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GAS CHROMATOGRAPHIC DETERMINATION OF ADSORPTION-DESORPTION RATES

INTERACTION OF HYDROGEN ON A NICKEL CATALYST

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SUMMARY

Under certain simplifying assumptions a simple mathematical model can be used to describe pulse broadening due to non-equilibrium chromatography. Neglecting diffusional effects and assuming linear rates of adsorption and desorption a system of partial differential equations was obtained and solved analytically. The solution, which is valid for any input pulse function, has been used to predict the effect of the rate parameters on the shape and position of the output pulse. Therefore, experimental curves can be compared with the model predictions in order to obtain the rate parameters. The chemisorption rates of hydrogen on a nickel catalyst were measured in the −30 to 25°C temperature range. The results are in good agreement with those obtained by the moments' equations and the plate height theory.

INTRODUCTION

· The development of gas–solid chromatography in its theoretical and practical aspects has led to new methods to evaluate physicochemical properties of solids, to measure transport of porous beds and to obtain kinetic data in heterogeneous catalysis. The relative simplicity of the experimental work in the chromatographic techniques contrasts with the difficulties faced in the interpretation of other experimental data, especially in those cases where the mathematical model takes into account the different physical and chemical processes that take place when a pulse of adsorbate or reactant passes through a porous bed.

One of the most general models, that of Kubin and Kucera[1-3], includes axial diffusion, external and internal diffusion resistances and finite rates of adsorption and desorption. The resulting system of partial differential equations cannot be solved analytically but a solution in the Laplace domain is possible. Since the inverse transformation is almost impossible to obtain, the chromatographic peaks are described by statistical moments.

Based upon this theory, Padberg and Smith[4] developed a method to determine rate constants and equilibrium parameters of hydrogen chemisorption on nickel. Experimentally they used the isotopic tracer technique first introduced by Ozaki et al.[5]. There are some inherent limitations in this method. First, second-order moments of the exit function must be calculated and this may lead to considerable error, especially when desorption is slow and pulse broadening is appreciable. Second, the moment expression as normally applied is valid for a delta input pulse which in practice is always a rough approximation.

Shigehara and Ozaki[6] have found comparable results using a different method of analysis and similar experimentation. They applied the plate height equation following the theoretical treatment for the C term as given by Giddings[7]. Here again the assumptions of a sharp input pulse and Gaussian elution peaks introduce a serious limitation for practical applications.

A different approach was taken by Villermaux[8], who treated the transient problem of pulse elution from a packed bed using concepts and theory of system dynamics. Each fundamental process taking place within the porous particles and those occurring in the interparticle space were described by linear relations and then characterized by a transfer function. The resulting expressions were then combined to obtain the transfer function for the whole column. In order to compare experimental data with the model predictions, a special numerical technique was use to obtain the inverse transform of the column transfer function, that is to relate the input and output concentrations. The author clearly demonstrated that the retention time of the peak maximum depends on the adsorption–desorption rates. An attractive feature in this approach is the possibility of dealing with the situation where the adsorption–desorption kinetics is complicated by the presence of different kinds of sites. If two kinds of sites are present a peak with two maxima may be expected. This theory was used to study the kinetics of H_2 adsorption on a Ni–Al_2O_3 catalyst. Here again the isotopic tracer method was applied.

The development of an alternative method to evaluate kinetic parameters without the above-mentioned difficulties appears as an attractive objective when we consider the importance of adsorption–desorption steps in heterogeneous catalysis.

It is always possible to reduce the mathematical treatment if we limit the generality of the Kubin and Kucera model. Assuming that pulse broadening due to axial diffusion is negligible compared with broadening produced by the adsorption–desorption processes, we obtain a simplified system of partial differential equations that may be solved analytically. The assumptions involved can be satisfied by proper selection of the experimental variables. The present approach leads to an equation that relates the adsorbate concentration at the bed exit with the kinetic parameters and the experimental variables. Therefore, it is possible to compare experimental and theoretical curves to obtain the parameters. In addition, one arrives at an equation which holds for input pulses of arbitrary shape. In this paper the solution for the simplified model is presented and its usefulness is demonstrated by studying the adsorption–desorption kinetics of hydrogen on a nickel catalyst.

