

RATE MULTIPLICITY DUE TO INTERACTIONS BETWEEN ADSORBED SPECIES

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Abstract—A generalized Langmuir-Hinshelwood mechanism for the reaction $A + 1/2B_2 \rightleftharpoons C$ has been studied. Lateral (nearest neighbor) interactions between the adsorbed species have been considered to analyze the multiple steady-states in the chemical reaction. Forward and reverse reaction rate constants have been evaluated via the lattice-gas model with the absolute rate theory. The simulation by the proposed model can predict multiple steady-states and hysteresis. Experimental correlation was made for the rate multiplicity observed by Sung [3] on CO oxidation reaction.

INTRODUCTION

When the chemical reactions occur on the catalytic surfaces, the activation energy may depend on the surface coverage [1]. This may be caused by either the intrinsic surface heterogeneity or the interactions between the surface and the adsorbed species, or by the combination of both. Temkin [2] has discussed in detail the influence of the surface heterogeneity on the reaction rate constants.

In order to obtain the pure intrinsic reaction rate data, it is often desirable to use the continuously pumped high vacuum reactor with the single crystalline catalyst [3]. The use of a single crystalline catalyst can rule out the heterogeneity of a catalyst surface. It might be presumed that the interactions between the adsorbed species are the only cause for the rate multiplicity. This interaction between the adsorbed species may be due to one or more of the followings [4]; 1. chemical interaction through the overlap of the molecular orbitals, 2. van der Waals forces, 3. London forces (dispersion forces), 4. dipole-dipole interaction and, 5. substrate-modulated interaction. The multiplicity phenomena have usually been analyzed in terms of the effect of chemisorption strength as shown by Eigenberger [5]. However it is supposed that the admolecular interactions must play a significant role in the rate multiplicity.

In this work, the lattice-gas model with the absolute rate theory is applied to consider the influence of the interactions on the rate constants. The generalized

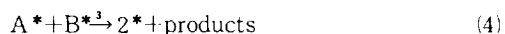
Langmuir-Hinshelwood(LH) mechanism has been analyzed for a simple bimolecular surface reaction. It is shown that the resulting model equations can predict the hysteresis phenomena.

THEORY

Consider a simple bimolecular surface reaction between A and B



proceeding through the following Langmuir-Hinshelwood(LH) type reaction steps



where * denotes an empty adsorption site. A adsorbs at single active site, while B_2 adsorbs dissociatively and desorbs associatively. The products, once formed, are assumed to leave the system immediately. This type of mechanism has recently been confirmed for the oxidation of carbon monoxide on the single crystalline platinum surface [3] where carbon monoxide corresponds to A and oxygen to B_2 .

According to the mass action law, the mass balance equations for the surface species A^* and B^* are as follows.

$$\frac{d\theta_A}{dt} = k_1 P_A (1 - \theta_A - \theta_B) - k_{-1} \theta_A - k_3 \theta_A \theta_B \quad (5)$$

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$$\frac{d\theta_B}{dt} = 2k_2 P_{B_2} (1 - \theta_A - \theta_B)^2 - 2k_{-2} \theta_B^2 - k_3 \theta_A \theta_B \quad (6)$$

where θ_A and θ_B are the fractional surface coverages of the adsorbed species A* and B* respectively.

In general the rate constants are the function of the surface coverages. The lattice-gas model with the absolute rate theory is applied to explain the influence of the interactions between the adsorbed species on the rate constants. For the application of the lattice-gas model a surface having M adsorption sites will be considered. Each adsorption site has z nearest neighbors, and can hold at most one adsorbed species. Our attention is confined to only the nearest neighbor interactions and accordingly an adsorbed species does not interact with the adsorbed species other than the nearest neighbor sites. The rate constants, k_1 , k_{-1} , k_2 , k_{-2} and k_3 should be obtained as functions of the surface coverages θ_A and θ_B .

The following sequence of derivations is similar to those given by Zhdanov [8]. The main point of the approach is presented here in order to avoid the notational complexities.

