JOURNAL OF CATALYSIS 36, 262-265 (1975)

Kinetics of Chemisorption: An Examination of the Elovich Equation

N. H. TURNER

Chemistry Division, Naval Research Laboratory, Washington, D. C. 20375

Received April 30, 1974

For many years the interpretation of the rate of chemisorption of a gas by a solid in numerous instances has been with the Elovich equation. The equation has been suggested as the best available procedure for describing the kinetics of chemisorption (*1,2*), however, others (*3,4*) have been critical of its use. The differential form of the Elovich equation is

$$dq/dt = ae^{-bq}, \qquad (1)$$

where q is the quantity of gas adsorbed, a and b are constants, and t is the time. Integration of Eq. (1) (when $q = 0$ at $t = 0$) gives

$$q = (2.3/b) \log (t + t_0) - (2.3/b) \log (t_0), \qquad (2)$$

where $t_0 = 1/ab$, and when $t >> t_0$ a plot of q vs log t is linear. Nonlinear behavior has been found in many systems and several explanations have been advanced: (a) an empirical value of t_0 has been chosen to linearize a q vs log $(t + t_0)$ plot (*5*), (b) small linear segments with different values of a and b (*1,6*), (c) a quantity of gas, q_0, that has been adsorbed "instantaneously," i.e., at $t = 0$ (*1*), and Eq. (2) becomes

$$q = (2.3/b) \log (t + k) - (2.3/b) \log t_0, \qquad (3)$$

where $k = t_0 \exp (bq_0)$.

In many systems where the Elovich equation has been used usually the entire extent of the reaction has not been observed in a single experiment (*1*). This has also been true if the coverage, θ, has been plotted instead of the amount of gas adsorbed vs log t. This, and other factors, have made it difficult to employ the concepts of standard chemical kinetics in chemisorption kinetics problems. Recently, however, Lopez-Sancho and deSegovia (*7*) have studied the kinetics of adsorption of oxygen on polycrystalline tungsten for coverages from zero to one.

In Fig. 1 are shown some of their results and one observation can easily be made. The reduction of the pressure by a factor of ten causes a shift to the right of the curve on the abscissa by a factor of ten. This suggests that in the first rate determining step the disappearance of oxygen is first order (*8*), and that the amount of gas introduced is much greater than could be adsorbed by the tungsten. It is also interesting to note that the shape of the curve is similar to that suggested by Low (*1*) to describe, in a general manner, the kinetics of chemisorption over a wide range of conditions. The following mechanism for the surface species was found to agree with the experimental data, and is given in general terms,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2A', \qquad (4a)$$

$$A' \xrightarrow{k_3} B, \qquad (4b)$$

$$B \xrightarrow{k_4} C, \qquad (4c)$$

with the following equations describing the appearance and disappearance of reac-

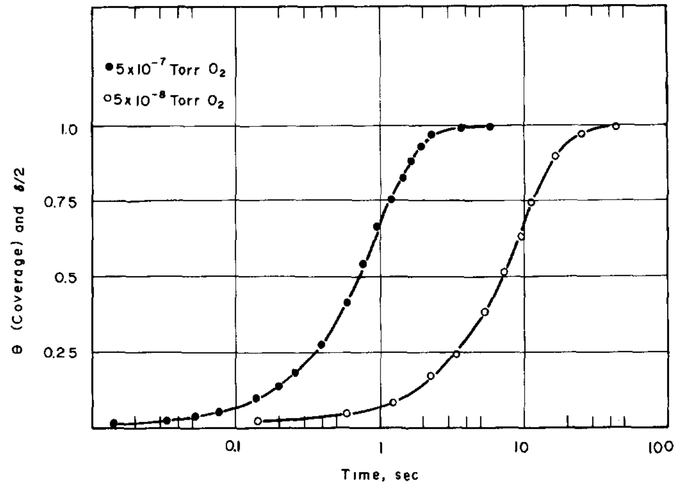

FIG. 1. Plot of coverage, θ, and $\delta/2$ vs log t for the adsorption of O_2 on polycrystalline tungsten from the data of Lopez-Sancho and deSegovia. The closed circles are at an O_2 pressure of 5×10^{-7} Torr and the open circles are at 5×10^{-8} Torr. The theoretical curves are discussed in the text.