Presentation and solution of equations
    The mass balance for a pulse of adsorbate passing through an isothermal and

isobaric bed in the plug-flow regime is given by the following set of partial differential equations:

$$\partial c/\partial t + u(\partial c/\partial z) + M(\partial q/\partial t) \div 0 \qquad (1)$$

$$\partial q/\partial t = k_1 c - k_2 q \qquad (2)$$

where c is the gas-phase concentration, q is the surface concentration, u is the carrier gas velocity and k_1 and k_2 are the adsorption and desorption rate constants, respectively. The constant M includes the bed porosity and the apparent density of the catalyst.

Diffusional effects in the interparticle space and in the pores have been neglected. This is an important requirement because mass-transfer resistance can seriously reduce the adsorption rate. In addition, the rate of adsorption is assumed to have a linear dependence on gas-phase concentration. Application of the isotopic tracer technique allows us to fulfil this requirement. A continuous flow of hydrogen was maintained over the catalyst and deuterium was used as a tracer. In this way a constant surface coverage was assured and the rate of chemisorption could be represented by a linear equation.

The proper initial and boundary conditions are:

$$c(z,0) = 0 \text{ and } c(0,t) = Q(t) \text{ for } t > 0$$

The Laplace transform of eqns. 1 and 2 permits one to obtain the following equation:

$$\ln \bar{c} = - (z/u) ((s^2 + Msk_1 \div sk_2) / (s \div k_2)) \div N$$

Applying the transformation to the initial condition, the constant N can be evaluated and the last equation rewritten as:

$$\bar{c} = \bar{Q} \times \exp(- z/u) ((s^2 + Msk_1 \div sk_2) / (s \div k_2)) \qquad (3)$$

In order to obtain the adsorbate concentration as a function of time, position and the model parameters, it is necessary to find the inverse transform of eqn. 3. Using some usual properties of Laplace transform and operating, one obtains:

$$c = \exp((z/u)(k_2 - k_1 M)) \times \int_{z/u}^{t} Q(t - v) \times \exp(-k_2 v) \times R \times$$

$$I_1(y) \, dv + \exp(-(z/u) k_1) \times Q(t - (z/u)) \qquad (4)$$

where

$$R = [(k_1 Mk_2 z) / (u(v - z/u))]^{1/2}; \quad y = 2 [(v - (z/u) \times (zk_1 Mk_2/u)]^{1/2}$$

and I_1 is a modified Bessel function of the first order.

Two important aspects may be emphasized in this result. First, the concentration function at the bed exit is determined only by typical experimental conditions, bed length and velocity, and two kinetic constants that depend on temperature. Thus, it is possible to compare directly experimental data with values calculated by means of eqn. 4 in order to evaluate the constants. Second, there is no restriction on the

input pulse function, the Dirac's delta being a special case. This generality is important because it allows us to include Gaussian input pulses that can be easily obtained experimentally. Another practical advantage of this feature is that we can use conveniently broadened input pulses in order to avoid sharp concentration gradients along the catalyst bed. Under this condition the assumption of negligible axial diffusion is more realistic.
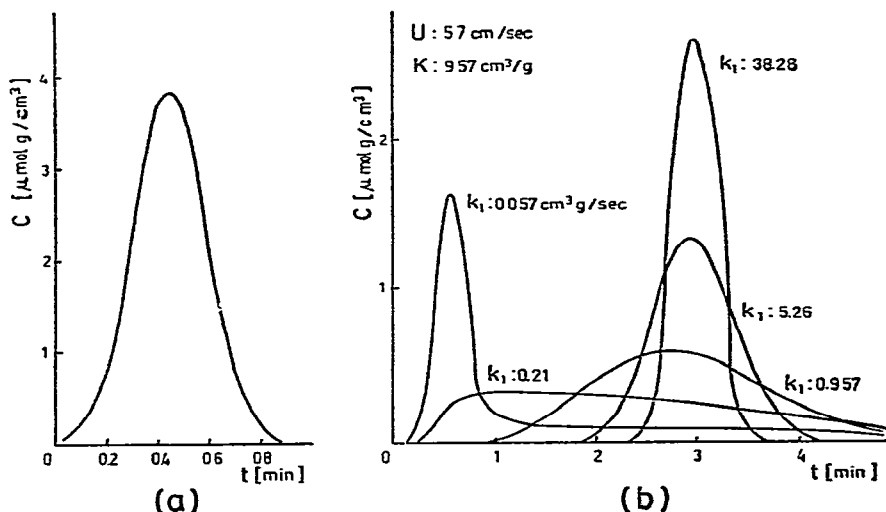

