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ADIABATIC ADSORPTION

By

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Abstract

A kinetic anomaly is described: it is necessary to use a negative, rather than the usual positive, constant with an integrated form of the Elovich equation to describe the course of certain isothermal chemisorption rate experiments. It is suggested that the cause of the anomaly is poor thermal conduction, leading to pseudo-adiabatic conditions. Adsorption under adiabatic conditions is considered, and an equation incorporating a negative parameter is derived for those conditions.

Recently, during a study of temperature and pressure effects on the rates of chemisorption of gases on solids, the rates of adsorption of hydrogen on kieselguhr-supported iron were measured, using previously described techniques[1],[2]. The data obtained were treated by the ELOVICH equation[3],[4],

$$dq/dt = ae^{-\alpha q} \tag{I}$$

where q is the amount of gas adsorbed at time t, and a and α are constants. This involved the use of an integrated from of the ELOVICH equation,

$$q = \frac{2\cdot 3}{\alpha}\log(t+k) - \frac{2\cdot 3}{\alpha}\log t_0 \tag{II}$$

where $t_0 = 1/\alpha a$, and k is a constant. The procedure is to plot values of q taken at various times t against $\log(t+k)$, with the value of k chosen to linearize the plot.

For experiments at 257°C at pressures of about 10 to 70 cm Hg the course of adsorption appeared to be satisfactorily described by Eq. (II) over the entire range of the observable reaction from about one minute (the earliest measurement) to about 500 minutes (when the experiments were stopped), with some scatter of point about the q-$\log(t+k)$ line. For comparable experiments at 200°, however, Eq. (II) was definitely not satisfactorily applicable, especially in the early stages of an experiment. The q-$\log(t+k)$ relations were such that no unique k value was applicable over the whole course of an experiment. Behavior typical of this is illustrated by the plots of Fig 1. Curve A of that

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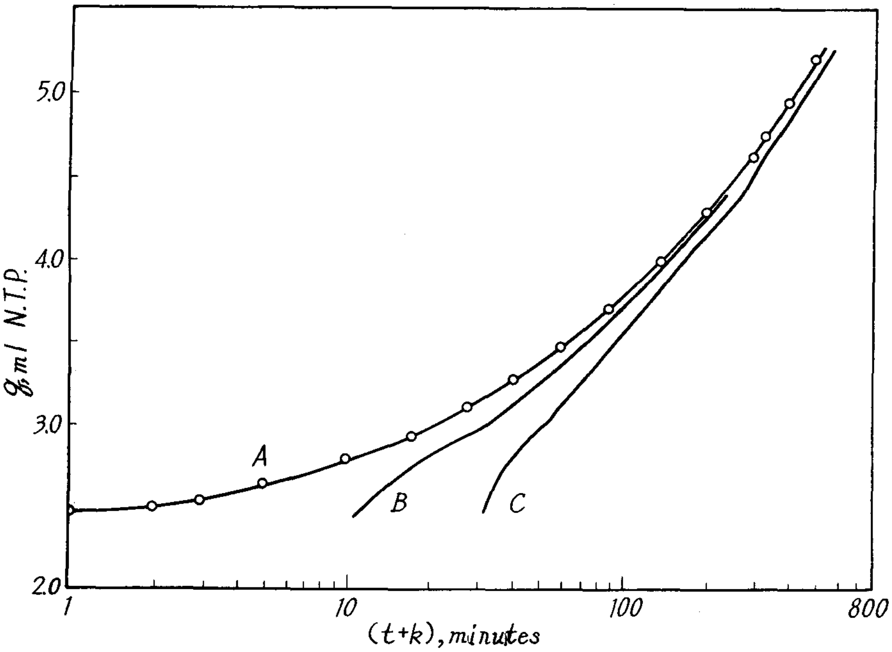

Fig. 1. Isothermal Adsorption of H_2 on Fe.
30 g kieselguhr-supported adsorbent, 28% Fe;
200°C; initial pressure: 44,5 cmHg.

figure is a plot of q versus $\log(t+k)$ with $k=0$, while curves B and C are similar plots of the same data with $k>0$.

For these experiments, a value of k chosen to linearize the first stage of the run has no linearizing effect on the later stages, while a relatively large k value shows the presence of an isothermal discontinuity or "break"[3),4)], but causes the curvature shown in the first portion of plot C. Intermediate values of k are altogether unsatisfactory, yielding S-shaped curves.

