The Kinetics and Mechanism of Hydrogen Adsorption and Hydrogen–Deuterium Equilibration on the Copper Surface

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The mechanism of H_2–D_2 equilibration reaction over the copper surface was studied in the 40—90 °C range of temperature and in the pressure range of 4—45 Torr. From the studies of the hydrogen adsorption and the reaction between gaseous deuterium and preadsorbed hydrogen, the reaction was confirmed to proceed *via* combination between hydrogen and deuterium atoms on the surface. The rate constants for the adsorption and the desorption were optimized by a computer simulation of the reaction-time course and were found to be in satisfactory agreement with the observed results. A marked isotope effect was found in these rates; its influence on the partial pressure dependence of the reaction was discussed.

It has been known that copper, a typical "s-metal," is different from a "d-metal" in its catalytic activity for reactions such as the hydrogenation of olefins and the decomposition of alcohols or formic acid. Surface hydrogen is supposed to play an important role in these reactions. However, there have been few detailed reports on the adsorption and reaction of hydrogen on the copper surface.

Allen and Mitchell[1)] have reported that hydrogen is not chemisorbed on the evaporated film of copper in the temperature range from 90 to 273 K. On the other hand, Prichard and Alexander[2)] have found, from their measurements of the surface potential, that hydrogen is chemisorbed spontaneously on the evaporated film between 242 and 337 K. Though Shield and Russell[3)] suggested that the adsorption of hydrogen is due to transition-metal impurities, Cadenhead and Wagner[4)] have found that carefully reduced copper powder can adsorb approximately 0.4 of a monolayer of hydrogen at 77 K. Recently, Momma and Yasumori[5)] have found, from a thermal desorption study, that there is only one dissociative state for the adsorbed hydrogen on copper powder.

In this work, we studied in detail the kinetics of the H_2-D_2 equilibration reaction in order to ascertain the behavior of adsorbed hydrogen on the copper surface.

Experimental

A circulating system of about 500 ml was used for the studies of adsorption and kinetics. This apparatus was incorporated with a reaction vessel, an inductance Bourdon gauge,[6)] gas reservoirs, and a high-vacuum line. The temperature of the reaction vessel was controlled within ±0.5 °C. Isotopes of hydrogen were analyzed by the use of a gas chromatograph with a column of Mn^{2+} coated γ-alumina.[7)]

The kinetics of the equilibration reaction was studied using an equimolar mixture of H_2 and D_2 in the temperature range of 40—90 °C at total pressures between 4 and 45 Torr. The dependences of the reaction rate on the partial pressures of H_2 and D_2 were also examined. Two series of experiments were carried out; in the first series, the initial pressure of H_2 (or D_2) was varied, while that of D_2 (or H_2) was kept constant, and in the second series, the fraction of hydrogen was varied under a constant total pressure.

During the course of the equilibration, the amounts of hydrogen and deuterium adsorbed on the surface were estimated from the introduced amounts and from the partial pressure of each isotopic molecule. The pressure change due to adsorption during the course of reaction was continuously followed by means of a Bourdon gauge. The rates of the adsorption and desorption of hydrogen and deuterium and the adsorption isotherms were determined using the same reaction vessel.

Copper powder, used as a catalyst, was prepared by the following procedure: cupric oxide was precipitated from an aqueous solution of copper nitrate by adding sodium hydroxide and was reduced with circulating hydrogen of 50—100 Torr at 180 °C. Guaranteed-reagent cupric nitrate was obtained from Wako-Pure Chemical Industries, Ltd. The reduction was continued for 50 hr until no decrease in the hydrogen or no trace of water could be found. The reduced copper powder was evacuated at the same temperature for several hours. The surface area of the catalyst was estimated as 4.4 m^2/g by means of the BET method using krypton at 77 K.

Transition-metal impurities in the cupric oxide were examined by emission spectroanalysis; the amounts of Fe and Ni were less than 5 ppm, and those of Co and Mn were less than 10 ppm. As for non-transition-metal impurities, the amounts of Al and Na were less than 2 and 0.5 ppm respectively, while those of Si and Mg slightly exceeded the limit of detection.

High-purity hydrogen, deuterium (HD less than 0.5%), and krypton purchased from the Takachiho Co., Ltd., were used without further purification.

