JOURNAL OF CATALYSIS **16**, 126–128 (1970)

NOTES

Comments on the Elovich Equation

The Elovich equation (*1, 2*) has been widely applied to chemisorption kinetics in its integrated form:

$$q = \frac{1}{\alpha}\ln(t + t_0) - \frac{1}{\alpha}\ln t_0. \qquad (1)$$

Here q is the amount chemisorbed at time t and α and t_0 are constants. The parameter t_0 is chosen to linearize a plot of q against $\ln(t + t_0)$ and α is calculated from the gradient of this plot. The differentiated equation is,

$$\frac{dq}{dt} = a\exp(-\alpha q), \qquad (2)$$

and $a = 1/t_0\alpha$ if $q = 0$ at $t = 0$.

Much debate exists as to the significance of t_0, α and a. Peers (*3*) has pointed out that t_0 must have a nonzero value, however small, but many authors obtain apparently linear plots of q against $\ln t$, i.e., $t_0 = 0$, and imply that Elovich kinetics apply from $t = 0$. It is worthwhile discussing this more explicitly.

The Parameter t_0

Here q^1 and t^1 are used for curves with $t_0 = 0$. A plot of $q^1 = (1/\alpha)\ln t^1$ is shown in Fig. 1 for $\alpha = 0.50$. A family of such curves exists, each with a different value of α but all passing through $(q^1 = 0, t^1 = 1)$. It is apparent that not only is (dq^1/dt^1) infinite at $t^1 = 0$ but also that $q^1 = -_\infty$ at $t^1 = 0$. Equations (1) and (2) have no physical significance when $t_0 = 0$ (*3*).

The value of α is determined by which of the family of q^1 against $\ln t^1$ curves applies to the kinetic process. The parameter t_0 is then concerned with the point on the curve at which the process begins. The origin is shifted by t_0 on the time axis (and hence by $1/\alpha \ln t_0$ on the q^1 axis) to give a new set of coordinates (q,t) which represent the chemisorption (Fig. 1)

$$\left.\begin{aligned} t &= t^1 - t_0 \\ q &= \frac{1}{\alpha}\ln t^1 - \frac{1}{\alpha}\ln t_0 = \frac{1}{\alpha} \\ &\qquad \ln(t + t_0) - \frac{1}{\alpha}\ln t_0 \end{aligned}\right\} . \qquad (3)$$

The parameter t_0 plays a purely mathematical role. Claims (*4*) for a precise physical meaning for t_0 are of doubtful validity. The parameters of possible physical significance are a and α.

Distinct breaks (*2*) often occur in Elovich plots. If $t_{0(j)}$ represents the t_0 value for a later Elovich section with a new value of $\alpha(=\alpha_{(j)})$ the data are well described by Eq. (1) if (*5, 6*)

$$t_{0(j)} = (t_0 + t^*), \qquad (4)$$

where t_0 is the constant originally chosen to linearize the plot and t^* is the time for which previous Elovich section(s) have

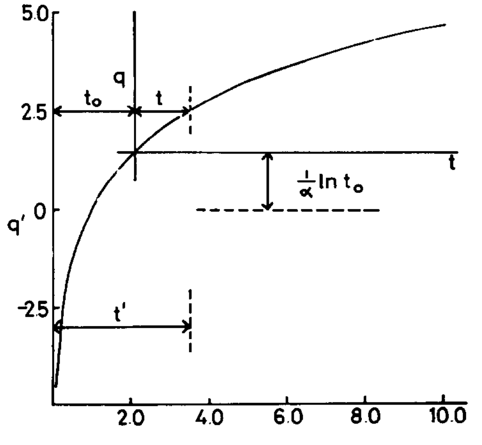

FIG. 1. Plot of $q^1 = (1/\alpha)\ln t^1$ for $\alpha = 0.50$ showing the significance of t_0 in the integrated Elovich equation.

been in force. This is confirmed if the origin is shifted so that the start of a second (or later) Elovich section becomes the point ($q = 0$, $t = 0$). An integrated Elovich plot can then be obtained for this section in the usual way and the disposable parameter necessary to linearize the plot turns out to have a value $(t_0 + t^*)$ in agreement with Eq. (4).