Re-examination of the 257° data showed that although q-$\log(t+k)$ plots appeared to be linear when an appropriate value of k was applied, some slight sigmoid character was inherent in the scatter of points about the q-$\log(t+k)$ lines.

The described behavior is reminiscent of sigmoid curves obtained on replotting, according to Eq. (II), some data on hydrogen adsorption on chromia. Such departure from the normal behavior was also found on replotting some data on the adsorption of nitrogen on iron of ZWIETERING and ROUKENS[6)]. Curve A of Fig. 2 is a plot of such data[7)] with $k=0$. With k values of 10 and

17 minutes, the sigmoid curves B and C of Fig. 2 respectively result. Numerical procedures[8] indicate the use of a k value of 32 minutes, resulting in curve D of Fig. 2. Similar results were obtained for nitrogen-iron data[7] at 199, 225, and 250°.

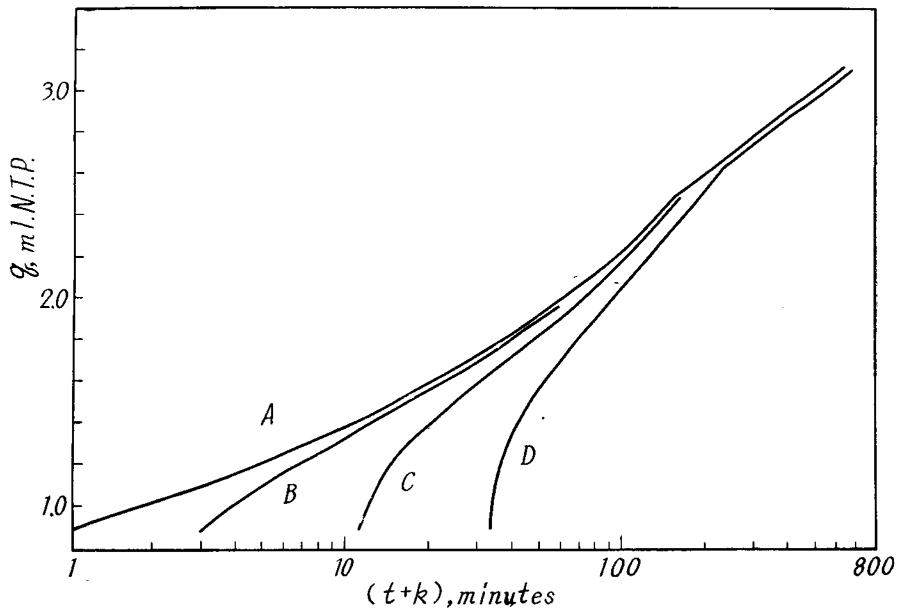

Fig. 2. Isothermal Adsorption of N_2 on Fe.
Data of ZWIETERING and ROUKENS, Figs. 2, 3.

It is obvious that a "best-linearized" plot such as D of Fig. 2 can be further linearized if a *negative* value of k is applied over the region of 0.9 to 1.6 ml. However, the appearance of sigmoid curves, negative constants, or failure of Eq. (II), signifies a distinct departure from the normal kinetic behavior already so well demonstrated[9]. Or, for certain experiments, the ELOVICH equation does not apply over a portion of each experiment. In view of the widespread applicability of the ELOVICH equation this behavior is anomalous. It is suggested that the cause of the anomaly is poor thermal conduction.

If thermal conduction is poor—as may well be the case with finely-powdered, insulator-supported adsorbents, or even with a powdered metal adsorbent—then the adsorption may occur under conditions that are not isothermal. In the initial stages of reaction, when gas take-up is rapid, the greatest local temperature increasss may be expected. In later stages of reaction, when the gas take-up is relatively slow, little or no temperature deviation need be expected because energy can be dissipated as quickly as it is released. Vigorous adsorption may thus occur under conditions that are pseudo-adiabatic during the initial stages. Such deviation from isothermal conditions could lead to the observed anomaly.

It can be shown, using previously described concepts[3], that similar behavior should obtain under conditions of adiabatic adsorption. By application of the thermal site generation mechanism postulated by VOLKENSHTEIN[10] it is suggested that under adiabatic conditions local temperature increases of the surface aggravate the site generation process.