The rate of a monomolecular desorption of molecules A in the presence of molecules B is defined as

$$\frac{dN_A}{dt} = -k_d(\theta_A, \theta_B) N_A \quad (7)$$

where $\theta_A = N_A/M$, $\theta_B = N_B/M$ are the fractional surface coverages, M is the number of elementary sites. Taking into consideration the non-configurational partition functions, F_A and F_{A^*} , and using the standard assumption of the absolute rate theory, we obtain ($\epsilon_{ij} < 0$ for attraction)

$$k_d = \frac{kT}{h} \frac{F_{A^*}}{F_A} \sum_{nm} P_{A, nm} \exp \{ - (E_d + \Delta\epsilon_{nm}) / kT \} \quad (8)$$

where $P_{A, nm}$ is the probability that particle A has n particles of A and m particles of B in the neighbor sites, E_d is the energy difference between an activated complex A* and a molecule A when the nearest sites to the molecules A and to the activated complex are empty,

$$\Delta\epsilon_{nm} = n(\epsilon_{A^*A} - \epsilon_{AA}) + m(\epsilon_{A^*B} - \epsilon_{AB}) \quad (9)$$

is the lateral energy difference between the activated complex A* and the molecule A, and ϵ_{ij} is the interaction energies of the nearest particles ij.

At present the exact calculation of the probability $P_{A, nm}$ is impossible. The most suitable method for the approximate calculations is the quasi-chemical approximation(QCA). According to this method $P_{A, nm}$ may be expressed through the probabilities P_{AA} , P_{AB} ...etc., where P_{ij} is the probability that the two nearest sites are occupied by the pair ij. In the following, the subscripts A and B represent the sites occupied by A and B respectively and the subscript O represents the

empty site. These probabilities are described by the equations

$$P_{AA} + P_{AB} + P_{AO} + P_{BB} + P_{BO} + P_{OO} = 1 \quad (10)$$

$$2P_{AA} + P_{AB} + P_{AO} = 2\theta_A \quad (11)$$

$$2P_{BB} + P_{AB} + P_{BO} = 2\theta_B \quad (12)$$

$$P_{AA}P_{OO}/P_{AO}^2 = 0.25 \exp(-\epsilon_{AA}/kT) \quad (13)$$

$$P_{BB}P_{OO}/P_{BO}^2 = 0.25 \exp(-\epsilon_{BB}/kT) \quad (14)$$

$$P_{AB}P_{OO}/P_{AO}P_{BO} = 0.50 \exp(-\epsilon_{AB}/kT). \quad (15)$$

Equations (13) to (15) are the representations of the quasi-chemical approximation for a system of two kinds of particles.

According to the QCA, the different pairs are considered to be independent, hence

$$P_{A, nm} = \frac{z!}{n!m!(z-n-m)!} \frac{P_{AA}^n \bar{P}_{AB}^m \bar{P}_{AO}^{z-n-m}}{(P_{AA} + \bar{P}_{AB} + \bar{P}_{AO})^z} \quad (16)$$

where $\bar{P}_{AB} = 0.5 P_{AB}$, $\bar{P}_{AO} = 0.5 P_{AO}$. After substituting eq.(9) and (16) into eq.(8), and rearranging them with the trinomial theorem, the function ϕ_d which describes the influence of the adsorbed particles interaction on the rate of desorption, can be defined as

$$\phi_d = \sum_{nm} P_{A, nm} \exp(-\Delta\epsilon_{nm}/kT) = \gamma_A^z \quad (17)$$

where

$$\gamma_A = P_{AA} \exp \{ (\epsilon_{AA} - \epsilon_{A^*A}) / kT \} + \bar{P}_{AB} \exp \{ (\epsilon_{AB} - \epsilon_{A^*B}) / kT \} + \bar{P}_{AO} / \theta_A \quad (18)$$

The desorption rate constant of A is then expressed as follows

$$\begin{aligned} k_{-1} (=k_d) &= \frac{kT}{h} \frac{F_{A^*}}{F_A} \exp(-E_d/kT) \cdot \phi_d = \nu_{dA} \phi_d \\ &= \nu_{dA} \gamma_A^z. \end{aligned} \quad (19)$$

The rate of monomolecular adsorption of A may be expressed as

$$dN_A/dt = k_a(\theta_A, \theta_B) N_A^g \quad (20)$$

where N_A^g is the number density of molecules A in the gas phase, and rate constant may be calculated in a similar way

$$\begin{aligned} k_a &= \frac{kT}{h} \frac{F_{A^*}}{F_A^g} (1 - \theta_A - \theta_B) \sum_{nm} P_{a, nm} \exp \{ - (E_a \\ &\quad + \Delta\epsilon_{nm}^*) / kT \} \end{aligned} \quad (21)$$

where $\Delta\epsilon_{nm}^*$ ($= n\epsilon_{A^*A} + m\epsilon_{A^*B}$) is the interaction energy of an activated complex and its environment. In general the number of activated complexes is small

($\epsilon_{rj}=0$, namely $\phi_a=1$). Using eqs.(20), (21) and (2), the rate constant of adsorption k_1 becomes as follows

$$k_1 = \frac{1}{Mh} \frac{F_A^*}{F_A^*} \exp(-E_a/kT). \quad (22)$$

An adsorption isotherm is defined by the equality between the desorption and adsorption rates.