In annealing, the copper powder was heated at definite temperatures up to 500 °C *in vacuo* below 10^{-6} Torr for an hour. Prior to each kinetic run, the annealed catalyst was evacuated again at room temperature for several hours.

The simulation and the numerical analysis of the reaction-time course were carried out by means of the Runge-Kutta-Gill method with the aid of a computer, HITAC 8700.

Results

The Adsorption of Hydrogen and Deuterium. The adsorption of hydrogen proceeded at a measurable speed at room temperature. Figures 1 and 2 show the time courses of the chemisorption of H_2 and D_2 respectively in the temperature range of 30—170 °C. It is evident that the chemisorption requires an activation energy. A marked isotope effect in the adsorption rate was found; the rate of hydrogen adsorption was about six times as fast as that of deuterium adsorption at room temperature. Figure 3 shows a linear relationship[8)] between the rate of adsorption and the pressure, where the points on each line were obtained as those

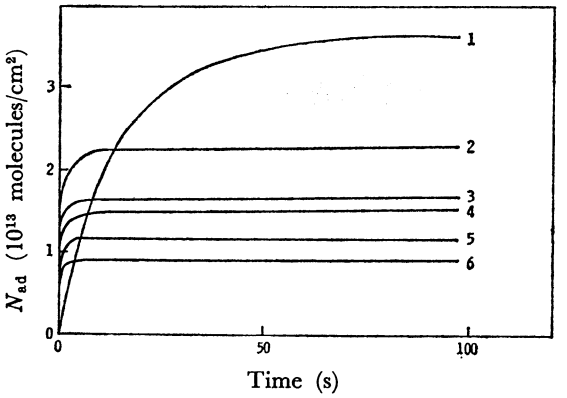

Fig. 1. Time course of hydrogen adsorption on copper at various temperatures.
1: 33.5, 2: 69, 3: 99, 4: 111, 5: 126, 6: 166 °C.

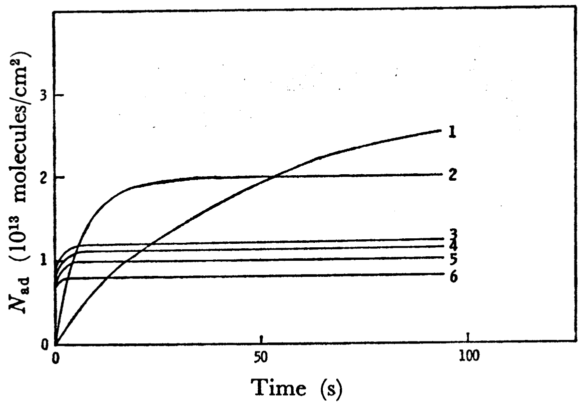

Fig. 2. Time course of deuterium adsorption on copper at various temperatures.
1: 36, 2: 62, 3: 99, 4: 111, 5: 126, 6: 166 °C.

for the same amount of adsorbed hydrogen from various time curves at 20 °C. The intercepts correspond to the desorption rates, which increase with the amount of adsorbed hydrogen. This result suggests that the adsorption is not controlled by any process such as diffusion in the gas phase or in surface migration, but by the simple collision of gaseous molecules with the surface.

The adsorption isotherms of hydrogen and deuterium were obtained in the temperature region from 0 to 60 °C and at pressures from 4 to 45 Torr. The adsorption of hydrogen was found to be reversible under these conditions. Plots of the reciprocal of $\sqrt{P_e}$ against the reciprocal of N^{e}_{ad} showed a linear relationship, where P_e is the equilibrium pressure and N^{e}_{ad} is the amount of adsorbed hydrogen. This result indicates that the adsorption isotherm obeys the Langmuir equation for dissociative adsorption. The monolayer capacity was evaluated as 2.8×10^{14} H atoms/cm^2. This value corresponds to approximately 20% of the surface copper atoms, 1.6×10^{15} atoms/cm^2, taken as the average of the (111) and (100) planes. The heats of adsorption of hydrogen and deuterium were determined to be 9.2 ± 1.0 kcal/mol and 10.3 ± 2.0 kcal/mol respectively.

