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Gas Chromatographic Determination of Reversible Adsorption of Hydrogen

VII. The Rate of Reversible Adsorption of Hydrogen on a Nickel Catalyst

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The rate of reversible adsorption of hydrogen was determined by means of plate height of a nickel catalyst column in gas chromatographic elution of deuterium by hydrogen, adopting Gidding equation for the plate height. The activation energy of desorption is derived from the variation of the desorption rate with temperature to be about 1.5 kcal/mole at low temperature (−195 to −183°C) and about 16 kcal/mole at around 0°C.

INTRODUCTION

A gas chromatographic method for the measurement of the rapid and reversible part of adsorption under stationary condition has been developed and applied to the adsorption of hydrogen over metals utilizing deuterium as a tracer (*1*, *2*). Those works disclosed an activation process of the hydrogen adsorption as appeared in the isobar of the deuterium retention.

It follows from the concept of activated adsorption that the adsorbed hydrogen is frozen at low temperature where the thermal energy cannot overcome the activation energy of desorption, whereas the rate of desorption increases exponentially with temperature, attaining a rate fast enough to establish the dynamic equilibrium at a higher temperature. The isobars of the deuterium retention over metals are quite reasonable on this concept. However no measurement has been done on the rate of desorption relevant to this kind of discussion, probably because of the experimental difficulty in the measurement of fast rate.

In this respect, the gas chromatographic method for the measurement of mass-transfer rate which has been related by Gidding (*3*) to the plate height equation seems to be promising. The present report deals with the rate of desorption of hydrogen determined by this method over a nickel catalyst.

Theoretical Basis for the Method

A chromatographic band injected at the column inlet as a narrow pulse becomes broadened as it migrates along the column. In the case of a linear isotherm the band contour approaches the shape of a Gaussian distribution. The theoretical plate height, H, of the column is defined in terms of the standard deviation, σ, of the Gaussian peak by

$$H = \sigma^2/L, \tag{1}$$

where L is the length of the column.

However the plate height is practically calculated by Eq. (2) transformed from the Eq. (1) assuming a band of Gaussian shape,

$$H = \frac{L}{16}\left(\frac{W}{V_R}\right)^2, \tag{2}$$

where W is the Gaussian band width and is expressed by the volume of carrier gas equivalent to 4σ, and V_R is the retention volume. It is required that both W and V_R are expressed in a same unit.

It is accepted that the plate height depends on the linear velocity, u, of the carrier gas in the column as expressed by the equation

$$H = A + B/u + Cu, \tag{3}$$

where A, B, and C are constants at any one temperature for any given column, solute or adsorbate, and carrier gas. The constant A represents the band broadening due to eddy diffusion and is expressed by (4)

$$A = 2\lambda dp, \tag{4}$$

where λ is a packing characterization factor and near unity for 50 mesh particle. This term is independent of the adsorbate or the operating conditions.

The second term, B/u, represents the contribution from the molecular diffusion, and is expressed by (4)

$$B = 2\gamma D_g, \tag{5}$$

where D_g is the coefficient of molecular diffusion in the gas phase and γ is a constant of about 0.6. The molecular diffusion coefficient, D_g, is given (5) by

$$D_g = D_0(T/T_0)^{1.75}, \tag{6}$$

where D_0 is the coefficient at a standard temperature, T_0°K.

The third term, Cu, represents the band-broadening due to mass transfer of adsorbate between gas and adsorbed phases. A number of theoretical treatments have been made on the term, Cu. Among them, the equation derived by Gidding (3) has particular relevance to gas-solid chromatography. It is given by

$$Cu = 2R(1 - R)u/k_{21}, \tag{7}$$

where R is the equilibrium fraction of molecules in the mobile phase and k_{21} is the first-order rate constant for the chromatographic process represented by a simple equilibrium

$$A_1 \underset{k_2}{\overset{k_{12}}{\rightleftharpoons}} A_2, \tag{8}$$

where subscript 1 represents the adsorbate involved in the gas phase and subscript 2, the adsorbate retained on the solid.