The rate of the associative desorption $2B^* \rightarrow B_2 + 2^*$ may be expressed as

$$\frac{dN_B}{dt} = -k_{ad}(\theta_A, \theta_B)M. \quad (23)$$

Taking into consideration the nonconfigurational partition functions we obtain

$$k_{ad} = \frac{kT}{h} \frac{F_{B^*B^*}}{F_B^2} \cdot Z \cdot \sum_i P_{BB,i} \exp\{-(E_{ad} + \Delta\epsilon_i)/kT\} \quad (24)$$

where $P_{BB,i}$ is the probability that two nearest sites are occupied by the pair BB and that this pair has the environment marked by the index i , E_{ad} is the energy difference between the activated complex and pair BB when the nearest sites are empty and $\Delta\epsilon_i$ is the lateral energy difference between the activated complex and the pair BB. The function, ϕ_{ad} , is defined to describe the influence of the particles interaction on the rate of the associative desorption,

$$\begin{aligned} \phi_{ad} &= \left[\sum_i P_{BB,i} \exp\left(\frac{\epsilon_{BB} - \Delta\epsilon_i}{kT}\right) \right] / \theta_B^2 \\ &= P_{BB} \gamma_B^{2z-2} \cdot \frac{\exp(\epsilon_{BB}/kT)}{\theta_B^2} \end{aligned} \quad (25)$$

where the last equality is obtained using QCA, together with

$$\begin{aligned} \gamma_B &= P_{BB} \exp\{(\epsilon_{BB} - \epsilon_{B^*B})/kT\} + \bar{P}_{AB} \exp\{(\epsilon_{AB} \\ &\quad - \epsilon_{B^*A})/kT\} + \bar{P}_{BO} / \theta_B. \end{aligned} \quad (26)$$

The rate constant of desorption, k_{-2} , is expressed as

$$k_{-2} = \nu_{dB} \phi_{ad}. \quad (27)$$

The rate of the dissociative adsorption is obtained in a similar way.

$$dN_B/dt = k_{da}(\theta_A, \theta_B) N_{B_2}^* \quad (28)$$

$$\begin{aligned} k_{da} &= \frac{kT}{h} \frac{F_{B^*B^*}}{F_{B_2}^*} \cdot Z \cdot \sum_i P_{Oo,i} \exp\{-(E_{da} \\ &\quad + \Delta\epsilon_i)/kT\} \end{aligned} \quad (29)$$

$$k_2 = \nu_{aB} \frac{P_{Oo}}{(1 - \theta_A - \theta_B)^2}. \quad (30)$$

The rate of the LH reaction, $A^* + B^* \rightarrow C + 2^*$ of the adsorbed molecules may be written as

$$dN_A/dt = dN_B/dt = -k_{LH}(\theta_A, \theta_B)M. \quad (31)$$

Taking the partition function into consideration,

$$\begin{aligned} k_{LH} &= \frac{kT}{h} \frac{F_{A^*B^*}}{F_A F_B} \cdot \frac{Z}{2} \sum_i P_{AB,i} \exp\{-(E_{LH} \\ &\quad + \Delta\epsilon_i)/kT\}. \end{aligned} \quad (32)$$

According to the quasi-chemical approximation, the probability $P_{AB,i}$ is expressed in terms of the probabilities, $P_{A,mm}$ and $P_{B,mm}$, and the following equation is obtained.

$$\sum_i P_{AB,i} \exp(-\Delta\epsilon_i/kT) = P_{AB} \gamma_A^{z-1} \gamma_B^{z-1} \quad (33)$$