Fig. 1. Concentration *vs.* time curves predicted by model. (a) Gaussian input pulse function. (b) Effect of rate constants on retention time and pulse shape.

The exit pulse concentration for different values of the parameters and variables has been calculated by numerical integration of eqn. 4 and the results for a Gaussian input pulse are shown in Fig. 1. The kinetic parameters were modified, while bed length, gas velocity and the equilibrium constant were kept unaltered. It is observed that the maximum pulse concentration passes through a minimum and the corresponding elution time (called here the retention time) is shifted towards larger values as the rate constants are increased. For very small values of k_1 and k_2 the retention time is equal to z/u and the adsorbate behaves like an inert gas. When k_1 and k_2 increase at fixed K, the slow desorption process causes appreciable tailing although pulse migration through the bed is mainly determined by the carrier gas velocity. A further increase in the values of k_1 and k_2 leads to a situation where the curve becomes broader and the concentration reaches a minimum. From this point on, the high rates have the opposite effect on pulse shape. Fig. 1 shows that the curves become sharper and symmetric with a notable increase in retention time. Eventually, the adsorption–desorption processes reach equilibrium, pulse broadening becomes null and the retention time is given by the familiar formula of ideal chromatography.

$$t_R = (z/u) (1 + K')$$

This analysis shows the usefulness of eqn. 4 to predict the effect of non-equilibrium adsorption on the shape and position of chromatographic peaks. Similar curves were

obtained by Funk and Houghton[9] using a film model derived for gas–liquid chromatography. The effect of k_1 and k_2 on retention time is also in agreement with the conclusion of Villermaux[8].

The effect of linear gas velocity is also of some interest. The model predicts an increase of the pulse width to retention time ratio when the gas velocity increases while holding all other conditions constant. This behavior is consistent with the plate height theory.

EXPERIMENTAL

A commercial nickel catalyst (Girdler G-49B, United Catalyst, Louisville, KY, U.S.A.) was used. Some physical data are shown in Table I. The nickel surface area of the catalyst was estimated from hydrogen adsorption isotherms determined at room temperature in a conventional volumetric adsorption apparatus. The catalyst was previously reduced in flowing hydrogen at 350°C for 14 h and then evacuated at the same temperature for 8 h. The hydrogen uptake was found to depend strongly on the equilibrium pressure at room temperature, i.e., a net surface coverage was not observed. Consequently, the metal surface area has been estimated on the basis of the amount adsorbed at the operating pressure (1 atm).

TABLE I

CATALYST PROPERTIES

BET surface area	112 m²/g
Metal surface area	29 m²/g
Nickel content	48.1%
Apparent density	1.94 g/cm³
Solid density	4.07 g/cm³
Average radius of macropores	950 Å
Average radius of micropores	20 Å
Pore volume	0.268 cm³/g
Porosity due to micropores	22%
Total porosity	52%
Particle radius	0.23 mm (4.2 mm I.D. column)
	0.12 mm (3.0 mm I.D. column)

The metal content was determined by the dimethylglyoxime method. The solid and apparent densities were obtained by helium–mercury picnometry and the average pore radius of macropores was determined from the pore size distribution curve obtained in a mercury porosimeter. For micropores, a nitrogen adsorption isotherm at liquid nitrogen temperature was obtained and the data were processed by the method of Orr and Dalla Valle[10].