In the present study, the relevant chromatographic process is the deuterium transfer between gas and adsorbed phases, the rate of which is expressed in terms of the equal rate of adsorption and desorption, r (molecules/cm^2 sec), under the established equilibrium condition. Namely,

$$r_{21} = 2rf_{Da} = 2rn_{Da}/n_a = k_{21}n_{Da}, \tag{9}$$

where $f_{Da} = n_{Da}/n_a$ is the atomic D fraction in the adsorbed phase, and n_a and n_{Da} the amounts of total hydrogen and of deuterium in the adsorbed phase, respectively (atoms/cm^2). Since the values of r and n_a are constant at a fixed temperature and pressure, $k_{21} = 2r/n_a$ may be regarded as a first-order rate constant for r_{21}. The reciprocal of the rate constant, k_{21}, is equivalent to mean time required for the desorption, t_d. Hence the Eq. (7) may be rewritten as

$$Cu = 2R(1 - R)t_d u. \tag{10}$$

This equation is an approximate description of the overall transfer between the gas stream and the stationary phase. Accordingly the mean desorption time should be interpreted as the average time for complete disengagement of an adsorbate molecule from the solid.

By substituting Eqs. (4)–(7) and (10) for those constants in Eq. (3), H is expressed as

$$\begin{aligned} H = 2\lambda dp &+ 2\gamma D_0(T/T_0)^{1.75}/u \\ &+ 2R(1 - R)t_d u. \end{aligned} \tag{11}$$

If the plate height is measured as a function of the linear velocity, u, the mean desorption time, t_d, can be obtained from the third term on the right hand of Eq. (11).

EXPERIMENTAL METHODS

Procedure. The apparatus and the procedure for the gas chromatographic measurement was essentially the same as described in the previous paper (1). Briefly, the deuterium sample was introduced into the carrier gas by means of a doser made of glass tubing, and was passed to the catalyst column packed in a glass tubing. Some improvements were made to realize a narrow pulse. Firstly the volume of doser was reduced to as low as 0.2 ml. Secondly the dead volume in the connecting tubes were minimized by adopting capillary tubings of 3 mm and by shortening the connection tubings. Total dead volume was about 3 ml. The conductivity cell as a detector had a fast time constant of less than 0.75 sec. The chart speed of the recorder was 6 cm/min.

Catalyst. The sample was taken from the same batch of nickel catalyst (50–60 mesh) as used in the previous work (*1*), i.e., the stabilized nickel catalyst No. 101 supplied by Nikki Kagaku Co. which involved kieselguhr (50 wt %) as a support. The amount of catalyst packed in the column (made from a glass U-tube 6 mm i.d.) was 14.5 g or 6.6 g, the length of which was 49.3 cm or 25.6 cm, respectively. This catalyst was reduced with a hydrogen stream at 350°C before use, and kept all the time in a hydrogen atmosphere. After reduction the BET area of the catalyst was 91 m^2/g, while the amount of chemisorption of carbon monoxide at −183°C was 7.6 ml/g, and the amount of chemisorption of hydrogen at 0°C was 8.5 ml/g from which the surface area of nickel is estimated to be 28 m^2/g.

Free space in the column. The volume of free space, V_g, in the packed column is required for the estimation of both the linear velocity, u, and the equilibrium fraction of molecules, R, in the gas phase.

V_g is given by the equation,

$$V_g = V_3 - (V_1 - V_2), \tag{12}$$

where V_1 is the apparent retention volume by the empty column, V_2 that of helium by the packed column and V_3 the real volume of empty column. The observed values for them were as follows.

