_2}}{dt} = \frac{1}{2} (v_{a,+} - v_{a,-}), \quad (17. ii)$$

with reference to $v_{a,+} \gg v_{a,-}$.

The value of $v_{a,+}/V_+$ at *ca.* $-\Delta G = 100$ kcal/mole is now evaluated as shown in Fig. 9 on the basis of Eqs. (14), (15) and (16), where the values dP^r/dt and dC^{CO_2}/dt were taken as inclinations of respective curves given in Fig. 3. One can see from the figure that the $\nu(a)$ -value is about 2 at higher temperatures, whereas the $v_{a,+}/V_+$ value is larger than 2 at temperatures

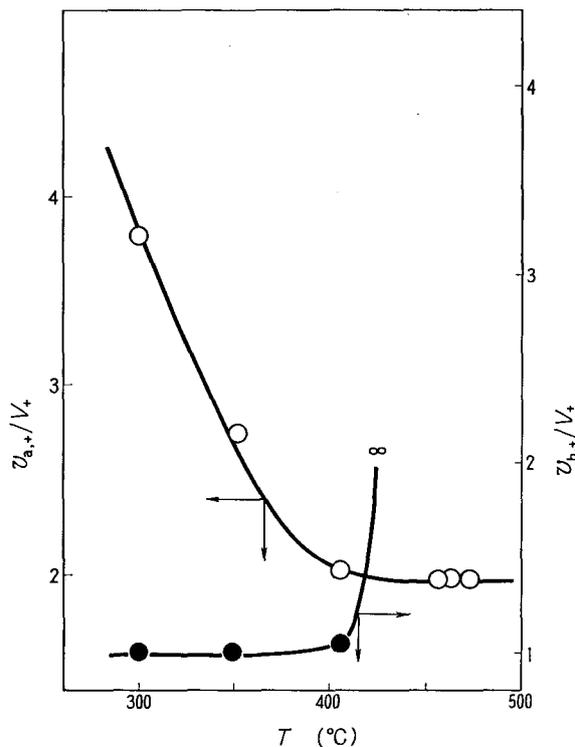


Fig. 9. Variations of $v_{a,+}/V_+$ and $v_{b,+}/V_+$ with temperature of reaction.

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lower than 400°C. These results clearly show that the rate-determining step switches over from one in path *b* to the other in path *a* with rise of temperature.

The same conclusion is derived as follows by comparison of the rate, V_+ , with the forward unidirectional rate of path *b*, $v_{b,+}$. The chemical affinity $-\Delta G$ of a reaction along with a single route²¹⁾ consisting of S steps is given as¹⁾

$$\Delta G = \sum_{s=1}^S \nu(s) \Delta G_s. \quad (18)$$

Provided that the overall reaction consists of comprising the paths, *b* and *a*, each effecting or not effecting the transfer of carbon-14 from carbon dioxide to carbon monoxide respectively, Eq. (18) is rewritten as

$$\Delta G = \Delta G_b + 2 \Delta G_a. \quad (19)$$

The ΔG_b or ΔG_a of path *b* or *a* is now given in terms of the forward or backward unidirectional rates, $v_{b,+}$ and $v_{b,-}$ or $v_{a,+}$ and $v_{a,-}$, of *b* or *a* respectively as

$$\Delta G_b = RT \ln \left(\frac{v_{b,-}}{v_{b,+}} \right) \quad (20)$$

or

$$\Delta G_a = RT \ln \left(\frac{v_{a,-}}{v_{a,+}} \right) \quad (21)$$

By eliminating $v_{a,+}$ and $v_{a,-}$ from Eqs. (16), (17,ii) and (21), the value of $-\Delta G_a$ is determinable and hence the value of $-\Delta G_b$ according to Eq. (19). The $v_{b,+}/V_+$ is thus determinable from Eq. (20) and the steady state condition of reaction (1) that

$$V = \frac{1}{\nu(b)} (v_{b,+} - v_{b,-}),$$

where the $\nu(b)$ is the stoichiometric number of path *b*, *i.e.*, unity in the present case. When path *b* is rate-determining and reaction (1) is far from its equilibrium as in the present experiments, V_- and $v_{b,-}$ is negligibly small as compared with V_+ and $v_{b,+}$ respectively, and hence we have

$$\nu(b) \cong v_{b,+}/V_+. \quad (22)$$

However, when path *b* is not rate-determining but in partial equilibrium, it follows that

$$V_+ \ll v_{b,+} \cong v_{b,-}$$

and hence $\nu(b)$ much higher than unity may be obtained. The $v_{b,+}/V_+$ is plotted in Fig. 9 against reaction temperature. It is seen that the ratio is nearly unity or larger than unity at temperatures below or above 400°C in conformity with the above conclusions.