It is appropriate to compare the values of Table I with those reported by other workers for the same catalyst. Shigehara and Ozaki[6] reported a total surface area of 91 m²/g and a nickel surface area of 28 m²/g. These values are in good agreement with those obtained by us. Padberg and Smith[4] give a total surface area of 205 m²/g and a metal surface area of 48 m²/g. A two-fold increase in total area is observed and this difference cannot be explained.

Apparatus

The apparatus had the basic components of a conventional gas chromatograph. Deuterium pulses were introduced into a hydrogen stream by means of a six-port valve and then passed through a dispersion column where sufficient pulse broadening was permitted in order to obtain a nearly Gaussian input pulse. It was constructed with 6 mm I.D. copper tubing, 15 cm long and filled with the catalyst used in the main column. This catalyst bed (held at room temperature) allows the conversion of $^2H_2$ into H^2H, which simplified the gas-phase analysis. After the dispersion column the H^2H pulse passed through one side of a thermal conductivity cell in order to measure the input pulse shape and then entered the main column. This column was made of 3.0 or 4.2 mm I.D. Pyrex glass tubing and the column length was 38 cm or 35 cm, respectively, depending on the mass of catalyst to be used.

After passing through the column the hydrogen stream entered the other side of the cell where the output pulse shape was recorded. The flow-rate was measured at the outlet with a soap-film meter and the total pressure was measured with a Wallace & Tiernan (Belleville, NJ, U.S.A.) manometer. The pressure drop through the catalyst was negligible. A column packed with $FeCl_3$-coated alumina[11] and held at 77°K was used to verify that total conversion of $^2H_2$ into H^2H took place in the dispersion column. The hydrogen used as a carrier gas was obtained from a commercial cylinder and freed from oxygen by passing it over a suitable catalyst at 300°C followed by a molecular sieve drying trap. Deuterium gas supplied by Union Carbide (New York, NY, U.S.A.) and reported to be 98.5% pure was used as received.

Experimental technique

Depending on the column size the catalyst weight was 3.5 or 5.4 g. The sample was reduced in flowing hydrogen at 350°C for 14 h and then cooled slowly to the operating temperature. The catalyst in the dispersion column was reduced by the same procedure. Deuterium pulses were injected using a 0.5-cm^3 sample loop. Input and output pulses were recorded at various temperatures between −30 and 25°C. The carrier gas flow-rate was varied from 21 cm^3/min to 165 cm^3/min (measured at room conditions) as the temperature increased, in order to minimize the contribution of axial diffusion to pulse broadening.

Several experiments were made at a given temperature and flow-rate to verify pulse shape and retention time reproducibility. Some measurements were carried out using helium as a tracer. In this way the dead volume in the column and the contribution of axial diffusion to peak broadening were estimated (see Results section).

Treatment of data

Input pulses traced on a high-speed recorder showed a slight asymmetry and therefore it was not appropriate to describe them by a normal Gaussian distribution function. They were best correlated by a modified Gaussian function like

$$Q(t) = c_0 \{exp [-(G(t) - G(\xi))^2/2\sigma^2]\}$$

where c_0 is the maximum input pulse concentration. $G(t)$ is a simple function as t^n with mean and variance given by $G(\xi)$ and σ, respectively. This equation has only two adjustable parameters which can be easily estimated[12]. Replacing $Q(t)$ in eqn. (4)