Catalyst wt (g)	V_1	V_2	V_3	V_g	$V_1 - V_3$ (dead vol)
14.5	17.4	15.8	14.4	12.8	3.0
6.6	11.2	10.5	6.5	5.7	4.7

The net amount of carrier gas involved in the column, V_0, can be calculated from V_g and temperature. The amount of V_0 specified for unit length of column, i.e., V_0/L is denoted by v_0 where L is the length of the column.

The equilibrium fraction of molecules in the gas phase, R, is given by

$$R = V_0/V_R, \tag{13}$$

where V_R is the net retention volume of the adsorbate and is obtained by subtracting dead volume from the apparent retention volume. The observed values of R and V_0, etc. are shown in Table 1 for a 14.5 g of catalyst.

TABLE 1

THE RETENTION VOLUME, ETC. FOR 14.5 g OF CATALYST

Column temp. (°C)	$V_0{}^a$ (ml; STP)	$V - V_0{}^a$ (ml; STP)	V^a (ml; STP)	R^a	$v_0{}^a$ (cm^3/cm)
−195	$44._9$	146	$190._9$	0.23_5	0.91
−183	$38._9$	$85._8$	$124._7$	0.31_2	0.79
$-31._0$	$14._5$	$123._2$	$137._7$	0.10_5	0.29_3
$-19._2$	$13._8$	123	$136._8$	0.10_1	0.27_8
$-11._5$	$13._4$	121	$134._4$	0.099_6	0.27_1
$-1._0$	$12._9$	$115._6$	$128._5$	0.10	0.26
$11._5$	$12._3$	111	$123._3$	0.099_6	0.24_9
$22._7$	$11\ _8$	$107._4$	$119._2$	0.099_3	0.24

[a] Abbrev.: V_0, net volume of carrier gas involved in the column; v_0, that per unit column; $V - V_0$, amount of reversible adsorption per 14.5 g; V, retention volume; and R, equilibrium fraction of molecules in the mobile phase.

The plate height is calculated from peak width, t_w (min), and retention time, t_r (min), in place of W and V_R in Eq. (2).

Results

Two series of measurements for different amounts of catalyst, i.e., 14.5 and 6.6 g, were carried out for the plate height, H, varying the linear velocity of carrier gas at two temperature ranges, −195 to −183° and −30 to 20°C. Those peaks on the chromatogram obtained in these temperature ranges were mostly symmetrical in their shape. For some exceptional cases where asymmetric peaks were obtained, the ratio of back side width to fore side one of the peak was recorded, and are attached to the data as shown in Figs. 4 and 5. The results of the plate height measurement are shown in Table 2 for 14.5 g of catalyst at −19.2°C.

Third term in the right side of Eq. (11) can be determined from dependency of H on the linear velocity; however, as pointed out earlier, there is the possibility that the term is affected by the band-broadening due to diffusion through a pore structure of the adsorbent. In order to estimate the contribution from the diffusion process, the plate height of helium was measured with the carrier gas of hydrogen and is plotted against reciprocal linear velocity, u^{-1}, in Fig. 1. The plots are linear, indicating that the third term can be regarded zero for helium. Accordingly the band-broadening due to the diffusion can be excluded and the third term in the case of deuterium sample can be regarded soley due to the adsorption process.

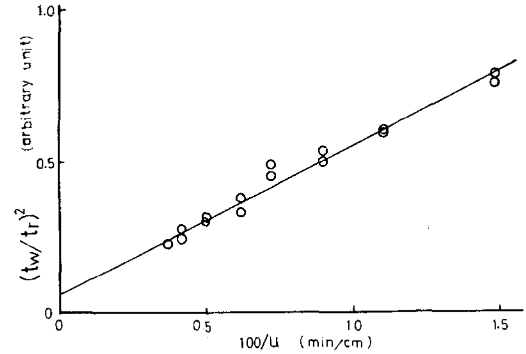

FIG. 1. The plate height of helium peak: column temp., −195°C; catalyst, 14.5 g.

