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A NEW APPROACH TO ELOVICH EQUATION

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THE chemisorption kinetic data are often analysed through a logarithmic relationship associated with Elovich.[1] Attempts[2-4] have been constantly made to rationalise this empirical equation by the use of suitable models based on the presence of site distribution on the surface of the solid. The integrated expression of the Elovich equation has the form:

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

where q is the amount of gas adsorbed (in cc NTP) at any time t and α and t_0 are constants. Since t_0 is usually small, it is often neglected and the experimental kinetic data are often examined through a plot of q as a function of log t, the slope of which yields the value of α and the intercept could be used to evaluate another constant of the Elovich equation, namely, 'a', through the relationship $t_0 = 1/a\alpha$. The dependence of these constants on temperature and pressure, though studied widely,[5] has not resulted in understanding the functional relationship of these parameters. In the present study, an attempt has been made to elucidate the physical significance of the parameters and to evolve methods for evaluating them from primary kinetic data on the chemisorption of hydrogen on iron oxide.

Iron oxide was prepared by the decomposition of AnalaR grade ferric nitrate in air at 400 ± 10° C. for 9 hours. The results reported here pertain to adsorption by 3·13 gm. of the oxide (Fe_2O_3) whose surface area was found to be 14·0 m^2 by the BET method. The measurements of adsorption were carried out in a volumetric apparatus similar to the one reported by Srinivasan.[6] Each adsorption experiment was preceded by evacuation for an hour at the temperature of the experiment, to avoid reduction by previously adsorbed hydrogen, followed by evacuation at 400° C. for 8 hours at 10^{-6} mm. Hg.

The evaluation of t_0.—Attempts to calculate q making use of the integrated equation have not resulted in getting values that were obtained experimentally, obviously on account of the omission of the constant t_0 in the plots of Elovich equation. In the present study a successive approximation procedure has been utilised to obtain the values of the integration constant t_0. This was done by successively regressing the value of t_0, obtained approximately from the intercept of the plot of q versus log t of the Elovich equation, till a self-consistent value for t_0 was reached.

The evaluation of 'a'.—A plot of the amount adsorbed as a function of time, with the condition that $q = 0$ at $t = t_0$, is made, and from the initial slope of this plot the value of 'a', the initial rate, can be obtained.

The values of the parameters obtained by the treatment of experimental data on the adsorption of hydrogen on iron oxide in the temperature range 299-433° K., by the above procedure are summarised in Table I. Recently, McIntock[7] has considered the parameters of

TABLE I

Parameters of the Elovich equation for the adsorption of hydrogen on iron oxide

At. Pr. = 76·0 cm.

Temp. °C.	Eq. Pr. cm. Hg.	t_0^1 min.	t_0^2 min.	a_1	a_2	t_b^1 min.	t_b^2 min.	q_b^1 CCNTP	q_b^2 CCNTP
26·5	At. pr.	0·432	4·21	6·22	2·19	14·55	..	0·56	..
56	49·51	0·724	1·73	3·80	2·30	6·45	42·56	0·58	1·41
56	At. pr.	0·419	0·17	3·67	1·91	3·62	26·30	0·58	1·62
80	49·60	0·582	..	2·66	..	33·19	..	1·53	..
80	At. pr.	0·284	..	2·39	..	46·88	..	2·14	..
100	29·87	0·275	..	4·84	..	7·24	..	1·18	..
100	49·59	0·302	..	2·82	..	9·31	..	1·22	..
100	At. pr.	0·374	..	2·01	..	9·91	..	1·63	..
142	29·30	0·0058	..	9·73	..	..	..	..	..
142	49·27	0·072	..	3·35	..	2·82	..	1·10	..
142	At. pr.	0·042	..	2·88	..	2·32	..	1·39	..
160	29·71	0·001	..	12·36	..	..	..	..	..
160	49·23	0·0086	0·019	3·42	3·07	12·85	..	2·14	..
160	At. pr.	0·0074	0·053	2·12	1·59	17·99	..	3·67	..

the Elovich equation and has concluded that t_0 has only a mathematical role in the equation and that no physical significance could be attributed to it. However, in the present instance, the plot of the amount adsorbed against logarithm of $(t + t_0)$ (in seconds) was seen to intersect the x-axis at time t_0, as shown in Fig. 1 indicating that the process of adsorption is initiated only after a time-lag of t_0.