The overall rate of adsorption may, therefore, reasonably be expressed as:

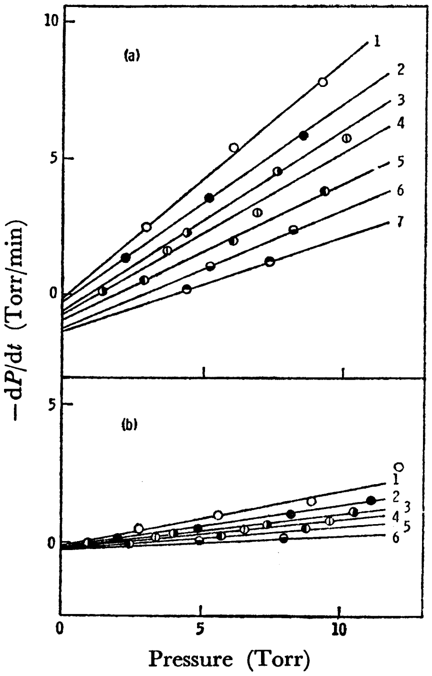

Fig. 3. Relationship between the net rate of adsorption and pressure at constant amount of adsorption at 20 °C.
a: H_2, b: D_2; 1: 0.306, 2: 0.612, 3: 0.918, 4: 1.22, 5: 1.53, 6: 1.84, 7: 2.14×10^{13} molecules/cm^2.

$$KV/\sigma_0{}^2S\cdot dP/dt = -k_aP(1-\theta)^2 + k_d\theta^2 \qquad (1)$$

where K is the conversion factor (molecules/ml·Torr), V is the volume of the reaction system, σ_0 is the monolayer capacity, S is the surface area, and k_a and k_d are the rate constants for adsorption and desorption respectively.

Adsorption Measurements during H_2-D_2 *Equilibration.* The change in the adsorption during the H_2-D_2 equilibration was followed volumetrically; the results at 14 °C are shown in Fig. 4. The amount of adsorbed hydrogen or deuterium is conventionally expressed by the virtual pressure of H_2 or D_2 which would be

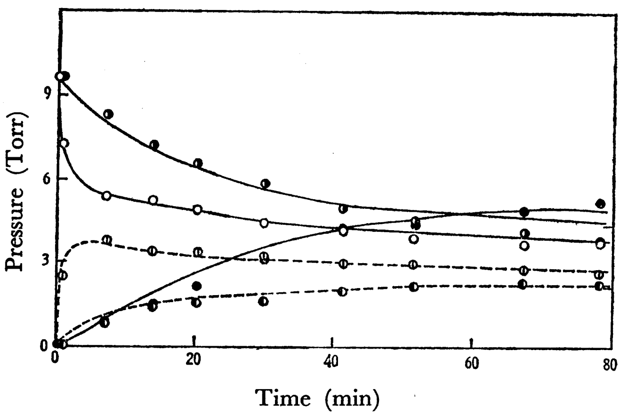

Fig. 4. Adsorption during the course of H_2-D_2 equilibration on copper at 14 °C. Lines indicate the best fitting curves obtained by computer simulation.
○: $H_2(g)$, ◑: $D_2(g)$, ●: $HD(g)$, ⦶: $H_2(a)$, ◐: $D_2(a)$.

expected if the adsorbed species were all present in the gas phase. When an equimolar mixture of H_2 and D_2 was introduced into the reaction system, the hydrogen in the gas phase decreased more rapidly than the deuterium. The adsorbed amount of hydrogen reached a maximum about ten minutes after the start of the reaction. As the reaction proceeded, the amount of adsorbed hydrogen decreased, whereas that of the adsorbed deuterium increased until it reached an amount similar to that of adsorbed hydrogen, their sum being almost kept constant after the maximum.

Exchange Reaction. In order to get information on the mechanism of the H_2-D_2 equilibration, the exchange reaction between the adsorbed hydrogen and gaseous deuterium was examined. Figure 5 shows the behavior of hydrogen species during the course of the exchange. In this case, H_2 was preadsorbed on the copper surface; then, the hydrogen in the circulating system was quickly replaced by deuterium except for the small amount of hydrogen in the catalyst vessel. An induction period for the HD formation and a maximum in the rate appeared, and the surface hydrogen was gradually displaced by deuterium.