The plate heights of deuterium are similarly plotted against u^{-1} in Figs. 2 and 3. As shown, the plots are curved in those

TABLE 2

LINEAR GAS VELOCITY AND PLATE HEIGHT AT −19.2°C, FOR 14.5 g OF CATALYST

u (cm/min)	t_w (min)	t_r (min)	H (cm)	$2\lambda dp$ (cm)	$\frac{2\gamma D_g}{u}$ (cm)	$2u(1-R)t_dR$ (cm)
$67._5$	0.97_1	7.2_2	0.88_9	0.03_5	0.71_9	0.14_2
	0.97_9	7.1_9	0.91_4	0.03_5	0.71_9	0.14_2
$90._6$	0.68_8	5.4_5	0.78_1	0.03_5	0.53_5	0.19_1
	0.66_8	5.4_3	0.75_6	0.03_5	0.53_5	0.19_1
$111._5$	0.53_6	4.4_6	0.70_9	0.03_5	0.43_5	0.23_5
	0.57_1	4.4_6	0.80_7	0.03_5	0.43_5	0.23_5
$138._9$	0.42_9	3.6_0	0.70_0	0.03_5	0.34_9	0.29_2
	0.42_3	3.5_8	0.68_6	0.03_5	0.34_9	0.29_2
$161._1$	0.36_2	3.0_8	0.68_4	0.03_5	0.30_1	0.33_9
$162._2$	0.36_8	3.0_6	0.71_4	0.03_5	0.29_9	0.34_2
$200._2$	0.30	2.4_9	0.72_5	0.03_5	0.24_2	0.42_1
$201._5$	0.30	2.4_5	0.72_5	0.03_5	0.24_1	0.42_4
238	0.25_6	2.0_8	0.75_3	0.03_5	0.20_4	0.50_1
241	0.24_8	2.0_4	0.73_4	0.03_5	0.20_1	0.50_7
272	0.22_5	1.7_9	0.78_1	0.03_5	0.17_8	0.57_3
273	0.23_3	1.7_8	0.78_1	0.03_5	0.17_7	0.57_5

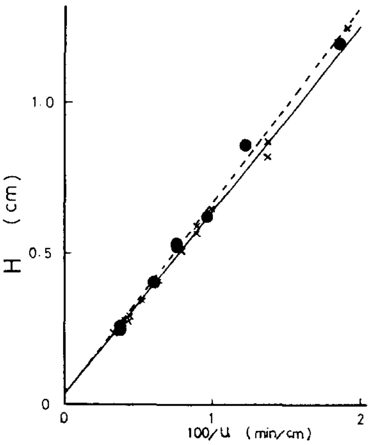

FIG. 2. The plate height of deuterium peak: catalyst, 14.5 g; ●, 22.7°C; ×, 11.5°C.

runs below 0°C, indicating an appreciable contribution of the third term, whereas straight lines are obtained in those runs at 11.5 and 22.7°C demonstrating that the rate of adsorption–desorption is fast enough to establish a dynamic equilibrium. This result again demonstrates that the value of *C* determined here is solely due to the adsorption process. Since the slopes of these straight lines are expressed by Eq. (5), the values of $2\gamma D_0$ can be obtained. The values of $2\lambda dp$ are also obtainable from the intercepts of the straight lines. Those values are tabulated as follows:

Temp. (°C)	Slope (cm²/min)	$2\gamma D_0$ (cm²/min)	Intercepts $= 2\lambda dp$ (cm)
11.5	$59._8$	$55._5$	0.03_5
22.7	63	$54._6$	0.03_5

For convenience of analysis of the results below 0°C, Eq. (11) may be rearranged to

$$H/u = 2\lambda dp/u + 2\gamma D_0(T/T_0)^{1.75}/u^2 + 2R(1-R)t_d, \tag{14}$$

where H/u is represented by an equation of second order in $1/u$. The third term on the right side of Eq. (14) may be obtained by an extrapolation of H/u to zero of $1/u$. H/u are plotted against $1/u$ on Figs. 4 and 5 for the series of 14.5 g of catalyst. However the extrapolation of H/u seems to be unreliable. Since those quantities other than $1/u$ and H/u are constant at a fixed temperature, Eq. (14) is rewritten as

$$H/u = L/u + M/u^2 + N. \tag{15}$$

These constants, *L*, *M*, and *N*, can be determined by the least square method. The best values thus obtained are as follows,

