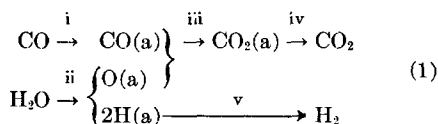# Locus of the Change in the Rate-Determining Step

It has been well recognized that a solid-catalyzed gaseous reaction comprises several consecutive chemical steps and that among them a rate-determining step or steps exist which govern the overall rate of reaction. Thus the determination of the rate-determining step has been the aim of numerous investigations in the field of heterogeneous catalysis. Several studies (*1–3*) have shown that the rate-determining step varies, depending on experimental conditions, particularly on reaction temperature and on the partial pressures of reactants and products. Recently, Happel and Mezaki (*4*) qualitatively demonstrated that the change of the rate-determining step may occur as solid-catalyzed gaseous reactions approach chemical equilibria.

In the present study we traced the changes of the adsorption rate of carbon monoxide for the water–gas shift reaction while the reaction proceeds and found that rate-determining step may change.

For the water–gas shift reaction over iron oxide catalyst, a number of reaction mechanisms have been proposed (*5–9*). Recent studies with deuterium (*5, 6*), carbon-14 (*7*), and oxygen-18 (*8, 9*) confirmed that the reaction sequence given below is most plausible and that the adsorption of carbon monoxide (i) and the associative desorption of hydrogen (*v*) are rate-determining.

$$
\begin{array}{c}
\overset{\text{i}}{} \quad \overset{\text{iii}}{} \quad \overset{\text{iv}}{} \\
CO \rightarrow \ CO(a) \Big\} \rightarrow CO_2(a) \rightarrow CO_2 \\
\overset{\text{ii}}{} \begin{cases} O(a) \ \Big\} \\ H_2O \rightarrow \begin{cases} \\ 2H(a) \xrightarrow{\quad\quad v\quad\quad} H_2 \end{cases} \end{cases}
\end{array} \tag{1}
$$

Hollingsworth (*10*) developed a relationship between the total Gibbs free energy change and the velocity ratios of all steps involved. Applying this relation to the reaction mechanism given by Eq. (1), we obtain

$$
\exp\left(-\frac{\Delta G}{RT}\right) = \left(\frac{v_{+i}}{v_{-i}}\right)^{v_i} \left(\frac{v_{+ii}}{v_{-ii}}\right)^{v_{ii}} \left(\frac{v_{+iii}}{v_{-iii}}\right)^{v_{iii}} \\
\left(\frac{v_{+iv}}{v_{-iv}}\right)^{v_{iv}} \left(\frac{v_{+v}}{v_{-v}}\right)^{v_v}, \tag{2}
$$

where v_j is the stoichiometric number of step (*j*).

For the water–gas shift reaction over an iron oxide catalyst, as described previously, the rates of steps (ii), (iii), and (iv) are extremely fast. Thus the following relation may hold:

$$
\frac{v_{+ii}}{v_{-ii}} \cong \frac{v_{+iii}}{v_{-iii}} \cong \frac{v_{+iv}}{v_{-iv}} \cong 1 \tag{3}
$$

Furthermore, the stoichiometric numbers of all the steps [steps (i) through (v)] are unity. Combination of Eqs. (2) and (3) gives

$$
\exp\left(-\frac{\Delta G}{RT}\right) = \left(\frac{v_{+i}}{v_{-i}}\right)\left(\frac{v_{+v}}{v_{-v}}\right). \tag{4}
$$

Note that a linear relationship should be obtained between $\exp(-\Delta G/RT)$ and (v_{+i}/v_{-i}), if and only if the value of (v_{+v}/v_{-v}) is constant.

In the present study we computed the values of $-\Delta G/RT$ and v_{+i}/v_{-i} from experimental data which were collected using oxygen-18 (*9*). The data were gathered using a closed-recyling type reactor at a total pressure of 80 mm Hg and reaction temperatures between 380 and 450°C. The analyses of reactants and products were performed by a Hitachi mass spectrometer, RMS-3B type. A detailed description of the experimental apparatus, the procedure, and the experimental conditions utilized in obtaining the data were presented elsewhere (*9*).

In Fig. 1, $\exp(-\Delta G/RT)$ is plotted against (v_{+i}/v_{-i}). As can be seen from the figure, a linear relationship does not hold for our experimental data. From Eq. (4) and Fig. 1 we see that the value of v_{+v}/v_{-v}
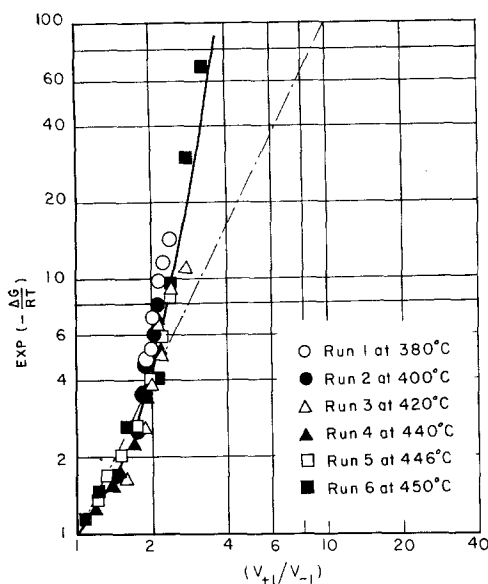
FIG. 1. The relationship between $\exp(-\Delta G/RT)$ and v_{+i}/v_{-i}.

is considerably greater than that of v_{+i}/v_{-i} during the earlier stage of the reaction, wherein carbon monoxide is abundant in the reaction system. This implies that the forward and reverse rates of step (i) are noticeably higher as compared to those rates of step (v) during this stage of the reaction. We further see that for experimental conditions closer to the chemical equilibrium (the origin of Fig. 1 corresponds to the chemical equilibrium of the water-gas shift reaction) the value of v_{+i}/v_{-i} is approximately equal to that of v_{+v}/v_{-v}. This fact indicates that in the neighborhood of equilibrium the rates of step (i) and step (v) contribute almost equally to the overall rate of the water-gas shift reaction. In the light of the results obtained in this investigation, perhaps, the rate-determining step gradually changes from dominance of step (v) to the dominance of step (v) and step (i) as the reaction conditions approach equilibrium.

As described previously, the rates of individual elementary steps of a solid-catalyzed gaseous reaction depends greatly on the partial pressures of reactants and products. Thus it seems unwise in certain cases to assume that rate-determining step remains unchanged for the entire range of experimental conditions. This state of affairs is especially true under circumstances wherein the partial pressures of reactants and products undergo substantial change, resulting in changes of the rates of elementary steps.

NOMENCLATURE

v_{+j} forward reaction rate of j-th elementary step

v_{-j} backward reaction rate of j-th elementary step

R gas constant

T absolute temperature

ΔG Gibbs free energy change

ν_j stoichiometric number of j-th elementary step

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