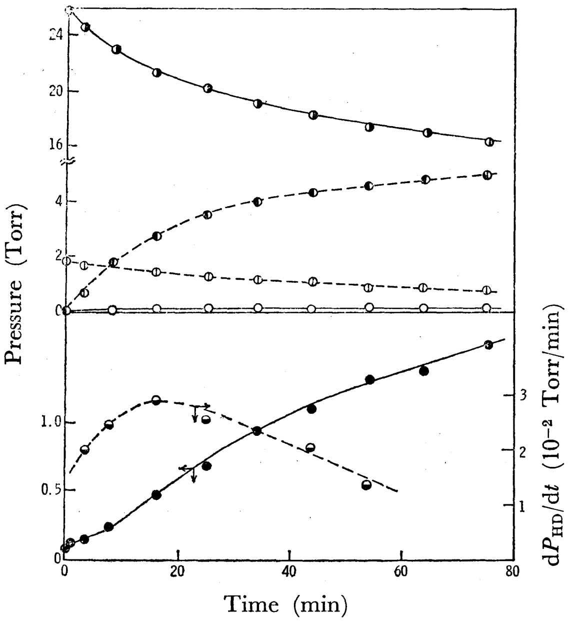

Fig. 5. Adsorption during the course of exchange reaction at 20 °C.
○: H_2(g), ◑: D_2(g), ●: HD(g), ⊖: the rate of HD formation, ⦶: H_2(a), ◐: D_2(a).

These results suggest that the equilibration takes place through the repetition of the dissociative adsorption of H_2 and D_2 and the desorption of HD. Hydrogen deuteride is formed from the recombination between the chemisorbed hydrogen and deuterium atoms; the rate of HD formation in this case should be proportional to the respective concentrations of adsorbed species. This view was further supported by a similar finding for the exchange between adsorbed D atoms and gaseous H_2 molecules.

If a reaction between adsorbed hydrogen atoms and gaseous deuterium molecules, $H(a)+D_2\rightarrow HD+D(a)$, occurs, a monotonous decrease in the rate may be observed, since the rate is expressed as $dP_{HD}/dt=k\theta_H P_{D_2}$.

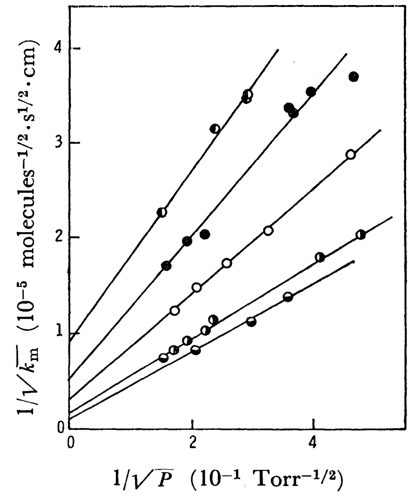

Fig. 6. Dependence of $1/\sqrt{k_m}$ on $1/\sqrt{P}$ at various temperatures.
◐: 43.5, ●: 51, ○: 64, ◑: 75.5, ⊖: 85 °C,

Kinetics of H_2-D_2 Equilibration. The rate of the equilibration in an equimolar mixture of H_2 and D_2 obeyed the usual first-order equation:

$$k_e = 1/t\cdot\ln(x_0-x_e)/(x_0-x_t) \quad (s^{-1}) \tag{2}$$

where x_0, x_t, and x_e represent the fraction of hydrogen deuteride at the beginning, at time t, and at equilibrium respectively. The absolute rate, k_m, is derived from the constant, k_e, as:

$$k_m = nk_e/S \quad (\text{molecules/cm}^2\cdot s) \tag{3}$$

where n is the total number of hydrogen molecules in the reaction system and where S is the surface area of copper.

The dependences of the absolute rate on the pressure and the temperature were studied in the ranges from 4 to 45 Torr and from 40 to 90 °C. The apparent order of the reaction was 0.8 with respect to the total pressure of hydrogen. Since a linear relationship holds between the reciprocals of $\sqrt{k_m}$ and $\sqrt{P}$, as is shown in Fig. 6, the rate may be represented by the equation:

$$k_m = k_0(\sqrt{KP}/1+\sqrt{KP})^2 \tag{4}$$

where k_0 is the rate constant and is estimated as an extrapolated value of k_m when the pressure rises to infinity. The apparent activation energy and the heat of adsorption were evaluated as 17.9±1.5 kcal/mol and 9.7±1.5 kcal/mol respectively.

