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The Effect of Back-Diffusion upon Rate Constant Determinations

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The effect of back-diffusion upon rate constant determinations has been illustrated by performing measurements at different flow rates for the deuterium exchange reaction between hydrogen and water on a nickel-chromia catalyst. The effect consists in yielding lower "apparent" values of the rate constants and is to be related to the magnitude of a "diffusion parameter." The flow rate dependence of the experimental rate constants could be explained within a standard error of 4% by diffusion effects for values of the diffusion parameter lying between 0.001 and 1.50.

In a former investigation of the activity of nickel-chromia catalyst for the deuterium exchange reaction between hydrogen and water vapor in the temperature range 50–150°C, deviations were found from the Arrhenius law (*1*). These deviations are expressed by the fact that at higher tempertures the measured activities remain below the values expected by extrapolation of the Arrhenius straight line obtained at lower temperatures as shown in Fig. 1. This behavior has then been attributed to an internal diffusion effect, but in order to account for the data unexpectedly low values of the effective diffusion coefficients in the catalyst grains (0.1–0.4% of the values corresponding to the free space) had to be assumed.

These deviations from the Arrhenius law could also be explained by remixing due to diffusion along the direction of flow (back-diffusion). This hypothesis is supported also by the fact that the deviations are more important at higher partial pressures of hydrogen, i.e., at higher values of the diffusion coefficients in the mixture. In the present work we tried to prove that the back-diffusion is responsible for the deviation reported above.

The theoretical treatment (*2*) of simultaneous flow, diffusion in the flow direction, and bimolecular isotopic exchange reaction in the range of small isotopic abundances, follows in the main way the treatment described by Noller, Andréu, and Schwab (*3*). It has been obtained that the mole fraction of the rare isotope in hydrogen is given, in the catalyst layer ($0 \leq \xi \leq \xi_1$) by

$$n_{\mathrm{II}} = n_e + (n_0 - n_e)[A \exp(r_1\xi) + B \exp(r_2\xi) + C \exp(r_3\xi)] \quad (1)$$

before the active zone ($\xi \leq 0$) by

$$n_{\mathrm{I}} = n_0 + (n_0 - n_e)(A + B + C - 1) \exp(r_4\xi) \quad (2)$$

and remains constant behind it ($\xi \geq \xi_1$).

$$n_{\mathrm{III}} = n_1 \quad (3)$$

The length coordinate x has been replaced by the dimensionless length ξ

$$\xi = (\alpha + \gamma)kv_1x/V \quad (4)$$

with the origin taken at the entrance in the catalyst bed and with X, respectively ξ_1, representing the length of the active zone.

In the former equations $n_e = (\gamma n_0 + N_0)/(\alpha + \gamma)$ is the equilibrium value, n_0 and N_0 are initial values ($\xi = -\infty$) in hydrogen and water vapor, respectively, and n_1 is the exit value of the mole fraction after the isotopic exchange has taken place. In Eq. (4) α is the isotopic equilibrium constant; γ, the ratio of molar flow rates of hydrogen to water vapor; k (mole/cc sec) is the rate constant; v_1, the

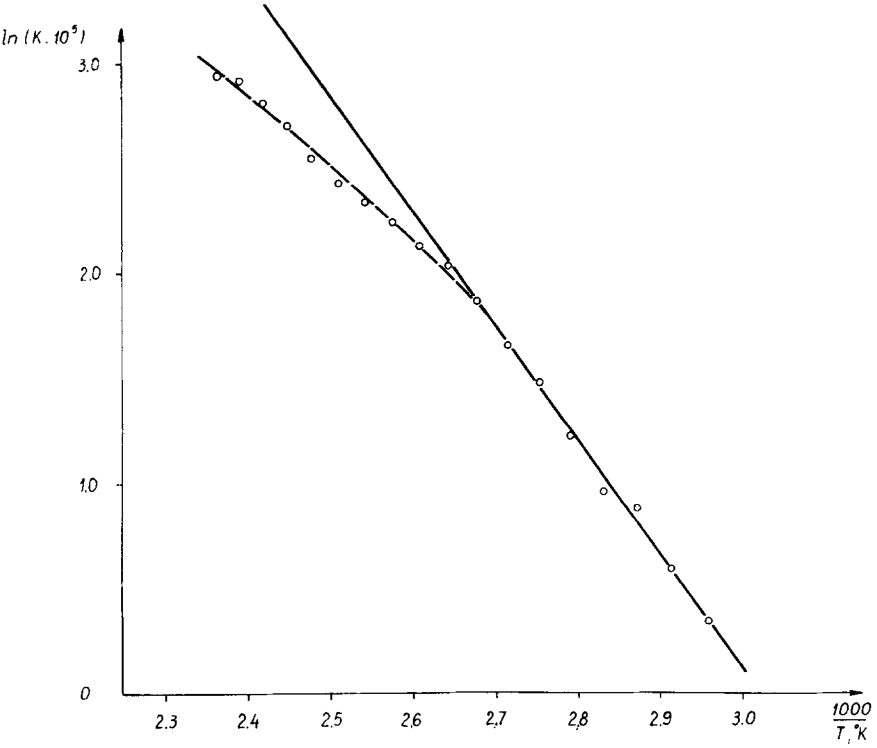

FIG. 1. Arrhenius plot for 5 l/hr, from ref. (*1*).