$2\lambda dp = 0.03_5$ cm
$2\gamma D_0 = 59._3$ cm²/min at −195 to −183°C
$55._3$ −30 to 0°C

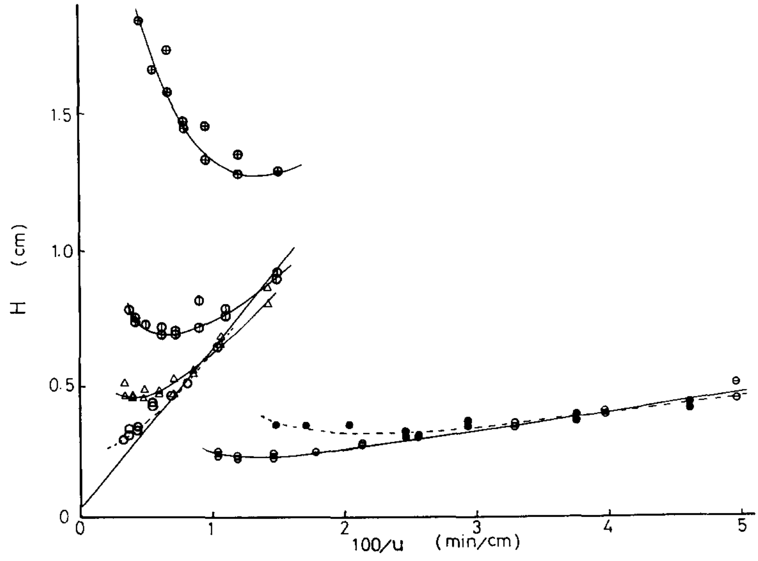

FIG. 3. The plate height of deuterium peak: catalyst, 14.5 g; straight line 11.5°C; ○, −1.0°C; △, −11.5°C; ⦶, −19.2°C; ⊕, −31.0°C; ●, −195°C; ⊖, −183°C.

TABLE 3

THE RATE CONSTANT OF ADSORPTION AND DESORPTION

Column temp. (°C)	$2R(1-R)t_d$ (×100) (min)	t_d (sec)	k_{21} (sec^{-1})	k_{12} (sec^{-1})	$n_a/2$ (mol cm^{-2})[b]	$k_{21}n_a/2$ (mol cm^{-2} sec^{-1})
−195	0.32_8	0.54_6	1.8_3	5.9_6	9.7 (× 10^{14})	1.8 × 10^{15}
−183	0.11_4	0.15_9	6.2_9	$14._9$	5.7	3.6
$-31._0$	0.87_3	2.8	0.35_7	3.2_2	8.2	0.29
$-19._2$	0.20_9	0.69_8	1.4_3	$13._0$	8.2	1.2
$-11._5$	0.08_2	0.29_7	3.3_6	$30._4$	8.0	2.7
$-1._0$	0.02_6	0.08_9	$11._3$	113	7.7	8.7
20			96[a]		7.2	68

[a] The value was derived from Fig. 5.

[b] mol = molecule(s).

giving an approximate value of 0.5 for γ by the calculated value of D_0 (=55.5 cm^2/min) from the literature (*5*). This is a reasonable value for γ. Above values of $2\lambda dp$ and $2\gamma D_0$ are in good agreement with those derived from the straight lines at 11.5 and 22.7°C in Fig. 2.

Such a consistency found in the observed value seems to allow the estimation of the kinetic mass transfer term, $2R(1-R)t_d$, by the above procedure. Thus the values of that term are obtained for each temperature and shown in the second column of Table 3. Those values together with the other constants obtained are used to reproduce the relation of Eq. (14) which is shown on Figs. 4 and 5 as smoothed curves (dotted and solid).