It is useful to define the following function,

$$\phi_R = \left[\sum_i P_{AB,i} \exp\left(\frac{\epsilon_{AB} - \Delta\epsilon_i}{kT}\right) \right] (2\theta_A \theta_B)^{-1} \quad (34)$$

which is a measure of the influence of the particles interaction on the rate of reaction. The rate constant becomes

$$k_3 = \nu_R \phi_R. \quad (35)$$

So far the rate constants, k_1 , k_{-1} , k_2 , k_{-2} and k_3 were obtained by considering the interactions between the adsorbed species. Inserting the rate constants into eq.'s (5) and (6) and arranging them lead to

$$\begin{aligned} \frac{d\theta_A}{dt} &= \nu_{aA} P_A (1 - \theta_A - \theta_B) - \nu_{dA} \theta_A \gamma_A^z \\ &\quad - \nu_R \bar{P}_{AB} q_{AB} (\gamma_A \gamma_B)^{z-1} \end{aligned} \quad (36)$$

$$\begin{aligned} \frac{d\theta_B}{dt} &= 2\nu_{aB} P_{B_2} P_{Oo} - 2\nu_{dB} (P_{BB} q_{BB}) \gamma_B^{2z-2} \\ &\quad - \nu_R \bar{P}_{AB} q_{AB} (\gamma_A \gamma_B)^{z-1} \end{aligned} \quad (37)$$

where, $q_{AA} = \exp(\epsilon_{AA}/kT)$, $q_{BB} = \exp(\epsilon_{BB}/kT)$, and $q_{AB} = \exp(\epsilon_{AB}/kT)$.

The time derivatives are zero at the steady state and the dimensionless rate(R) can be given by eq. (38).

$$R = \bar{P}_{AB} q_{AB} (\gamma_A \gamma_B)^{z-1} \quad (38)$$

Arranging eq.'s (36) and (37) leads to

$$P_A' (1 - \theta_A - \theta_B) = EA \cdot \theta_A \gamma_A^z + R \quad (39)$$

$$P_{B_2}' P_{Oo} = EB \cdot P_{BB} q_{BB} \gamma_B^{2z-2} + R \quad (40)$$

where

$$P_A' = \frac{\nu_{aA} P_A}{\nu_R}, \quad P_{B_2}' = \frac{2\nu_{aB} P_{B_2}}{\nu_R}, \quad EA = \frac{\nu_{dA}}{\nu_R}, \quad EB = \frac{2\nu_{dB}}{\nu_R}.$$

The equations (38), (39) and (40) will be solved simultaneously together with the QCA of equations (10) to (15). Nonlinear regression techniques were employed for the numerical computations to solve the simultaneous nonlinear algebraic equations.

DISCUSSION

The CO oxidation reaction carried out by Sung [3] was analyzed to demonstrate the experimental correlation with the present model. The reaction was studied over Pt(110) single crystal catalyst from 300 to 900 K with CO and oxygen partial pressures from 3×10^{-7} to 5×10^{-7} Torr in a continuously pumped vacuum reactor. A plot of typical steady state kinetic data is shown in Fig. 1. The ordinate is the natural logarithm of ΔP_{CO_2} ($= P_{\text{CO}_2}$ -background P_{CO_2}). In the continuously pumped system ΔP_{CO_2} is proportional to the reaction rate ($\Delta P_{\text{CO}_2} \propto R$).

The values of the parameters in simulation were selected as in Table 1 based on CO oxidation on the (110) surface of Pt single crystalline catalyst [3]. It is assumed that the interaction energies, $\epsilon_{AA} = -1.6$ Kcal/mole and $\epsilon_{AB} = \epsilon_{BB} = 0$ by the trial and error in simulation in order to match with the experimental results observed by Sung [3]. The experimental data in Fig. 1 are very close to the simulation results (to be shown in Fig. 4 later on). It was explicitly assumed that the interaction energy between the adsorbed species A^* and A^* is much larger than that between the adsorbed species B^* and B^* ($|\epsilon_{AA}| \gg |\epsilon_{BB}|$). As P_A increases slowly from the low value at a constant P_{B_2} , A can easily displace B from the surface because of the low attraction energy, ϵ_{BB} . The reaction rate increases. This corresponds to the left branch of the kinetic curve in Fig. 2. If P_A increases a bit further, A displaces most of B_2 from the surface. It is difficult for B to be adsorbed because of the large attraction energy among the adsorbed species of A (A-blocking). This point cor-