an analytical expression for the output pulse concentration function was available. There was no great advantage treating the input pulse data in this way except for the simple convenience of reducing the amount of data to be fed into the computer. In order to fit the experimental data the proper values of k_1 and k_2 were obtained by a trial-and-error procedure. Some typical results are shown in Fig. 2.
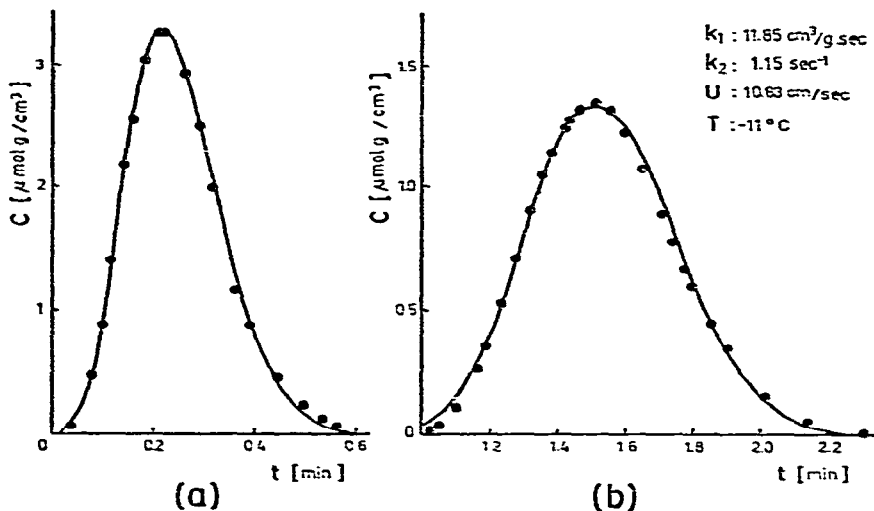

Fig. 2. Experimental data fitted by the proposed model. (a) Input pulse. (b) Output pulse.

RESULTS

The dead volume in the connecting lines and the dead volume in the column were estimated by measuring the retention time of a helium peak for both the packed and the empty column. In a typical case, at $-11°C$, with a flow-rate of 40.38 cm³/min, the retention times were 0.25 min (see Fig. 3) and 0.28 min, respectively. Therefore the dead volume in the column was $4.85 - ((0.28 - 0.25) \times 40.38) = 3.6$ cm³, where 4.85 cm³ was the volume of the empty column. For the connecting lines the dead volume was $(0.28 \times 40.38) - 4.85 = 6.5$ cm³. Similar measurements and calculations were performed at other conditions.

The low-temperature experiments (-21 and $-27°C$) were carried out with the 4.2 mm I.D. column using a relatively low gas velocity. At these temperatures pulse broadening was very appreciable, reflecting the influence of low adsorption-desorption rates. Non-adsorbable pulses showed that axial diffusion, although present, could be neglected. At higher temperatures and with the same gas velocity (10.8 cm/sec) the contribution of diffusion to pulse broadening becomes significant because of the higher rates. Fig. 3 (He peaks) clearly shows the effect of diffusion. Under these conditions an anomalous rate constant dependency on gas velocity was observed (see the values at $-11°C$ in Table II). In order to estimate to what extent the broadening of the H²H peaks was caused by diffusion they were compared with the helium peaks. For such a comparison an appropriate parameter was the time-
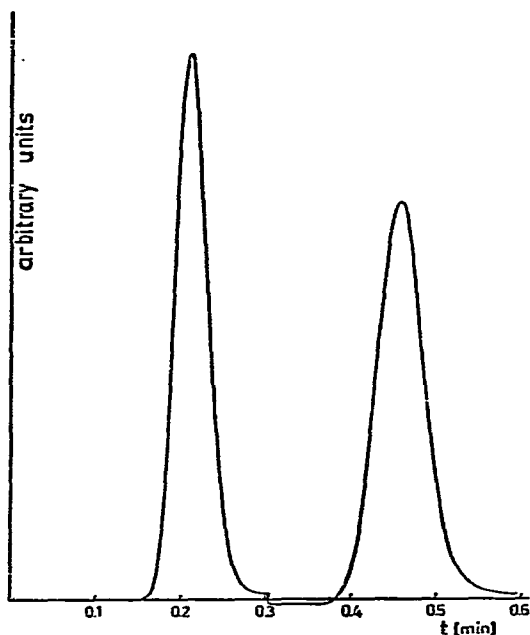
Fig. 3. Peak broadening due to gas-phase diffusion for the data in Fig. 2. Input and output helium pulses.