molar volume of hydrogen; and V (cm/sec), the mean linear speed of flow in the packed bed based on an empty tube. The characteristic equation for the roots r_1, r_2, and r_3 is

$$a\epsilon^2 r^3 - b\epsilon r^2 + (1 - c\epsilon)r + 1 = 0 \quad (5)$$

$$r_4\xi = Vx/D_n$$

The integration constants A, B, C, can be obtained by solving the simultaneous equations

$$\begin{aligned}(r_1 - \eta)A + (r_2 - \eta)B + (r_3 - \eta)C &= -\eta \\ r_1A\exp(r_1\xi_1) + r_2B\exp(r_2\xi_1) + r_3C\exp(r_3\xi_1) &= 0 \\ (r_1^2 - \eta)A\exp(r_1\xi_1) + (r_2^2 - \eta)B\exp(r_2\xi_1) + (r_3^2 - \eta)C\exp(r_3\xi_1) &= 0\end{aligned} \quad (7)$$

where

$$a = \delta(\alpha + \gamma)^2;\ b = (\alpha + \gamma)(1 + \delta);$$

$$c = \gamma + \alpha\delta;\ \delta = \frac{D_N}{D_n}$$

D_N and D_n are the diffusion coefficients in free space for HDO and HD, respectively, in the mixture of H_2O and H_2, and is the

$$\epsilon = kfD_nv_1/V^2 \quad (6)$$

diffusion parameter, with f defined as the ratio of effective diffusion coefficients in the catalyst bed to diffusion coefficients in free space. The product $r_4\xi$ is given by

with $\eta = 1/\epsilon(\alpha+\gamma)$.

By solving Eqs. (5) and (7) for a given set of physical parameters one obtains from Eq. (1) the exit mole fraction $n_1 = n_{\mathrm{II}}(\xi_1)$. Then, it is possible to obtain the conversion ratio

$$\frac{n_1 - n_e}{n_0 - n_e} = A\exp(r_1\xi_1) + B\exp(r_2\xi_1) + C\exp(r_3\xi_1) \quad (8)$$

and to predict an apparent value for the rate constant

$$k_a = \frac{V}{(\alpha + \gamma)v_1 X} \ln\left(\frac{n_0 - n_e}{n_1 - n_e}\right) = \frac{G}{(\alpha + \gamma)W} \ln\left(\frac{n_0 - n_e}{n_1 - n_e}\right) \quad (9)$$

where G is the molar flow rate of hydrogen and W is the volume of the catalyst bed. This apparent value k_a is expected to be lower than the real value k, the lowering being more important at higher values of the diffusion parameter ϵ, that is for lower flow rates and higher temperatures.

In the former measurements (*1*) the hydrogen flow rate has been limited up to about 5 l/hr by the appearance of catalyst fluidization. For the run presented in Fig. 1 of the previous paper (*1*), this resulted in ϵ values of the order of 0.01–0.02 at lower temperatures and 0.10–0.20 at higher temperatures and that would affect the apparent values of the rate constant by about 3–6% and 15–25%, respectively. In fact, the deviations observed are of this order of magnitude.

In order to decide between internal and back-diffusion, measurements have been performed at different flow rates of hydrogen, because the effect of back-diffusion is changed by the flow rate while that of internal diffusion is not. A catalyst sample of nickel-chromia with 85 atomic % nickel of about the same activity as used earlier (*1*) has been chosen. In order to cover the most interesting range of values for the diffusion parameter ϵ, operation at higher flow rates has also been necessary. Catalyst fluidization has been avoided by downward flowing of the reagent mixture through the catalyst bed. The procedure described in another paper (*4*) has been used with the modified reactor shown in Fig. 2. The hydrogen flow was saturated at 63.5°C by bubbling through water with 5.22 atomic % deuterium. The saturation degree was tested by measuring the equilibrium value n_e of the deuterium mole fraction in hydrogen at different flow rates. The measurement of saturation was performed at 63.5° and 154°C in the saturator and catalytic cell, respectively, using 2 g of a catalyst sample of high activity (*4*). By increasing the hydrogen flow rate from 2 to 30 l/hr only a slight change, about 2%, of the equilibrium value n_e was observed. A preheating coil was placed between the saturator and the catalytic cell in the vapor jacket of the catalytic cell. The coil was very outsized in order to ensure the preheating of the mixture at flow rates about ten times the maximum flow rate used.