Dependence of the Rate on the Composition of the Reactant. In order to ascertain the dependence of the rate on the partial pressures of H_2 and D_2, two series of experiments were carried out. Figure 7 shows the initial rate of HD formation obtained at 79 °C, where the partial pressure of H_2 or D_2 was kept constant. A marked isotope effect was observed; when the partial pressure was lower than 3.2 Torr, the rate of reaction under a constant D_2 pressure was faster than that under a constant H_2 pressure. Plot of $\log P_{H_2}$ or $\log P_{D_2}$

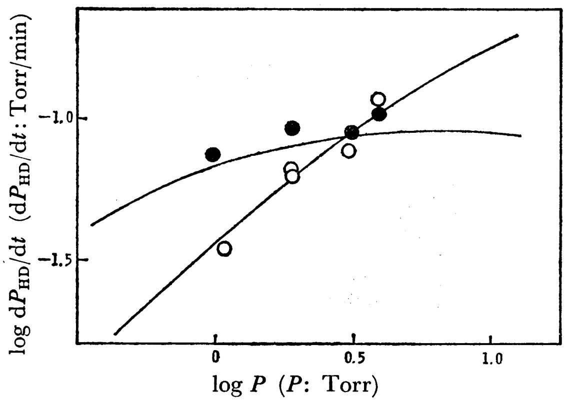

Fig. 7. Variation of initial rate of HD formation with hydrogen or deuterium pressure. Initial pressure was 3.2 Torr. Solid lines show theoretical curves. ○: initial $P_{H_2}=3.2$ Torr, ●: initial $P_{D_2}=3.2$ Torr.

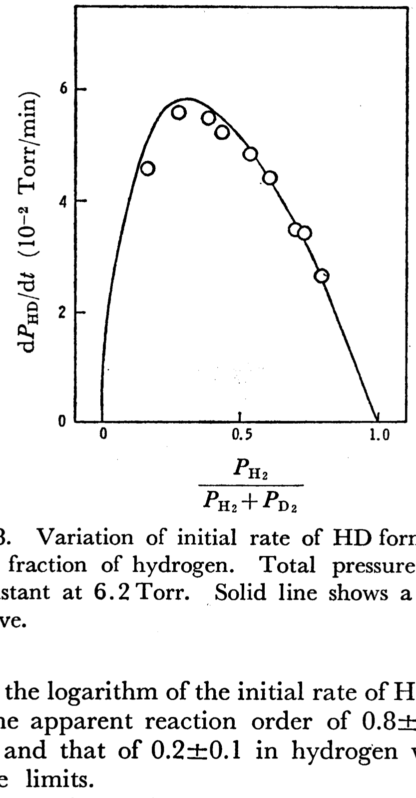

Fig. 8. Variation of initial rate of HD formation with the fraction of hydrogen. Total pressure was kept constant at 6.2 Torr. Solid line shows a theoretical curve.

against the logarithm of the initial rate of HD formation gives the apparent reaction order of 0.8±0.1 in deuterium and that of 0.2±0.1 in hydrogen within these pressure limits.

Figure 8 shows the correlation between the initial rate of HD formation and the fraction of hydrogen under a constant total pressure of 6.2 Torr at 84 °C. The maximum in the rate appears at a hydrogen fraction of 0.3—0.4; it deviates from the point of an equimolar composition. This result can be attributed to the kinetic isotope effect in the adsorption and desorption processes.

Effect of Annealing. The dependences of the reaction velocity and the apparent activation energy on the annealing temperature are shown in Table 1; the activity per unit of weight of copper decreased on annealing. However, it was found that the annealing also decreased the surface area of copper and that the reaction rate per unit of surface area remained almost unchanged.