TABLE II

ADSORPTION–DESORPTION RATE CONSTANTS

T $(°C)$	u (cm/sec)	K (cm^3/g)	k_1 $(cm^3/g\ sec)$	k_2 (sec^{-1})	k_1 $(cm^3/g\ sec)$ [*]	k_2 (sec^{-1}) [**]
−27	4.8	8.6	3.05	0.36	2.85 (−30°C)	0.35 (−31°C)
−21	10.4	9.63	6.74	0.70	6.11 (−22.5°C)	1.4 (−19°C)
−11.7	10.8	10.28	11.85[***]	1.15[***]		
	38.1	9.94	17.79	1.79	14.54 (−15°C)	3.3 (−11°C)
−8.0	38.7	10.10	23.84	2.36	32.1 (−7.5°C)	
0.0	50.6	10.90	35.05	3.21	64.9	11 (−1°C)
	72.8	10.35	35.00	3.38		
21.5	54.5	9.95	109.5	11.00	244.2 (24°C)	
	79.3	10.02	109.3	10.90		

[*] From ref. 4.
[**] From ref. 6.
[***] Values affected by axial diffusion.

based variance σ^2 (an additive variable), which is equal to $t_w^2/16$ for a Gaussian peak. The pulse width, t_w, was taken as the baseline distance determined by the tangents to the sides of the peaks. From Figs. 2 and 3 we obtained $\Delta\sigma^2_{He} = 0.0005$ min^2 and $\Delta\sigma^2_{H^2H} = 0.036$ min^2. Thus the contribution of diffusion to peak broadening, $\Delta\sigma^2_{He}$, amounted to 1.5% of the total variance $\Delta\sigma^2_{H^2H}$ (12% if standard deviations are compared). It is clear that a large fraction of this dispersion has originated in the extracolumn volume, because the average time spent by the helium peak in the

column was $35/(10.8 \times 60) = 0.05$ min, which is much less than the total retention time for the helium peak (0.25 min). With a higher gas velocity, 38.1 cm/sec, diffusional effects were again minimized. In this case the variance σ^2_{He} for input and output pulses was about the same.

For the runs at 0 and 21°C a column with a smaller cross-sectional area and smaller particles ($d_p = 0.024$ cm) was used in order to increase the gas velocity while maintaining a reasonable flow-rate in the thermal conductivity detector.

Reasonably good reproducibility of results was observed for successive injections at a given temperature. However, the retention times of pulse maxima slowly increased after each reduction treatment at 350°C.

Finally, it must be pointed out that the slight asymmetry observed in the input pulses was still present after it passed through the catalyst bed. This indicated a symmetrical pulse broadening in accord with the model prediction. The rate constants estimated using the procedure given above are shown in Table II along with the results of other workers. Taking into account the total gas-phase concentration, and assuming a negligible isotope effect[13], the hydrogen desorption rates were calculated as a function of temperature. The Arrhenius plot shown in Fig. 4 predicts an activation energy of 14 kcal/g mol. This value is in agreement with the isosteric heat of adsorption at complete coverage reported by Schuit and Van Reijen[4] for a Ni–SiO$_2$ catalyst.
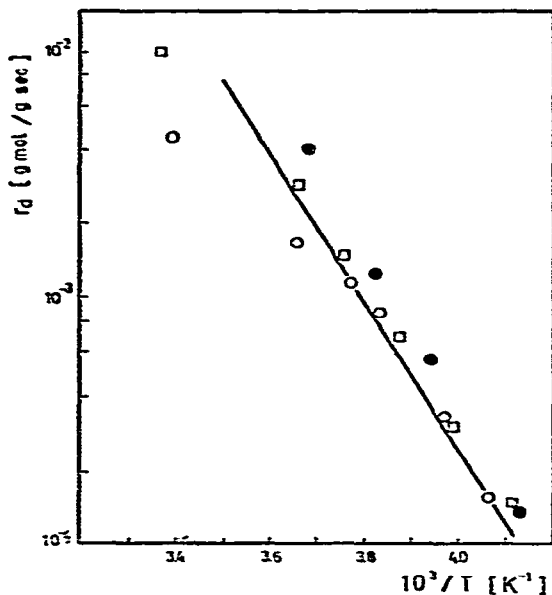