The activation heat, E_a , is estimated as 50.0 kcal/mole or 64.5 kcal/mole at temperatures below or above 390°C respectively, as shown in Table 13.

TABLE 13. Activation Heat of Carbon Monoxide Oxidation in the Presence of Platinum

| No. of run | T_1 (°C) | T_2 (°C) | V_1 (mmHg/hr) | V_2 (mmHg/hr) | E_a (Kcal/mole) |
|------------|---------------|---------------|--------------------|--------------------|----------------------|
| 1 | 428 | 440 | 4.16 | 7.70 | 61.7 |
| 2 | 395 | 404 | 0.67 | 1.75 | 64.5 |
| 3 | 405 | 420 | 0.40 | 1.07 | 64.8 |
| 4 | 380 | 390 | 1.26 | 2.61 | 62.9 |
| 5 | 380 | 390 | 1.20 | 2.52 | 64.1 |
| 6 | 310 | 320 | 0.90 | 1.78 | 50.0 |
| 7 | 310 | 320 | 0.68 | 1.40 | 47.2 |
| 8 | 350 | 360 | 0.64 | 1.20 | 50.0 |
| 9 | 350 | 360 | 0.60 | 1.10 | 48.2 |
| 10 | 360 | 370 | 6.20 | 11.64 | 49.8 |
| 11 | 350 | 380 | 0.18 | 1.18 | 50.8 |
| 12 | 350 | 380 | 0.31 | 2.03 | 49.2 |

These results also support the above conclusion that the rate-determining step of reaction (1) is different with each other at these two temperature regions.

Possible mechanisms for reaction (1) summarized in Table 14 are now discussed on the basis of the results described above as follows.

Mechanism I has been proposed by HEYNE and TOMPKINS,¹⁷⁾ where step (iii) is rate-determining. If their mechanism is valid, the stoichiometric number of rate-determining step estimated by using carbon-14 will be unity, conflicting with the present experimental results that the $\nu(r)$ -values is ∞ or 2 at lower or higher temperature.

LANGMUIR¹⁸⁾ has, on the other hand, proposed mechanism II, where step (iii) is rate-determining. According to LANGMUIR's mechanism, the experimental values of $\nu(r)$ must be 2 independent of reaction temperature, which

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TABLE 14. Possible mechanisms for reaction (1)

| Sequences | elementary step |
|-----------|--|
| I | $O_2 \longrightarrow O_2(a)$ (i) |
| | $CO \longrightarrow CO(a)$ (ii) |
| | $CO(a)+O_2(a) \longrightarrow CO_3(a)$ (iii) |
| | $CO_3(a)+CO(a) \longrightarrow 2CO_2$ (iv) |
| II | $O_2 \longrightarrow 2O(a)$ (i) |
| | $CO \longrightarrow CO(a)$ (ii) |
| | $CO(a)+O(a) \longrightarrow CO_2$ (iii) |
| III | $O_2 \longrightarrow 2O(a)$ (i) |
| | $CO+O(a) \longrightarrow CO_2$ (ii) |

contradicts with the present results. Furthermore, from the heat of adsorption of oxygen or carbon monoxide on platinum catalyst, 70 kcal/mole or 48 kcal/mole respectively,^{19,20)} and the heat of carbon dioxide formation, 67.5 kcal/mole, the heat of reaction of step (iii) is estimated as -15.5 kcal/mole, which suggests that step (iii) may be absent so far as the entropy change of this step is not largely negative. Thus, these two mechanisms will be safely excluded in the present case.

In consequence, mechanism III in Table 14 is proposed as the most probable one, where step (i) or (ii) is rate-determining at temperatures below or above *ca.* 390°C respectively.

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