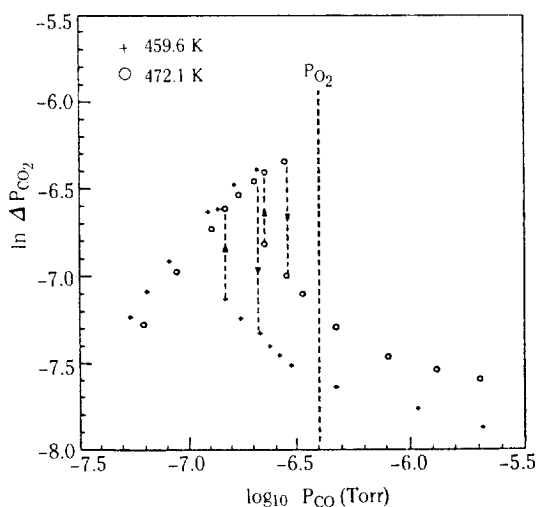


Fig. 1. Multiple steady states for CO oxidation on Pt (110) surface [3].

Table 1. Values of the system parameters used in the simulation

Parameter	Remark
$M = 1 \times 10^{15}/\text{cm}^3$	
$Z = 4$	
$\nu_{aA} = 2.72 \times 10^5 (\text{Torr})^{-1} \text{sec}^{-1}$	nonactivated
$\nu_{aB} = 1.11 \times 10^5 (\text{Torr})^{-1} \text{sec}^{-1}$	"
$\nu_{dB} = 0 \text{ sec}^{-1}$	non-desorption
$\nu_{dA} = 1 \times 10^{12} \exp(-27000/\bar{R}T) \text{sec}^{-1}$	Temp-dependent
$\nu_R = M(0.84 \times 10^{-11}) \exp(-10500/\bar{R}T) \text{sec}^{-1}$	"
$\epsilon_{AA} = -1.6 \text{ Kcal/mol}$	
$\epsilon_{BB} = 0$	
$\epsilon_{AB} = 0$	

Note: The values of the parameters were selected based on CO oxidation on Pt single crystalline catalyst [3].

responds to the downward transition in Fig. 2. The reaction rate at the downward transition point drops by more than one order of magnitude, which was observed by Sung [3]. Golchet and White [6] postulated that such an abrupt downward transition may be accompanied by the condensation-like accumulation of adsorbed species. Fig. 3 shows such a possibility quite clearly (i.e., θ_A jumps from 0.1 to 0.9).

Inversely as P_A decreases slowly from a high value of P_A , B_2 cannot easily displace A from the surface even at the pressure of the downward transition because of the attractive interaction among A's. When P_A decreases a bit further from the pressure of the

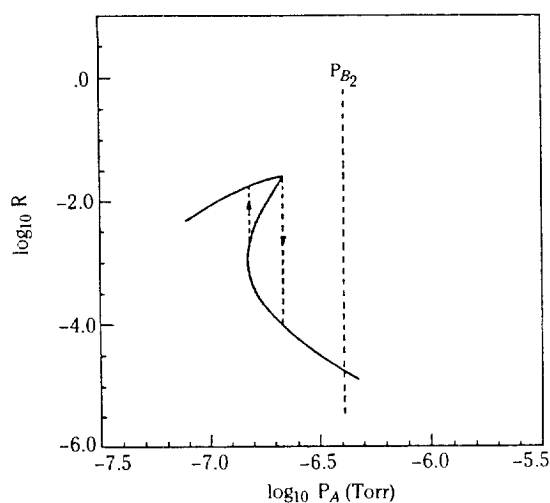


Fig. 2. The clockwise hysteresis for the reaction rate vs. P_A at 460 K and $P_{B_2} = 4 \times 10^{-7}$ Torr.

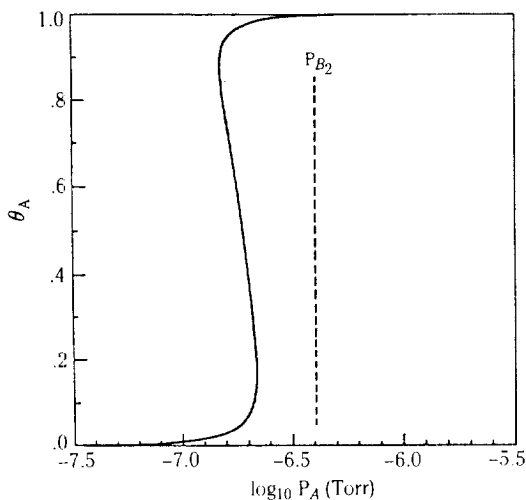


Fig. 3. The fractional surface coverage θ_A vs. P_A at 460°K and $P_{B_2} = 4 \times 10^{-7}$ Torr.

downward transition, the A-A attractive interaction decreases and B begins to displace A. And the reaction rate increases abruptly at this point. This point corresponds to the upward transition in Fig. 2. According to the history of P_A variation at the pressures between the upward and the downward transitions, there exist multiple steady states at the same value of P_A .