Fig. 4. Temperature dependence of desorption rates. □, From Padberg and Smith, ref. 4; ●, from Shigehara and Ozaki, ref. 6; ○, this work.

DISCUSSION

The main results of this work are compared with those obtained by Padberg and Smith[4] and Shigehara and Ozaki[6] in Table II using the moments' equations and

the plate height theory, respectively. Two temperature ranges can be established for the analysis. At low temperatures (-27 to $-8°C$) it is clear that the simplified model gives results similar to these of the more rigorous treatment of Kubin and Kucera. The agreement is certainly good, particularly if one takes into account the differences in the method used for the interpretation of the pulse experiments. It should be noted that there are also some differences in the experimental conditions. For example, at $-8°C$ we have used a gas velocity of 38.7 cm/sec with particles of 0.23 mm in radius. Padberg and Smith measured the moments of the chromatographic curves as a function of gas velocity for each temperature and particle size. They varied the carrier gas flow-rate by a factor of 4, between 5 and 20 cm/sec, and they were able to work with particles of 0.114 mm without having a significant pressure drop.

When our results are compared with those of Shigehara and Ozaki, important differences are observed as the temperature was increased. Only at $-27°C$, where adsorption–desorption predominates, are the results in good agreement. Since all their values for k_2 are higher than expected, it indicates that the plate height theory tends to overestimate the contribution of axial diffusion to pulse broadening. This situation probably arises because of the low gas velocities used in their experiments. It was estimated from their data at $-19°C$ and 4.5 cm/sec (maximum velocity) that the diffusion process amounted to 25% of the plate height. At $-1°C$ its incidence amounted to 60%. Consequently, the authors were only able to obtain the rates at temperatures below 0°C.

In the high-temperature range (0–21°C) our values differ substantially from those of Padberg and Smith. Because the rates were now near equilibrium, input and output pulses were not much different. Therefore, it was essential to reduce further the diffusional effects. As higher velocities were used the detector response fell sharply and consequently the chromatographic curves were measured with more error. Thus, in this range the model fails because it is not possible to find the proper experimentals conditions to satisfy the assumptions.

However, the discrepancy may be due to other factors. The Arrhenius plot of Fig. 4 exhibits a deviation which is typical of diffusional limitations. We have to consider the possibility of external and internal diffusion resistance. The first hypothesis can be neglected because it can be shown by calculation that a 100% increase in gas velocity leads to a 40% increase in the external mass transfer coefficient. Experiments carried out at 33 cm/sec and 67 cm/sec did not indicate any change in the rate constants. The incidence of internal diffusion is more likely because the catalyst had an appreciable microporosity and therefore concentration gradients within the pores may be present at high adsorption–desorption rates. In principle, this problem should be eliminated by using smaller particles ($d_p < 0.024$ cm) but in our case it tended to increase the pressure drop which in turn invalidates the constant-pressure assumption.

