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THE RATE OF CHEMISORPTION OF NITROGEN
ON IRON: COMMENTS ON A STATEMENT
BY T. KWAN

By

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In a recent communication¹⁾ KWAN commented on the validity of the ELOVICH equation as an expression for nitrogen chemisorption kinetics, claiming the power rate law to be adequate for that purpose. We claim the ELOVICH equation to be precise for that purpose.

KWAN based his comments on apparent curvature of $\log\left(-\frac{1}{p} \frac{dp}{dt}\right)$ versus θ plots. Such treatments based on approximated rates are not precise and may lead to inclusive or wrong results^{2,3)}.

The ELOVICH equation

$$\frac{dq}{dt} = ae^{-aq} \quad (1)$$

is most easily and correctly applied to experimental data in one of its integrated forms, *viz.*

$$\begin{aligned} q &= 1/\alpha \ln(1 + \alpha a t), \\ q &= 1/\alpha \ln(t+t_0) - 1/\alpha \ln t_0 \end{aligned} \quad (2)$$

Application requires a simple plot of q versus $\log(t+t_0)$. Evaluation of the parameters t_0 , (a) and α may be made by means of objective numerical methods⁴⁾.

Mathematically, from equation (1), a plot of the logarithms of the momentary rates at various times as a function of q should also be

* M. J. D. L. and H. A. T.: Wm. H. Nichols Laboratory, New York University, New York, U. S. A.

1) Bull. Chem. Soc. Japan **31**, 247 (1958).

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

3) H. A. TAYLOR, P. C. *Reilly Lectures*, Vol. XII, Univ. of Notre Dame Press, 1956, Notre Dame, Indiana.

4) J. N. SARMOUSAKIS and M. J. D. LOW, J. Chem. Phys. **25**, 178 (1956).

linear and furnish similar information. There are two practical difficulties connected with this latter procedure. The first, as TAYLOR and THON pointed out, depends on the presence of an initial massive adsorption which occurs much more rapidly than the succeeding slow adsorption. The apparent rates observed initially are therefore markedly higher than those calculated from t_0 and must be reduced by this initial adsorption which, from the plot of equation (2), may be determined as the value of q at time t_0 . Obviously, if the apparent rates are plotted logarithmically against values of q , no straight line can result, since the earliest values are inconsistent with the later ones. In the second place, for equation (1) it is the instantaneous rates, dq/dt , which must be used. These may be determined from the experimental data of values of q at various times t , either as average rates, $\Delta q/\Delta t$, over short time intervals, or from the slopes of tangents to a direct plot of the data. Either method is fraught with difficulty, especially in the early stages of adsorption where the rate is changing rapidly and may lead to erroneous conclusions.

An excellent example of this is provided by the chemisorption kinetics of nitrogen on iron, shown to be ELOVICHIAN by TAYLOR⁵⁾ and, more recently in a comparative study, by SCHOLTEN and ZWIETERING⁶⁾, which is disputed by KWAN⁷⁾. An occurrence similar to that found with the data of KWAN was found with data of rates at various times given by BRUNAUER, LOVE and KEENAN⁶⁾ which did not plot linearly as $\log(\text{rate})$ versus q . It appeared, however, on close scrutiny that these were not new data but earlier data of EMMETT and BRUNAUER⁷⁾ "recalculated" to give rates. TAYLOR and THON had already shown that the original data plotted linearly as q versus $\log t$.

Let us therefore consider the data of KWAN. For example, the 400° run⁸⁾.

The plot¹⁾ of $\log(-1/P \, dP/dt)$ versus $(P_0 - P)$ is again reproduced as plot A in Figure 1. It is apparent that there is considerable scatter of points and that the plot could be curvilinear or could consist of two interesting straight lines. Curve B of Figure 1 is a plot of $(P_0 - P)$ versus $\log t$, constructed from the same data⁸⁾. It is obvious that the

5) J. J. F. SHOLTEN and P. ZWIETERING, *Trans. Faraday Soc.* **53**, 1363 (1957).

6) S. BRUNAUER, K. S. LOVE and R. G. KEENAN, *J. Am. Chem. Soc.* **64**, 751 (1942).

7) P. H. EMMETT and S. BRUNAUER, *J. Am. Chem. Soc.* **56**, 35 (1934).

8) T. KWAN, *this Journal*, **3**, 109 (1955); Table 2, p. 114 gives pressures, declining from $P_0 = 1.728$ mmHg at $t=0$, as a function of time.