There is no obvious reason why this parameter should be related to the time for which previous Elovich section(s) have lasted. This situation indicates not only a sharp change in the rate of decrease of (dq/dt) but also in (dq/dt) itself. It is easily verified that the rate (dq/dt) at the end of an Elovich section cannot equal that at the start of a following section if α changes in value and $t_{0(j)} = (t_0 + t^*)$. These rates are only equal if

$$t_{0(j+1)} = \frac{\alpha_{(j)}}{\alpha_{(j+1)}} (t_0 + t^*).$$

The Parameters a and α

The constant a represents the rate of chemisorption at the beginning of an Elovich section. Its physical significance is fairly straightforward. In certain circumstances (*6, 7*) its variation with temperature may be used to calculate activation energies for chemisorption.

In chemisorption models where Elovich kinetics follow from an activation energy (E) which increases linearly with coverage a certain physical significance can be attached to α since (*2, 8*)

$$E(q) = E(0) + \alpha q, \tag{5}$$

where $E(q)$ is the activation energy at coverage q. Otherwise the significance of α is less clear and it is loosely taken to represent the deceleration of the uptake. "Breaks" in Elovich plots indicate an abrupt change in α. To account for this it is assumed that distinct sets of adsorption sites exist and that each has a characteristic value of α. Abrupt "breaks" are taken to result from complete filling of the first set of sites before significient adsorption begins on the second set. This model does not seem realistic. A more convincing explanation of abrupt changes in α would be a sudden change in the character of the surface at a particular q value. Models of site creation (*9*) or of aggregation of adsorbate (*7*) may be more appropriate in explaining the abrupt alterations in α. The fact that (dq/dt) also changes abruptly is of relevance here.

The electronic theory (*10*) of catalysis on semiconductors deals successfully with many aspects of chemisorption on these solids but its application to chemisorption kinetics (*11–14*) leads to an Elovich rate law only in specific circumstances. Kuznetsov (*13*) has shown that Elovich kinetics should apply to the particular case of chemisorption on a "quasi-isolated" (*10*) semiconductor surface when the Fermi level passes near the upper boundary of the band edge. The kinetics should then follow:

$$N = \frac{4\pi m^* kT}{h^2} \ln \left\{ \exp\left(\frac{h^2 N_0}{4\pi m^* kT}\right) + \frac{xPN^*h}{4\pi m^* kT}\, t \exp(fg + fs - f^+ + E_{1p} - Q_a) \right\}, \tag{6}$$

where N is the amount chemisorbed at time t. The symbols in Eq. (6) are defined in Ref. (*13*) but comparison of Eqs. (*1*) and (6) shows that $\alpha = (h^2/4\pi m^* kT)$ where m^* is the effective mass of carriers in the surface band. For chemisorption at constant temperature changes in α could only result from changes in m^*. It would be tempting to equate sharp breaks in Elovich plots with abrupt changes in m^*.

It is dangerous to yield too easily to such temptations. Elovich kinetics apply to chemisorptions on a wide range of solids and not only on surfaces which could have the specific characteristics described by Kuznetsov. It has been stressed (*2*) that adherence of data to Elovich kinetics does not prove a particular mechanism of chemisorption. It has not been stressed, however, that the Elovich rate law also describes a wide variety of reactions outside the field of chemisorption. For example, such diverse processes as the following obey Elovich kinetics: (a) the oxidation of metals (*15*); (b) the oxidation of coals and chars (*16*); (c) decomposition of surface formate on nickel (*17*); (d) decay of photoconduction in semiconductors (*18*, *19*); (e) decay of photogenerated free radicals in a photosynthetic system (*20*) and in melanin (*21*); (f) graphitization of carbon (*22*); (g) annealing of films of carbon (*23*) and silicon carbide (*24*); and (h) ion transport across cell membranes (*25*). A profusion of models exists to explain Elovich kinetics in these systems.