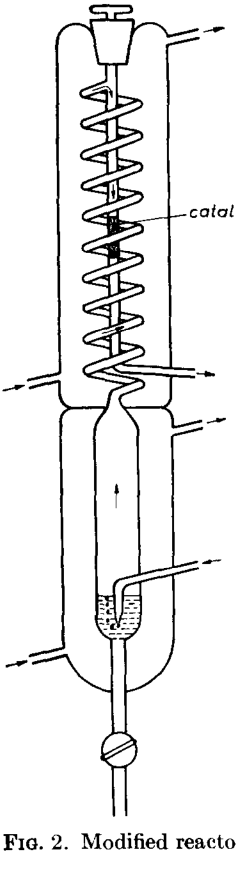

FIG. 2. Modified reactor.

The kinetic measurements were performed for six values of flow rate from 2 to 30 l/hr and for five values of temperature between 79° and 154°C. The same catalyst sample, 0.1 g, with grain size 0.2–0.3 mm, was used for all the measurements. The dimensions of the catalyst bed were 0.62 cm in diameter and 0.31 cm in height. Each series of runs at a given temperature and different flow rates was preceded by a reactivation, as described in a previous paper (*4*). The mean reproducibility of rate constants is about 5%. This figure may be higher under extreme conditions (high temperatures at low flow rates and low temperatures at high flow rates yielded values of about 95% and 5%, respectively, for the conversion ratio n/n_e), while under intermediate conditions the reproducibility can be better.

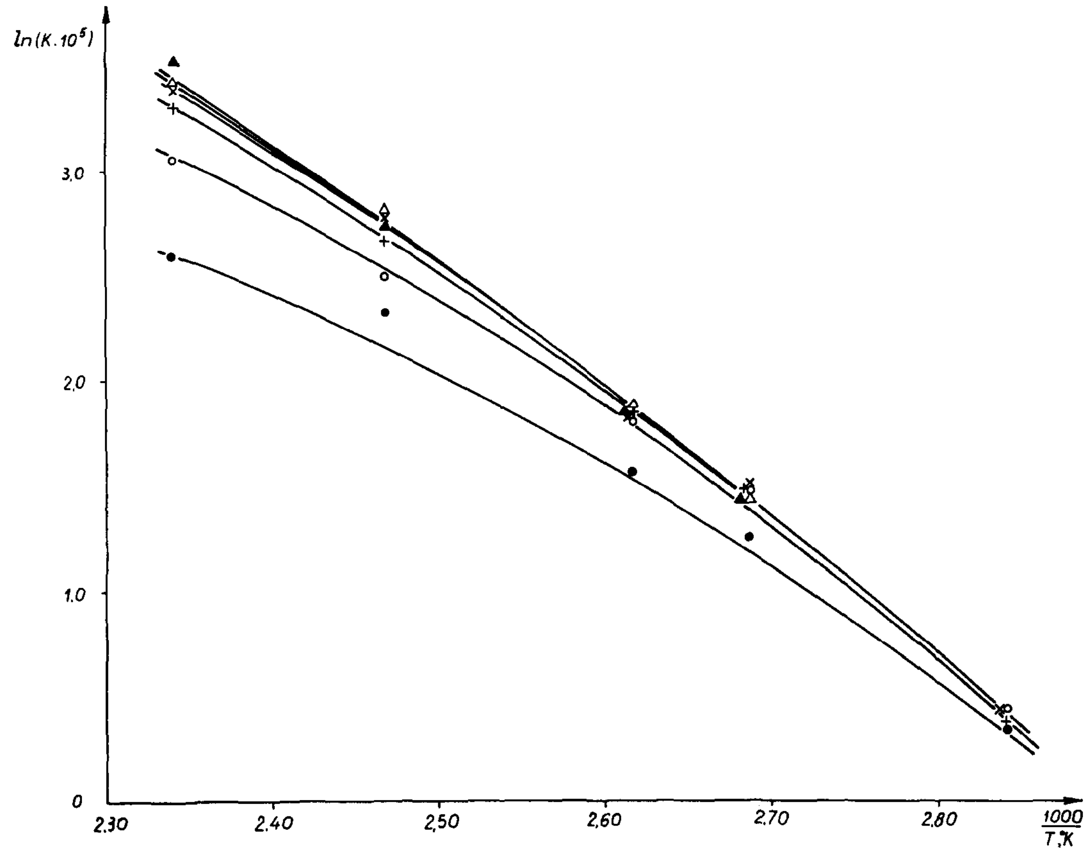

FIG. 3. Arrhenius plot of the apparent rate constant k_a for different flow rates of hydrogen (liters/hour at room temperature): ●, 2 l/hr; ○, 5 l/hr; +, 10 l/hr; ×, 15 l/hr; △, 20 l/hr; ▲, 30 l/hr. The continuous lines represent calculated values of the apparent rate constant k_a.