An order-of-magnitude analysis can be useful to assess the influence of internal diffusion resistance in our data. Using the information in Table I an effective intraparticle diffusivity, D_e, can be calculated by the random-pore model. At 0°C a value of 0.5×10^{-2} cm²/sec was obtained. The relation d_p^2/D_e allows an estimation of the mean diffusion time, which in this case ($d_p = 0.24$ cm) is equal to 10^{-2} sec. This value is of the same order of magnitude as the average time required for free molecules to adsorb; $V_d/(k_1 \times m) = 1.8/(35 \times 3.5) = 1.5 \times 10^{-2}$ sec. Based

on this result we may conclude that our high-temperature values are affected by mass-transfer resistance within the pores. However, it is important to notice that at lower temperatures, where the agreement between our values and those of Padberg and Smith was certainly good, similar considerations lead to the same conclusion as the decrease in k_1 is compensated by an increase in particle size ($d_p = 0.046$ cm). In fact Padberg and Smith were able to show experimentally (by changing the particle size) that intraparticle diffusion was very small at all temperatures. However, it is seen in Fig. 4 that their data at room temperature do not correlate well with the points at low temperature. Therefore, we conclude that the deviation of our data at 0 and 21 °C may be partially due to internal diffusive resistance, but mainly reflects the fact that pulse broadening was detected with a large experimental error.

An attempt was made to compare our rate constants with those obtained by Villermaux[8] for a Ni–Al$_2$O$_3$ catalyst, but it was unsuccessful for two reasons. First the experiments were carried out at higher temperatures (21–100°C) than those used here. Second the catalyst surface apparently was not fully reduced (pretreatment conditions were not given) as NiO sites are considered to be active, along with Ni sites, in the adsorption–desorption process. The equilibrium constant at room temperature was much lower than that reported here (0.6 cm^3/g) and the adsorption rate constant at 50°C was an order of magnitude smaller than our value at 21°C. At higher temperature (78°C) considerable pulse broadening was observed and this was ascribed to an increasing participation of NiO sites in the rates. In fact we have performed a few experiments at > 21°C and an increase in retention time with increasing temperature was noticed. This behavior, however, is more likely to be associated with a new exchange mechanism involving water adsorbed on the catalyst surface[15]. With a very dry hydrogen stream (< 10 ppm) the retention time was found to decrease as temperature increased and peak broadening or tailing were not observed.

One apparent anomaly of our data is the temperature dependency of the equilibrium constant. As the concentration in the gas phase decreases slowly as temperature increases, then, since K increases, the concentration in the surface tends to increase and this is not reasonable. Equilibrium constants, as determined by Padberg and Smith, do not vary over the whole temperature range and do agree with our value at 0°C. Shigehara and Ozaki have obtained values that decrease slightly with temperature. As mentioned before, we have observed an increase in deuterium retention time after each reduction cycle. Therefore, the anomalous trend of our data actually reflects the order in which the experiments were performed. This change in retention time may be due to the formation of new centres for hydrogen adsorption as a result of metal sintering. However, we did not observe variation in metal surface area in samples that were reduced at 350°C several times. Specific experiments designed to investigate the existence of different kinds of sites were not performed.

The results presented here clearly demonstrate the usefulness of our mathematical model for the determination of adsorption–desorption kinetics. We have been able to remove one standard assumption regarding input pulse shape and to obtain an equation that allows a straight fitting of experimental data. Compared with the existing model the new one requires less experimental data and has the advantage of reduced computational work. One difficulty encountered in practical applications is the proper selection of the experimental conditions that could satisfy the simplifying

assumptions. It has been shown above that they cannot be independently selected.

Finally, it is important to state that a solution similar to eqn. 4 can be obtained when a first-order reaction term is included in the model. In principle, this result should allow us to determine simultaneously adsorption and surface reaction rate constants.

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NOTATIONS

c gas-phase concentration of tracer
c_0 maximum input pulse concentration
d_p particle diameter
D_e effective intraparticle diffusivity
k_1 adsorption rate constant
k_2 desorption rate constant
K adsorption equilibrium constant
K' retention constant
m mass of catalyst
$Q(t)$ input pulse function
q concentration of adsorbed tracer
r_d desorption rate
t time
t_R retention time
t_w pulse width
T temperature
u carrier gas velocity
v convolution variable
V_d column dead volume
z bed length
σ variance

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