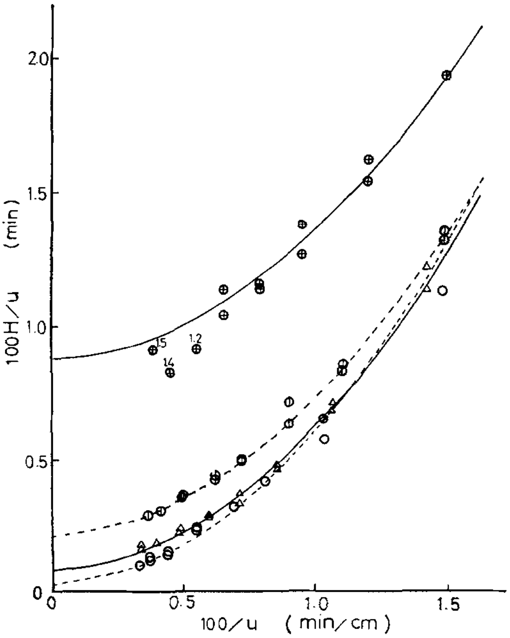

FIG. 4. The plots of H/u vs. reciprocal linear velocity: ○, −1.0°C; △, −11.5°C; ⦶, −19.2°C; ⊕, −31.0°C.

The values of t_d on the third column are obtained with the predetermined value of R (Table 1). The k_{12} and k_{21} are derived from

$$k_{21} = 1/t_d \qquad k_{12} = k_{21}(1-R)/R.$$

The rate of desorption which is equal to that of adsorption is obtained by multiplying k_{21} by $n_a/2$. The results are summarized in Table 3.

The magnitudes of the three terms are given in the last three columns of Table 2 for the sake of comparison with H. It was found that the sum of two terms, molecular and eddy diffusion in the gas phase, amounted to 24–84% of the plate height.

Activation Energy of Desorption

The rate of desorption is generally expressed in terms of surface coverage with a functional form depending on homogeneity of surface and kind of surface species. If Langmuir model is applied, the rate of desorption is given as follows: (a) undissociated adsorption

$$r = K(n_a/2)\exp(-E/RT),$$

(b) dissociated adsorption

$$r = K'(n_a/2)^2\exp(-E'/RT),$$

where K is a constant independent of tem-

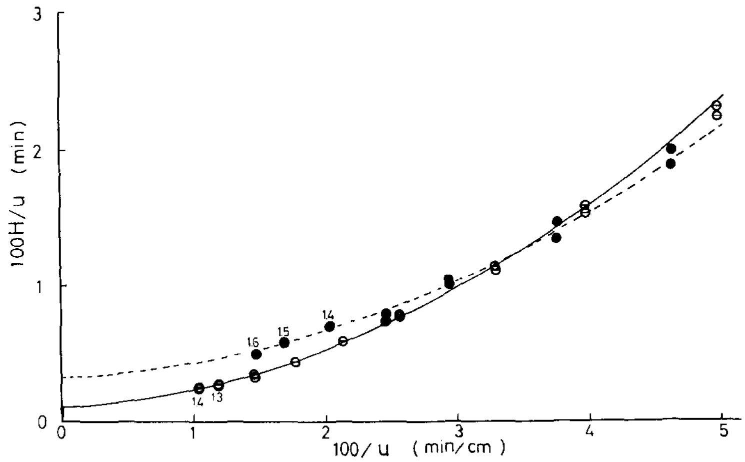

FIG. 5. The plots of H/u vs. reciprocal linear velocity: ●, −195°C; ⊖, −183°C.

perature and E the activation energy of desorption. As previously reported, the reversibly adsorbed hydrogen on the same nickel catalyst is evidentially undissociated at low temperature from —195 to −183°C, i.e., case (a), while dissociated at higher temperature from −30 to 60°C, i.e., case (b). Since r is given by $(\frac{1}{2})n_a k_{21}$, E and E' can be estimated from the Arrhenius plots of k_{21} and k_{21}/n_a, respectively. Those values of E and E' thus obtained from Fig. 6 are as follows (kcal/mole): low temperature range, 1.5, room temperature range, $16._4$.