Table 1. Effect of annealing on catalytic activity

Annealing temp. (°C)	Surface area (m^2/g)	Specific activity (molecules/s·g)	k_m (molecules/ s·cm^2)	E_{ap} (kcal/mol)
180	4.4	2.48×10^{14}	5.6×10^{9}	12.6
280	4.1	2.15×10^{14}	5.2×10^{9}	12.6
380	3.4	1.72×10^{14}	5.1×10^{9}	12.2
480	2.2	0.69×10^{14}	4.4×10^{9}	11.9

Discussion

In the present study, it is revealed that hydrogen is dissociatively adsorbed on the copper surface and that an activation energy is needed for this process. The results obtained from the adsorption measurements during the course of the exchange reaction confirm that the equilibration reaction occurs *via* the dissociative adsorption of H_2 and D_2 and the desorption of HD as a result of a recombination of the chemisorbed hydrogen and deuterium atoms.[9] A recent study of the thermal desorption supports this mechanism; the desorption spectra showed only one dissociatively-adsorbed state for hydrogen on the reduced copper powder. The desorption was found, from the dependence of the peak shift on the amount of adsorption, to be second-order with respect to the surface concentration of hydrogen; further, the complete mixing of the hydrogen and deuterium atoms was observed.

There is no alternative mechanism for explaining the equilibration reaction. Since the Rideal-Eley mechanism[10] involves a surface reaction between the chemisorbed hydrogen atom and the physically-adsorbed molecule as the rate-controlling step, it does not accord with the present results on the exchange reaction. The Schwab-Killmann mechanism,[11] which presumes a molecular adsorption of H_2 and D_2 and a bimolecular rearrangement between them on the surface, also does not hold because the adsorbed hydrogen is in a dissociative state, as has been discussed above.

Subsequently, the results of the adsorption measurements during the H_2-D_2 equilibration can be analyzed according to the following scheme:

$$H_2 \underset{k_d{}^H}{\overset{k_a{}^H}{\rightleftharpoons}} 2H(a) \tag{I}$$

$$HD \underset{k_d{}^{HD}}{\overset{k_a{}^{HD}}{\rightleftharpoons}} H(a) + D(a) \tag{II}$$

$$D_2 \underset{k_d{}^D}{\overset{k_a{}^D}{\rightleftharpoons}} 2D(a) \tag{III}$$

where k_a and k_d are the rate constants for the adsorption and the desorption respectively, as defined above.

The rates are expressed in the same way as in Eq. (1):

$$KV/\sigma_0{}^2S\cdot dP_H/dt = -k_a{}^HP_H(1-\theta_H-\theta_D)^2 + k_d{}^H\theta_H{}^2 \tag{5}$$

$$KV/\sigma_0{}^2S\cdot dP_{HD}/dt = -k_a{}^{HD}P_{HD}(1-\theta_H-\theta_D)^2 + k_d{}^{HD}\theta_H\theta_D \tag{6}$$

$$KV/\sigma_0{}^2S\cdot dP_D/dt = -k_a{}^DP_D(1-\theta_H-\theta_D)^2 + k_d{}^D\theta_D{}^2 \tag{7}$$

This set of simultaneous differential equations was solved numerically by applying the Runge-Kutta-Gill

TABLE 2. RATE CONSTANTS FOR DESORPTION AND ADSORPTION AT 14°C

	k_d (cm^2/molecules·s)	k_a (cm^2/molecules·Torr·s)
H_2	7.9×10^{-17}	5.4×10^{-18}
HD	7.0×10^{-17}	3.0×10^{-18}
D_2	1.7×10^{-17}	7.2×10^{-19}

method with the aid of a computer. The rate constants as parameters were chosen so as to obtain the best-fitting curves to the experimental time course by using the least-squares method. The rate constants thus determined are listed in Table 2; the coincidence of the theoretical curves with the experimental results is evident, as is shown in Fig. 4. The rate constants at 0 and 89 °C were also evaluated from the results of adsorption during the equilibration by means of the computer simulation procedure. The activation energies for the adsorption and desorption were determined from these constants at 0, 14, and 89 °C by combining the separate data of the adsorption rates of H_2 and D_2 at temperatures between 0 and 20 °C. These values are summarized in Table 3. The rate constants estimated from the adsorption and desorption rates of H_2 and D_2 at 20 °C are compared with those determined by the simulation in Table 4. The agreement between the calculated and the observed values offers an additional evidence for the validity of computer simulation. Therefore, it is confirmed that the reaction proceeds *via* the so-called Bonhoeffer-Farkas mechanism.