tants:

$$dA/dt = -k_3(k_1A/k_2)^{1/2}, \qquad (5a)$$

$$dB/dt = k_3(k_1A/k_2)^{1/2} - k_4B, \qquad (5b)$$

$$dC/dt = k_4B. \qquad (5c)$$

A rapid equilibrium between A and A' and the steady-state approximation for A' with $k_2 > k_3$ have been assumed.

Equations (5a)-(5c) are only valid at times when A is greater than zero. Component B will disappear in a simple first order manner after the value of A is zero, i.e., the first term in the right-hand side of Eq. (5b) is zero. The solutions to Eq. (5) with the boundary conditions noted above are (after conversion to dimensionless variables)

$$\alpha = (1 - \tfrac{1}{2}\tau)^2, \qquad (6a)$$

$$\beta = [\zeta(2 - \tau) + 1 - e^{-\zeta\tau}(2\zeta + 1)]/2\zeta^2, \qquad (6b)$$

$$\gamma = 1 - \alpha - \beta, \qquad (6c)$$

with $\alpha = A/A_0$, $\beta = B/A_0$, $\gamma = C/A_0$, $\zeta = k_4(k_2A_0/k_1)^{1/2}/k_3$ and $\tau = k_3t(k_1/k_2A_0)^{1/2}$, A_0 is amount of A at $t = 0$, and it has been assumed at $t = 0$ that $B = C = 0$. $\delta = \beta + 2\gamma$ and is defined as the extent of reaction; δ ranges in value from 0 to 2 (*9*). A plot of $\delta/2$ (curve) and θ (solid circles) vs log time is shown in Fig. 1 for an oxygen pressure of 5×10^{-7} Torr for the results of Lopez-Sancho and deSegovia. For this curve A_0 and $k_3(k_1/k_2)^{1/2}$ are set equal to 1.0 and the value of k_4 is 1.25. The curve is displaced so that it coincides with the experimental points by noting that log $\tau =$ log t + log $k_3(k_1/k_2A_0)^{1/2}$, and the data fall close to the theoretical curve over the entire extent of the reaction. Similar procedures are used for the results of an oxygen pressure at 5×10^{-8} Torr.

From this analysis a mechanism can be suggested and rate constants evaluated. From Fig. 1 for an oxygen pressure of 5×10^{-7} Torr the value of $k_3(k_1/k_2A_0)^{1/2}$ has been found to be 1.25 s^{-1}, and A_0 has been determined by Lopez-Sancho and deSegovia to be 4×10^{14} atoms/cm^2. The following mechanism is consistent with the preceding analysis:

$$W_2 \xrightleftharpoons[k_2]{k_1'} 2W, \qquad (7a)$$

$$\mathrm{W} + \mathrm{O_2} \xrightarrow{k_3'} \mathrm{WO} + \mathrm{O}, \qquad (7b)$$

$$\mathrm{WO} + \mathrm{O_2} \xrightarrow{k_4'} \mathrm{WO_2} + \mathrm{O}, \qquad (7c)$$

$$\mathrm{O} + \mathrm{O} \longrightarrow \mathrm{O_2}. \qquad (7d)$$

Since the amount of O_2 is much larger than W, $k_3'(k_1'/k_2')^{1/2}\ [O_2] \cong k_3(k_1/k_2)^{1/2}$ and $k_4'[O_2] \cong k_4$, then $k_3'(k_1'/k_2')^{1/2} \sim 7.8 \times 10^{-4}$ cm/s atom$^{1/2}$ and $k_4' \sim 9.7 \times 10^{-11}$ cm^3/s atom.