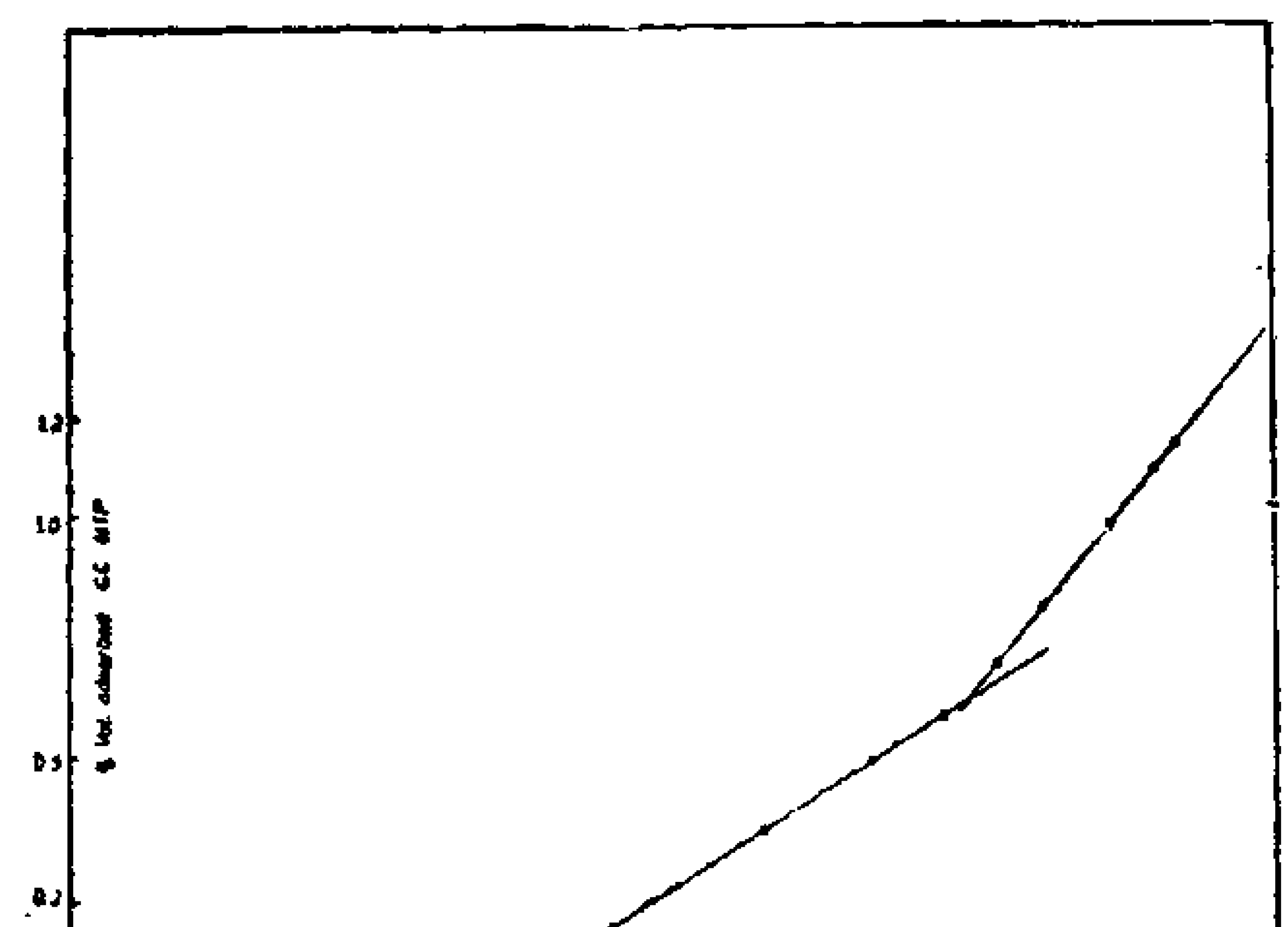

FIG. 1. Elovich plot for hydrogen adsorption on iron oxide at 56° C. and atmospheric pressure (× axis $t+t_0$ in seconds).

This induction period could be associated with the activation of the gas molecules for adsorption. Such a physical significance for t_0 has been taken into consideration in the evaluation of the values of the initial rates 'a', and the values thus obtained have been used in finding out the activation energy for the adsorption of hydrogen of iron oxide at atmospheric pressure using Arrhenius relationship. The value was found to be 2·6 K.cal./mole in the temperature range 299-433° K. It was found that the values of 'a' obtained by omitting t_0 in the Elovich equation did not vary consistently with temperature whereas the initial rate evaluated by the present procedure shows a consistent variation with temperature thus enabling one to get a meaningful value for the activation energy.

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