Following convention, assuming that site generation is ARRHENIAN,

$$d \ln n/dT = Q/RT^2$$

where n is the number of sites, Q is the heat of formation of sites, and R is the gas constant. This heat Q could be supplied by the heat of adsorption. It has been suggested[3] that the heat of adsorption is a composite of two factors, the heat liberated by the adsorption proper, and the heat liberated by site decay. Consider the total heat evolved accompanying the adsorption of q ml of gas. An amount Q' results from the formation of surface complexes by the q ml, and Q'' results from the site decay that has occurred during the adsorption. If the initial site density is n_0 and that when q ml have been adsorbed is n, then $(n_0 - n)$ is the number of sites which have decayed. The total heat evolved per mole of gas adsorbed is then

$$H = Q'^*/q + Q''/n_0 (1 - e^{-\alpha q})$$

since[3] $n = n_0 \exp(-\alpha q)$, where Q'^* and Q''^* include the numerical factor expressing ml gas in moles. This may be written:

$$H = H' + H_0''/(1 - e^{-\alpha q})$$

For a single type of site H' is a constant, independent of coverage, hence

$$dH/dq = -\alpha H_0'' e^{-\alpha q}/(1 - e^{-\alpha q})^2$$

Expressing $dH = C\,dT$, where C is the surface heat capacity, probably itself a function of q, substitution in the site generation expression gives

$$\frac{-d \ln n}{dq} = \frac{\alpha Q H_0'' e^{-\alpha q}}{C R T^2 (1 - e^{-\alpha q})^2} = \frac{-d \ln n/dt}{dq/dt} \qquad \text{(III)}$$

From Eq. (II),

$$dq/dt = \left[\alpha (t+k)\right]^{-1}$$

whence

$$\frac{-d \ln n}{dt} = \frac{Q H_0'' e^{-\alpha q}}{C R T^2 (1 - e^{-\alpha q})^2} \cdot \frac{1}{(t+k)} \qquad \text{(IV)}$$

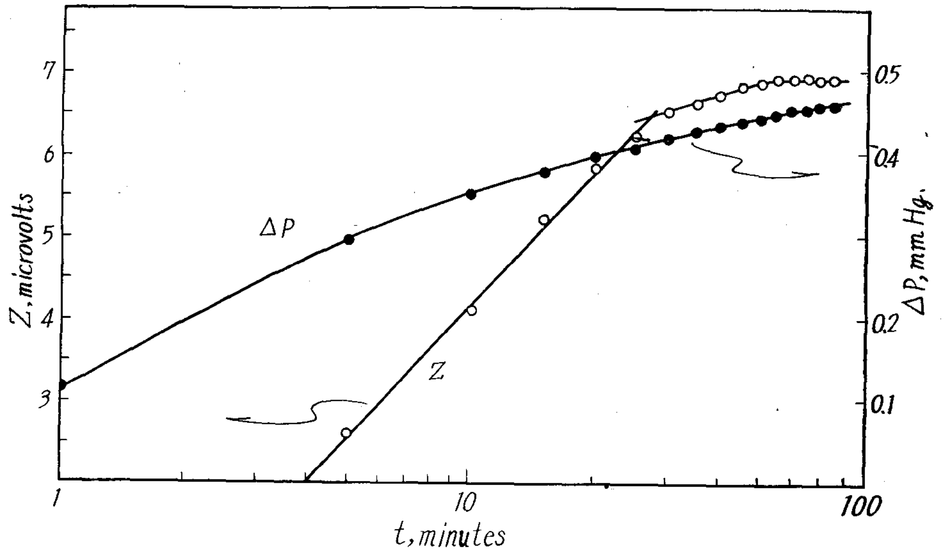

Fig. 3. Adiabatic adsorption of H_2 on Ni.
Data of MAGNUS and SARTORI, Table I.
50 g Ni; 25°C; initial pressure: 0.516 mmHg.

Site generation means that $d \ln n/dt$ is positive. Hence in Eq. (IV) the term $(t+k)$ must be negative. This requires k to be larger than t and to be negative.

Some data obtained under adiabatic conditions are given by MAGNUS and SARTORI[11], who measured adsorption kinetics as well as the temperature rise produced by adsorption of hydrogen on nickel contained in a calorimeter. Fig. 3 shows an ELOVICH plot of increments of Z (thermocouple potential proportional to temperature increase) and one of the pressure decrease in the system, ΔP (inversely proportional to the amount of gas adsorbed). The latter plot requires a negative value of k for linearity and hence is analogous to the plots of Fig. 1 and 2.

A further complication may be introduced if the TAYLOR-THON site generation mechanism[3] holds, whereby multiple sites are produced in quasi-explosive fashion on the surface at the initial moment of contact with the adsorbable gas. For a temperature rise the new site generation act could result in an amplification of the effects of relatively small temperature changes.

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