A similar result obtained by the column of 6.6 g catalyst is also shown in Fig. 6. The results of the two series of experiments are in good agreement. This confirms the above mentioned values of activation energies for desorption.

The heat of adsorption of hydrogen on the same catalyst was separately measured and reported (*2*) already as follows (kcal/mole): low temperature range (−195 to −100°C), 1.7–2.8; room temperature range (−30 to 60°C), 12–15. Consequently the activation energy for adsorption is estimated to be nil for low temperature range and 1–4 kcal/mole for room temperature range.

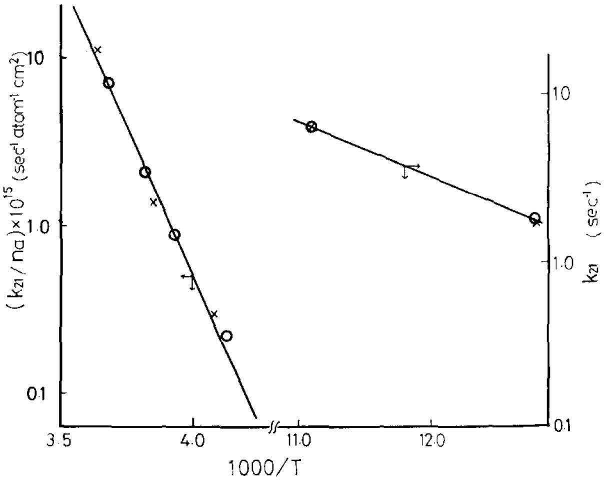

FIG. 6. Arrhenius plots of k_{21} or k_{21}/n_a: catalyst, ○, 14.5 g; and ×, 6.6 g.

Discussion

Applicability of the Gas Chromatographic Method of Adsorption Rate Measurement

There are two essential requirements for the experimental method presented above. First, the adsorption isotherm should be linear. Second, the adsorption process should be nearly in equilibrium. Otherwise the symmetric peak cannot be obtained. On the other hand, if the rate of desorption is too fast, the contribution of the mass transfer term would be too small to be measured, as observed in those runs above 0°C. The faster the rate of desorption, the higher the linear velocity of carrier gas should be, whereas the larger the pressure drop across the column would be. A too low linear velocity of carrier gas is also unfavorable because the gas-phase diffusion becomes large in the process as shown in Table 2. In conclusion the rate of desorption is measurable by this method at a selected temperature range, provided that a Gaussian chromatogram is available.

Relevance to Other Work

It has been known that there are two kinds of hydrogen adsorptions, fast and slow, on nickel at low temperature, while the rate data are meager. Gundry and Tompkins (*6*) at low temperatures, and Leibowitz *et al.* (*7*) at higher temperatures, studied the rate of adsorption applying the Elovich equation. An initial rate of adsorption may be estimated from their data as follows:

Catalyst	Temp. (°C)	Initial pressure, P_i (mm Hg)	Rate (mol/sec cm²)	Ref.
Wire	−195	5×10^{-3}	10^{15}	(*6*)
		760	10^{17}[a]	
Ni–kieselguhr	216	639	$10^{29} \sim 10^{32}$	(*7*)

[a] Estimated by a reported relation, rate $\propto P_i$.

The rate value at −195°C is 10^2 times as large as observed here and another one at 216°C is extraordinarily larger than expected from the present value of 10^{16} molecules sec^{-1} cm^{-2} at 0°C and 16 kcal/mole of the observed activation energy. These discrepancies must be, at least partially, due to difference in the surface coverage.