The Rate of Chemisorption of Nitrogen on Iron

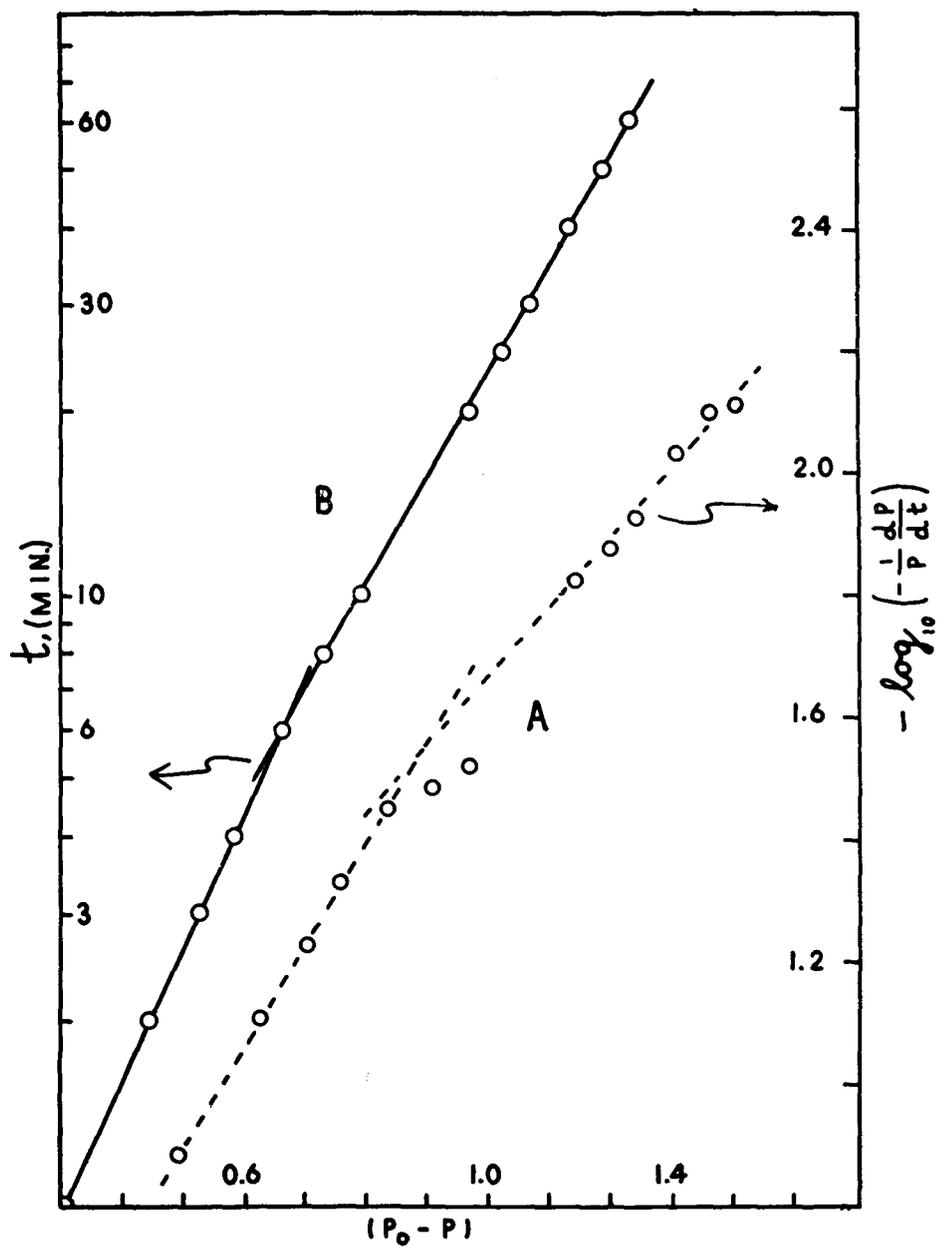


Fig. 1.

approximation to linearity in each portion is excellent. Such breaks in $q-\ln t$ plots have been found previously and have been interpreted as being due to different sites^{2,3}. Behaviour analogous to the above is found with the rest of the nitrogen adsorption data. Unwarranted difficulties are then introduced through the use of rates calculated from successive q and t values. The approximation of these momentary rates is not adequate. It is obvious that a simple and direct treatment of experimental data is preferable to an indirect one involving approximations if both treatments are mathematically equivalent. It is further obvious that should momentary rates be derived, these may be precisely calculated from the rate parameters.