The Arrhenius plot of the values obtained is given in Fig. 3. The data, expressed in mole/g sec units to avoid density uncertainties ($\rho = 1.07$ g/cc), show the same deviations from the straight line. For 5 l/hr the behavior is the same as in the earlier data. As expected, the lowering of rate constants is more important at lower flow rates and higher temperatures so that it can be attributed to back-diffusion rather than to internal diffusion.

In order to compare at a given temperature the observed dependence of the rate constant k_a on flow rate to the theoretical prediction described above, effective diffusivities in the given catalyst are needed. Theoretical prediction of binary molecular diffusion coefficients in free space (*7*) have been used to obtain equivalent diffusion coefficients of small amounts of HD and HDO in the H_2 and H_2O mixture (*8*). Axial dispersion due to the flow pattern (*9–11*) has not been taken into account because under our experimental conditions axial dispersion added to molecular diffusivity does not alter by more than about 1% the calculated rate constant values based on molecular diffusivity alone. This is to be explained by the fact that at small flow rates the axial dispersion term is small compared to the molecular diffusivity (2% at 2 l/hr and 6% at 5 l/hr), whereas at our highest flow rate [30 l/hr, Re = 0.47 based on effective diameter (*10*)], where the axial dispersion term rises to about 35% of the molecular diffusivity, the overall effect upon the apparent rate constant value is small. As we did not know the f value for our sample we proceeded by interation, adjusting the two unknown parameters k and f to obtain the best fit, for the highest temperature $T = 154$°C, which showed the largest effect.

TABLE 1

THE RATE CONSTANTS AT DIFFERENT TEMPERATURES AND FLOW RATES

T (°C)	Rate constant type[a]	G(l/hr) 2	5	10	15	20	30	$k \times 10^5$
79°	a	1.39	1.53	1.45	1.56	—	—	1.54
	b	1.38	1.48	1.52	1.53	—	—	
	c	+0.7	+3.4	−4.6	+2.0	—	—	
99°	a	3.53	4.40	4.40	4.47	4.28	4.28	4.50
	b	3.42	4.14	4.41	4.46	4.48	4.49	
	c	+3.2	+6.3	−0.2	+0.2	−4.4	−4.7	
109°	a	4.85	6.02	6.33	6.15	6.53	6.33	6.44
	b	4.52	5.73	6.16	6.32	6.37	6.41	
	c	+7.3	+5.1	+2.8	−2.7	+2.5	−1.2	
132°	a	10.3	12.2	14.5	16.1	16.8	15.9	16.4
	b	8.7	12.9	15.0	15.6	16.0	16.2	
	c	+18.4	−5.4	−3.3	+3.3	+5.0	−1.9	
154°	a	13.4	21.2	27.3	30.0	30.6	33.9	32.2
	b	13.5	22.0	27.5	29.7	30.6	31.4	
	c	−0.7	−3.6	−0.7	+1.0	0.0	+8.0	

[a] a, experimental values of $k_a \times 10^5$, mole/g sec; b, calculated values of $k_a \times 10^5$, mole/g sec; c, relative deviations $(k_{a,\mathrm{exptl}} - k_{a,\mathrm{calc}})/k_{a,\mathrm{calc}}$, %.

Care must be taken to use in Eqs. (4) and (6) rate constant values converted to mole/cc sec units. The best fit yielded the values $k = 32.2 \times 10^{-5}$ mole/g sec and $f = 0.62$. This f value has been maintained and used in the calculation of k_a values at the other temperatures, by adjusting only one parameter (k). The calculated data of k_a, mole/g sec, are listed together with the experimental data, the relative deviations, and the real values k in Table 1. The point $T = 132$°C, $G = 2$ l/hr, exhibits a deviation 3.5 times the standard error (5.2%) and can therefore be excluded. The other points show a standard error of 3.9%, so that the dependence of the apparent rate constant on flow rate is explained by back-diffusion within the experimental errors. The f value obtained seems to be plausible for an overall porosity of about 88% (*5*, *6*), as for our catalyst sample.

The real rate constants k obtained enable an Arrhenius plot free of back-diffusion effects. In our case the five points scatter from the straight line with a standard deviation of 6%.

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