As can be seen in Fig. 2, the catalyst surface is mainly saturated with B for the left branch of the kinetic curve and with A for the right branch. The predictions of the surface coverage variation with P_A under the reaction conditions as shown in Fig. 3 generally

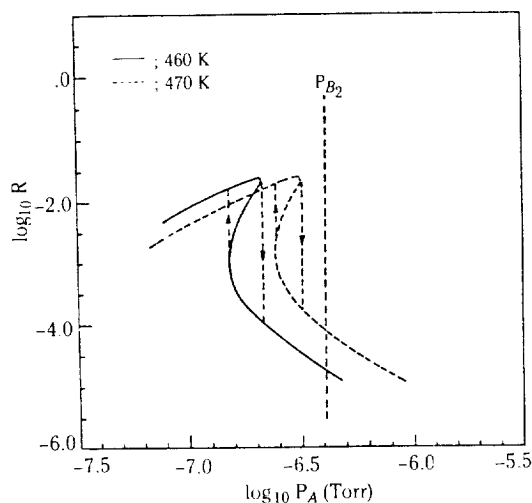


Fig. 4. The effect of temperature on the clockwise hysteresis at $P_{B_2} = 4 \times 10^{-7}$ Torr.

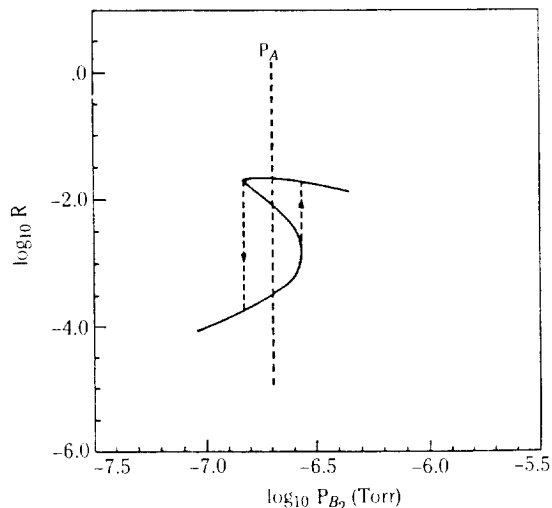


Fig. 5. The counter-clockwise hysteresis for the reaction rate vs. P_{B_2} at 470°K and $P_A = 2 \times 10^{-7}$ Torr.

agree with the data reported by Golchet and White [6].

Fig. 4 shows the clockwise hysteresis for two different temperatures. The hysteresis loops become smaller with increasing temperature. The shrinking rate of the loops is smaller than that of the experimental loops in Fig. 1. The reaction rate on the left branch is not sensitive to the temperature variation, but the right branch shifts appreciably with the temperature. The sensitivity to the temperature can be explained if B_2 starts to desorb at a higher temperature (i.e., ~ 800 K) as well as if A at a temperature near to the hysteresis range (i.e., ~ 400 K) [3].

The counter-clockwise hysteresis phenomena are shown in Fig. 5 when P_{B_2} varies at a fixed P_A . This is expected from the P_A and P_{B_2} effect in Fig. 2. Because the A-A attraction is bigger than the B-B attraction, B cannot easily displace A. Fig. 6 shows the extent to which B displaces A from the surface with increasing P_{B_2} . It can be seen that considerable portion of the surface is covered by A even after the upward transition. The reaction rate will be still high. This corresponds to the right branch of the kinetic curve in Fig. 5. Inversely as P_{B_2} decreases slowly from the high value, the reaction rate decreases abruptly at the lower value of the P_{B_2} than the pressure for the upward transition. This results in the counter-clockwise hysteresis loop, which is a good contrast to the clockwise hysteresis loop in Fig. 2.