The rate of adsorption of hydrogen is closely related to the rates of isotopic exchange of hydrogen and of ortho–para conversion. It is known (*8*) that the parahydrogen conversion on nickel catalyst at low temperature is poisoned by a dissociatively adsorbed hydrogen. Emmett and Harkness (*8*) measured the rate of the conversion over a nickel catalyst after exposing to hydrogen at 300°C and obtained a value of 2.7×10^{-3} sec^{-1} at −190°C while the rate of reversible adsorption of hydrogen at −195°C observed here is 5.9 sec^{-1}, an about 10^3 times larger value. This is in agreement with the previous observation that the deuterium pulse eluted by carrier gas, hydrogen, from the nickel catalyst column retained unexchanged D_2 in spite of an appreciable retention by the catalyst column. These results show that the adsorption at low temperature does not necessarily result the parahydrogen conversion or the isotopic exchange and that the rate-determining step of those reactions is the surface reaction itself at this temperature.

On the other hand, at 20°C, the rate of parahydrogen conversion is estimated to be about 10^{16} molecules sec^{-1} cm^{-2} on a nickel wire (*9*) and on a nickel film (*10*) and the rate of the H_2–D_2 exchange reaction $10^{15} \sim 10^{17}$ molecules sec^{-1} cm^{-2} on a nickel–silica (*11*). These values are close to the rate of adsorption at 20°C given in Table 3. This indicates that the hydrogen adsorption at this temperature necessarily results in the isotopic exchange and the conversion, which is in agreement with the previously proposed view on the isobaric variation of deuterium retention with rising temperature.

It has been claimed by Horiuti (*12*) that the adsorption of hydrogen is the rate-determining step in ethylene hydrogenation over nickel at low temperature. In this respect it is interesting to compare the rate data of the hydrogenation with the adsorption. The rates of hydrogenation of ethyl-

TABLE 4

RATE OF ETHYLENE HYDROGENATION OVER NICKEL CATALYST

Form	Reaction temp. (°C)	Initial pressure (mm Hg)		Rate of reaction (mol sec^{-1} cm^{-2})	Ref.	Rate of adsorption (mol sec^{-1} cm^{-2})
		H_2	C_2H_4			
Film	0	50–25^0	50–250	1 ($\times 10^{16}$)	(*13*)	9×10^{15}
Wire	0	8	5.2	3	(*14*)	9×10^{15}
	20	32.5	21.5	5	(*15*)	7×10^{6}

ene over nickel film and wire are estimated from the literature and are tabulated in Table 4.

As described in the previous paper, the rate of ad- and desorption of hydrogen under the stationary condition seems to be insensitive to hydrogen pressure, because the amount of reversible adsorption of hydrogen was less dependent on the hydrogen pressure. Accordingly the above values of adsorption rate observed here under 1 atm may be not so different at low pressures adopted for the hydrogenation. Both rates of hydrogenation and adsorption appear to agree with each other.

According to Jenkins and Rideal (*16*), a large part of nickel surface is covered by ethylene during the hydrogenation. The rate of hydrogen adsorption on such a surface would be of the same magnitude as that on the hydrogen-covered surface which was observed in the present study. Thus the agreement of both rates mentioned above seems to be reasonable if the rate of hydrogenation is determined by the step of hydrogen adsorption.

Note added in proof. Recently, a study by G. Padberg and J. M. Smith on the chemisorption rate of hydrogen on nickel by means of gas chromatography appeared in this Journal **12**, 172 (1968). Although their method of analysis was different, these authors have concluded that the adsorption of hydrogen on nickel at around 0°C appears to be essentially nonactivated. It has been known, however, that the fast adsorption of hydrogen on nickel at —195°C is followed by slow and activated adsorption which is believed to be dissociative. The reversible adsorption observed at around 0°C in the present study seems to be identified as the slow adsorption at low temperature. The observed value of activation energy is reasonable.

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