It would be prudent not to attribute undue physical significance to Elovich parameters unless a general mechanism can be suggested to take account of its widespread applicability. It may turn out that the Elovich equation represents only an empirical approximation to actual behavior. If this is *not* the case it could eventually prove to be of fundamental significance.

REFERENCES

1. ROGINSKY, S. Z., AND ZELDOVICH, J., *Acta Physicochim. USSR* **1**, 554 (1934).

2. LOW, M. J. D., *Chem. Rev.* **60**, 267 (1960).

3. PEERS, A. M., *J. Catalysis* **4**, 672 (1965).

4. CIMINO, A., MOLINARI, E., AND CIPOLLINI, E., *Actes Second Congr. Intern. Catalyses, 2^e, Paris 1960* **1**, 263 (1961).

5. MCLINTOCK, I. S., AND RITCHIE, M., *Trans. Faraday Soc.* **61**, 1007 (1965).

6. MCLINTOCK, I. S., *Nature* **216**, 1204 (1967).

7. ALLEN, J. A., AND SCAIFE, P. H., *Australian J. Chem.* **19**, 2015 (1966).

8. HAYWARD, D. O., AND TRAPNELL, B. M. W., "Chemisorption." Butterworths, London, 1964.

9. TAYLOR, H. A., AND THON, N., *J. Am. Chem. Soc.* **74**, 4169 (1952).

10. VOLKENSHTEIN, F., *Advan. Catalysis* **12**, 189 (1960); and "The Electronic Theory of Catalysis on Semiconductors." Macmillan, New York, 1963.

11. PESHEV, O., *Russ. Chem. Rev.* **35**, 761 (1966).

12. VOLKENSHTEIN, F., AND PESHEV, O., *Kinetics Catalysis (USSR) (Eng. Transl.)* **6**, 79 (1965).

13. KUZNETSOV, V. S., *Kinetics Catalysis (USSR) (Eng. Transl.)* **5**, 471 (1964).

14. KUZNETSOV, V. S., *Kinetics Catalysis (USSR) (Eng. Transl.)* **4**, 772 (1963).

15. KUBASCHEWSKI, O., AND HOPKINS, B. E., "Oxidation of Metals and Alloys." Butterworths, London, 1962.

16. NEWMAN, J. O. H., STANLEY, L., EVANS, P. L., COLDRICK, A. J. T., KEMPTON, T. J., *Nature* **213**, 280 (1967).

17. FUKUDA, K., NAGASHIMA, S., NOTO, Y., ONISHI, T., AND TAMARU, K., *Trans. Faraday Soc.* **64**, 522 (1968).

18. NOBBS, J. MCK., *Phys. Chem. Solids* **29**, 439 (1968).

19. PAGNIA, H., *Surface Sci.* **10**, 239 (1968).

20. COPE, F. W., *Proc. Natl. Acad. Sci. U. S.* **51**, 809 (1964).

21. COPE, F. W., *J. Chem. Phys.* **40**, 2653 (1964).

22. MIZUSHIMA, S., *Proc. Conf. Carbon, 5th, Univ. Park, Penna., 1961* **2**, 439 (1963).

23. MCLINTOCK, I. S., AND ORR, J. C., unpublished results.

24. MOGAB, C. J., AND KINGERY, W. D., *J. Appl. Phys.* **39**, 3640 (1968).

25. COPE, F. W., *Bull. Math. Biophys.* **27**, 99 (1965).

I. S. MCLINTOCK

Isotopes Laboratory
University of Dundee
Dundee, Scotland

Received May 13, 1969