Through close examination of Fig. 4 it is possible to predict the behavior of the reaction rate, R , with temperature at a fixed P_A and P_{B_2} . The resulting curve

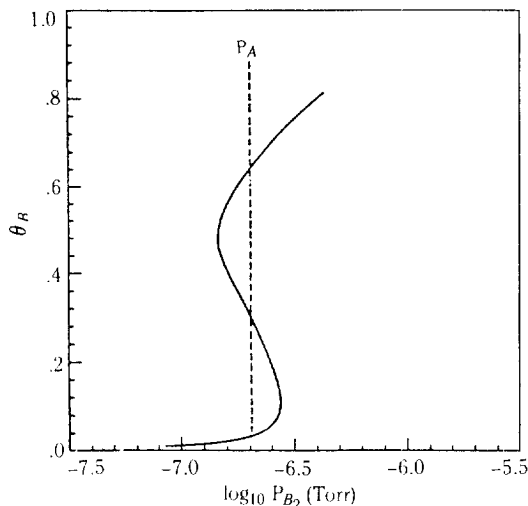


Fig. 6. The fractional surface coverage θ_B vs. P_{B_2} at 470°K and $P_A = 2 \times 10^{-7}$ Torr.

exhibits the counter-clockwise hysteresis as shown in Fig. 7.

Eigenberger [5] also proposed that the clockwise and the counter-clockwise hysteresis can be caused by so called "A- and B-blocking" respectively. However A- or B-blocking was explained by the big difference in the chemisorption strength, which is the attractive force between A or B and the surface. It is rather interesting that the two different approaches (one, which is the present study, is based on the interaction among the adsorbed species and the other on the chemisorp-

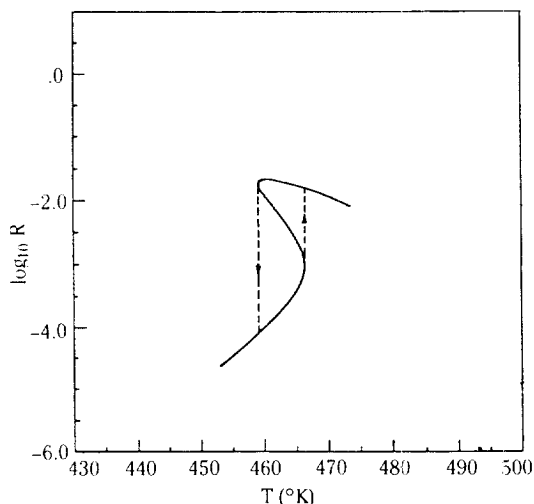


Fig. 7. The counter-clockwise hysteresis for the reaction rate vs. temperature at $P_A = 2 \times 10^{-7}$ Torr and $P_{B_2} = 4 \times 10^{-7}$ Torr.

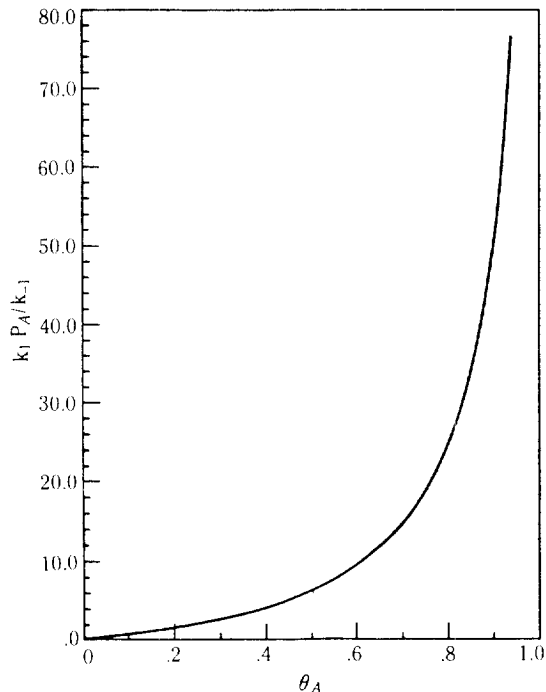


Fig. 8. The chemisorption strength in terms of $k_1 P_A / k_{-1}$ vs. θ_A at 460°K and $P_{B_2} = 4 \times 10^{-7}$ Torr.

tion strength) result in the same explanation on the hysteresis phenomena. From the present analysis, the chemisorption strength can be represented by $k_1 P_A / k_{-1}$. Fig. 8 shows that up to $\theta_A \cong 0.8$, the strength increases very slowly, but above the value the strength increases very fast and the A-blocking will appear. Sung [3] observed the difference of the multiplicity between the lattice planes of the single crystal, e.g. Pt(110) and Pt(100). They may be predicted by the newly-proposed model where z depends on the particular type of surface lattice. It would be difficult to predict them by the model based on the strong chemisorption. Additionally confirmation has been made through numerical computations that the variations of ϵ_{AA} and ϵ_{BB} can result in the clockwise and the counter-clockwise hysteresis respectively.