In the example above the available surface limited the amount of reaction; in many other systems that have been investigated the quantity of gas introduced has been much less than could have been adsorbed. For such systems where the disappearance of gas has been observed the following equations (assuming simple kinetic behavior with respect to the gas) have been derived following earlier procedures (*8*)

$$\begin{aligned} q_r &= 1 - \frac{n_g}{n_{g_0}} \\ &= 1 - [1 + (\mathrm{n} - 1)\, k n_{g_0} t]^{1/(1-n)}, \qquad (8) \end{aligned}$$

when $n \neq 1$, and

$$q_r = 1 - \exp\,(-k n_{g_0} t), \qquad (9)$$

when $n = 1$. n_g is the number of moles in the gas phase at time t, n_{g_0} is the amount of gas introduced into the system, n is the order of the reaction, k is the rate constant, and q_r is ratio of gas adsorbed at time t to that at infinite time, i.e., $q_r = 1$ at infinite time. Plots of q_r vs log t with values of n that vary over the range usually encountered in simple reactions have shapes that are similar also to the curve suggested by Low (*1*). In the case where the amount of gas introduced is double the amount that can be adsorbed, then the following relationship has been found (based upon the work of Frost and Schwemer (*10*)) for the reaction $G + S \xrightarrow{k} G \cdot S$

$$q_r = (e^{\phi} - 1)/(2e^{\phi} - 1), \qquad (10)$$

$$\text{with } \phi = S_0 kt = ln\ [(\eta + 1)/2\eta] \quad (11)$$

S is the surface available at time t, S_0 is this quantity at time 0, and $\eta = S/S_0$. A plot of q_r (which in this case has a limiting value of 0.5), or θ, vs log t also gives a curve that is similar to those suggested earlier (*1*). It should be noted that none of the curves just mentioned can be made to coincide over the entire extent of the oxygen–tungsten reaction (*8,9*). However, if q_r is 0.1 or less the q_r vs log t plots are almost linear and nearly overlap. An increase in temperature, which would be expected to increase k, should then shift the observed curve to left on the abscissa of a q vs log t plot if all of the other experimental conditions are the same. This has been observed by Walker *et al.* (*6*) for the chemisorption of oxygen on Graphon for the temperature range of −78 to 160°C and a pressure of 100 mTorr. At the lowest temperature only a small amount of gas was adsorbed; however, increasing the temperature resulted in more gas being adsorbed at a given time and the appearance of curvature in the plots (*6*, Fig. 2). The onset of curvature appeared earlier as the temperature increased, as would be expected from Eqs. (10) or (11). More investigations using the method of dimensionless variables to describe the kinetics of chemisorption would appear to be desirable.

ACKNOWLEDGMENTS

The author appreciates the permission of Dr. J. L. deSegovia to use his data on the kinetics of oxygen adsorption on tungsten. Also acknowledged are many helpful discussions with members of the Surface Chemistry Branch at the Naval Research Laboratory.

REFERENCES

1. Low, M. J. D., *Chem. Rev.* **60**, 267 (1960).

2. Aharoni, C., and Tompkins, F. C., *Advan. Catal. Relat. Subj.* **20**, 1 (1970).

3. Laidler, K. J., "Catalysis" (P. H. Emmett, Ed.), Vol. 1, pp. 189–191. Reinhold, New York, 1954.

4. Coekelbergs, R., Frennet, A., Lienard, G., and Resibois, P., *J. Chem. Phys.* **39**, 585 (1963).

5. Taylor, H. A., and Thon, N., *J. Amer. Chem. Soc.* **74**, 4169 (1952).
6. Bansal, R. C., Vestola, F. J., and Walker, P. L., Jr., *J. Colloid Interface Sci.* **32**, 187 (1970).
7. Lopez-Sancho, J. M., and deSegovia, J. L., *Surface Sci.* **30**, 419 (1972).
8. Frost, A. A., and Pearson, R. G., "Kinetics and Mechanisms," pp. 14, 15. John Wiley and Sons, New York, 1961.
9. Frost, A. A., and Pearson, R. G., "Kinetics and Mechanisms," p. 169. John Wiley and Sons, New York, 1961.
10. Frost, A. A., and Schwemer, W. C., *J. Amer. Chem. Soc.* **74**, 1268 (1952).