TABLE 3. ACTIVATION ENERGIES FOR DESORPTION AND ADSORPTION

	E_a (kcal/mol)	E_d (kcal/mol)
H_2	9 ± 1	17 ± 1
HD	9 ± 1	17 ± 2
D_2	10 ± 1	18 ± 2

TABLE 4. RATE CONSTANTS FOR DESORPTION AND ADSORPTION AT 20°C

	k_d (cm^2/molecules·s)		k_a (cm^2/molecules·Torr·s)	
	Obsd	Calcd	Obsd	Calcd
H_2	1.5×10^{-16}	1.5×10^{-16}	5.5×10^{-18}	7.4×10^{-18}
D_2	4.2×10^{-17}	3.6×10^{-17}	1.1×10^{-18}	1.0×10^{-18}

It may be seen that the rates are empirically represented by Eq. (4), which is derived on the basis of this mechanism by neglecting the isotope effect. The linear relationship shown in Fig. 6 is, however, rather accidental; Eq. (4) predicts that the reaction order of H_2 or D_2 must not exceed 0.5. The solid lines in Figs. 7 and 8 were obtained by the use of evaluated rate constants involving the isotope effect and were in good agreement with the experimental results.

Accordingly, the considerations given above indicate that the isotope effect can not be ignored in interpreting the pressure dependence of the reaction.

The equilibration reaction can now be precisely analyzed on the basis of the present results and the transition-state theory. It can easily be shown that the rate constants of adsorption, k_a, and desorption, k_d, are given by:

$$k_a = kT/h\cdot F^{\ddagger}/F_g F_{s2}\cdot\exp(-E_a/RT)\cdot k'/T\cdot s/2L \tag{8}$$

$$k_d = kT/h\cdot F^{\ddagger}/F_{H(a)}{}^2\cdot\exp(-E_d/RT)\cdot s/2L \tag{9}$$

where L is the total number of sites per unit area of copper, s is the number of adjacent sites, and F_g, $F_{H(a)}$, F_{s2}, and $F^{\ddagger}$ are the partition functions of gaseous hydrogen, the adsorbed hydrogen atom, the dual sites, and the activated complex respectively. The constant, k', in Eq. (8) is the conversion factor in unit of molecules·deg/Torr·ml. The transmission coefficient is assumed to be unity. The rates at 14 °C were evaluated by assuming F_{s2}, $F^{\ddagger}$, and $F_{H(a)}$ to be unity, and s to be 6, and by assuming L as 2.8×10^{14} sites/cm^2. The results for hydrogen were:

$$k_a = 6.0\times10^{-18} \quad (\text{cm}^2/\text{molecules}\cdot\text{Torr}\cdot\text{s})$$

$$k_d = 7.9\times10^{-15} \quad (\text{cm}^2/\text{molecules}\cdot\text{s})\,.$$

As is shown in Table 2, the calculated rate constant of adsorption is in satisfactory agreement with the experimental value. However, in the case of desorption, the theoretical value is larger than the experimental value by a factor of 10^2. This discrepancy is presumably a result of the low vibrational frequencies of the adsorbed hydrogen atom on the real surface.

By combining the difference between the zero-point energies of the molecular vibrations of H_2 and D_2, 1.8 kcal/mol with the values of the activation energies shown in Table 3, it is possible to estimate the difference between the zero-point energies of the Cu-H and Cu-D vibrations on the surface. The value, 0.9 kcal/mol, obtained for this difference seems reasonable in comparison with the value, 0.92 kcal/mol, of that between the dissociation energies of diatomic molecules, CuH and CuD.

It has been considered by several investigators that defect structures in metal surface may play an important role in heterogeneous catalysis. Uhara *et al.*[12] studied the effect of annealing on the catalytic activity of copper for the decomposition of benzene diazonium chloride and suggested that the fall in catalytic activity was attributable to a decrease in the concentration of dislocation which occurred around 400 °C. In the present study, the total activity per unit of weight decreased upon annealing in a way similar to that observed by them. However, the surface area also decreased upon annealing, and the reaction rate per unit of surface area was almost unvaried. Therefore, this reaction is not structurally sensitive, but belongs to a category of "facile" reaction[13] which depends only on the degree of exposure of metal atoms. Besides, it is known that the points or lines of the emergence of defects at silver films[14] and the lattice imperfection on silver crystals[15] are unimportant for the decomposition of formic acid. Woodward *et al.*[16] indicated that dislocations on silver do not act as active sites for the oxidation of ethylene. The present findings, together with these observations, lead us to conclude that the structural defects in s-metals do not play a dominant role in heterogeneous catalysis.

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