CONCLUSION

The rate multiplicity was assumed to occur due to the interactions between the adsorbed species, and the interactions were elucidated by applying the lattice-gas model with a statistical approach. A generalized Langmuir-Hinshelwood mathematical model was chosen for the analyses. The simulation results were shown to predict all the detailed patterns of the hysteresis loop

with respect to the reaction variables. Both the clockwise and the counter-clockwise hysteresis phenomena were obtained for the same values of the kinetic parameters. It is rather interesting that two different approaches, one based on the lateral interaction and the other on the chemisorption strength, result in the same explanation on the hysteresis phenomena.

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NOMENCLATURE

EA	: defined by ν_{dA}/ν_R
EB	: defined by $2\nu_{dB}/\nu_R$
E_a	: energy difference between an activated complex A* and the molecular A for the adsorption
E_d	: energy difference between an activated complex A* and the molecular A for the desorption
E_{ad}	: energy difference between an activated complex B* and the molecular B ₂ for the associative desorption
E_{da}	: energy difference between an activated complex B* and the molecular B ₂ for the dissociative adsorption
E_{LH}	: energy difference for the Langmuir-Hinshelwood reaction step
F_A, F_{A^*}	: nonconfigurational partition functions of A, A*
F_{B_2}, F_{B^*}	: nonconfigurational partition functions of B ₂ , B*
h	: Plank's constant
k	: Boltzman's constant
k_1, k_{-1}	: rate constant of A for the adsorption, for the desorption in eq. (2)
k_2, k_{-2}	: rate constant of B for the dissociative adsorption, for the associative desorption in eq. (3)
κ_3	: rate constant for the surface reaction in eq. (4)
k_a	: rate constant of A for the monomolecular adsorption
k_d	: rate constant of A for the monomolecular desorption
k_{ad}	: rate constant of B for the associative desorption
k_{da}	: rate constant of B for the dissociative adsorption
k_{LH}	: rate constant for the surface Langmuir-Hin-

	shelwood reaction
LH	: Langmuir-Hinshelwood
M	: number of the elementary sites
N_A	: number of the adsorbed A (molecules/cm ²)
N_A^g	: number of the A molecules in the gas phase (molecules/cm ³)
N_B	: number of the adsorbed B
$N_{B_2}^g$: number of the B ₂ molecules in the gas phase
N_T	: equal to M
P_A	: partial pressure of A
P_A'	: defined as $\nu_{dA}P_A/\nu_R$
P_{B_2}	: partial pressure of B ₂
P_{B_2}'	: defined as $\nu_{dB}P_{B_2}/\nu_R$
$P_{A, nm}$: probability that the particle A has n particles of A and m particles of B in the neighbor sites
$P_{BB, i}$: probability that two nearest sites are occupied by the pair BB and that the pair has the environment marked by the index i
P_{ij}	: probability that two nearest sites are occupied by the pair ij
\bar{P}_{ij}	: defined as 0.5 P_{ij}
Q_{ij}	: defined as $\exp(\epsilon_{ij}/kT)$
\bar{R}	: dimensionless reaction rate
R	: gas constant (= 1.987 cal K ⁻¹ mol ⁻¹)
T	: absolute temperature (°K)
Z	: number of the nearest neighbors to an adsorption site
γ_A, γ_B	: functions defined by eq. (19), by eq. (28)
ϵ_{ij}	: interaction energy of the nearest particle pair ij
$\Delta\epsilon_{nm}$: lateral energy difference defined as $n(\epsilon_{A^*A} - \epsilon_{AA}) + m(\epsilon_{A^*B^*} - \epsilon_{AB})$
$\Delta\epsilon_{nm}^*$: interaction energy between the activated complex and the neighbor particles
θ_A	: fractional surface coverage of the adsorbed species A*
θ_B	: fractional surface coverage of the adsorbed species B*
ν_{dA}, ν_{dA}	: rate constant of A for the adsorption, for the desorption without admolecular interaction
ν_{dB}, ν_{dB}	: rate constant of B for the dissociative adsorption, for the associative desorption without admolecular interaction
ν_R	: reaction rate constant without admolecular interaction

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