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NOTES

A Practical Method for the Evaluation of the Net Rates of Adsorption and Desorption from Adsorption–Time Curves*

The rate of adsorption observed experimentally is, in general, the difference between the rates of adsorption and desorption. Therefore the evaluation of an adsorption rate, whether from direct measurement or by applying a rate equation to the time course, is usually limited to a small surface coverage where the desorption rate is supposed to be negligible. In the case of a heterogeneous surface, however, the activation energies of adsorption and desorption are functions of surface coverage, so that it becomes necessary to measure the rates at various surface coverages. The objective of this note is to propose a method for obtaining the rates of both adsorption and desorption which are applicable to any surface and surface coverage and requires only adsorption–time curves observed at various concentrations of adsorbate. For convenience, the matter will be discussed for a gas–solid system.

In the time course of adsorption, a typical one being shown in Fig. 1 for illustration, the overall rate of adsorption, da/dt, is generally expressed by the net rates of adsorption (r_a) and desorption (r_d) as

$$da/dt = r_a - r_d = k_a f(p) g(\theta) - k_d h(\theta)$$

where $f(p)$ is a function of gas pressure, and $g(\theta)$ and $h(\theta)$ are functions of surface coverage. For example, $f(p) = p$, $g(\theta) = 1 - \theta$, and $h(\theta) = \theta$ for the Langmuir-type adsorption on a homogeneous surface, and $f(p) = p$, $g(\theta) = \exp(-u\theta)$, and $h(\theta) = \exp(v\theta)$ for the Frumkin-Temkin-type adsorption (the rate is the Elovich type).

When $\Delta a/\Delta t$ is calculated graphically at the same amount of adsorption, say at a_1, from the adsorption–time curves observed at various pressures, p_1, p_2, etc. as shown in Fig. 1, $g(\theta)$ and $h(\theta)$ are now constant for all pressures at this particular adsorbed amount a_1, so that

$$(\Delta a/\Delta t)_{a_1} = A_1 f(p) - B_1$$

where A_1 and B_1 are constant. Then the plot of $\Delta a/\Delta t$, calculated at various a, against $f(p)$ should give, as illustrated in Fig. 2, a straight line with a positive slope and a negative intercept on the ordinate. The

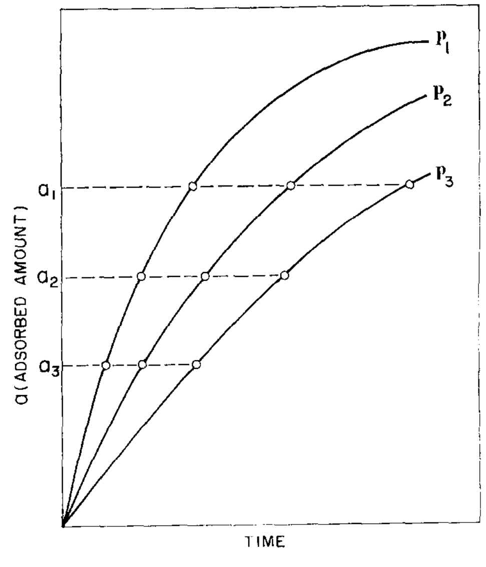

FIG. 1. Time course of adsorption; p is the pressure at which the adsorption was measured.

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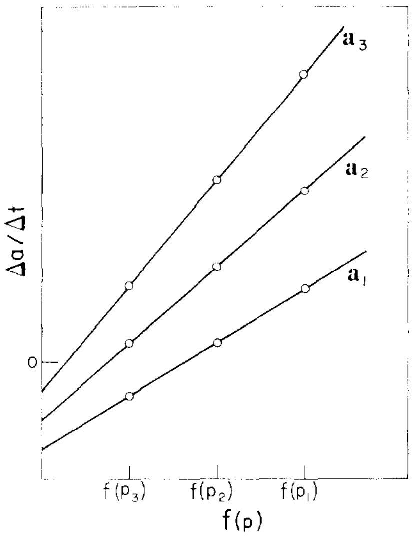

FIG. 2. Plot of $\Delta a/\Delta t$ against $f(p)$.

slope is $k_a g(\theta)$ and the intercept is $k_d h(\theta)$, the desorption rate.

Thus we can separate respective rates of adsorption and desorption from the overall rate of adsorption. Fortunately $f(p) = p$ in most cases unless the adsorption is controlled by other processes such as diffusion or surface migration. Measurement of adsorption at a constant pressure makes the above treatment easier, but is not always necessary if the initial pressure for adsorption is varied over a wide range and the pressure is known at the point where $\Delta a/\Delta t$ is calculated.

Figure 3 represents the results of hydrogen adsorption on alumina as an example of the present method. The preparation and treatment of alumina have been described elsewhere (*1*). The measurement of adsorption was made by following the pressure change in a constant volume. Figure 3 shows that $\Delta a/\Delta t$ is linear in pressure, and that the slope of the plot of $\Delta a/\Delta t$ versus p decreases as the adsorbed amount increases, while the intercept increases with the adsorbed amount. Although the range of adsorbed amount is not sufficiently wide in this example, the slope (A) and the intercept (B) can, in principle, be used to elucidate the form of the functions, $g(\theta)$, $h(\theta)$. Thus, for molecular adsorption of the Langmuir type, an A–a plot should give a straight line with a negative slope, and a B–a plot should be a straight line with a positive slope which goes through the origin. Plots of $A^{\frac{1}{2}}$–a and B–a^2 may be used as diagnostic tests for dissociative adsorption. For a heterogeneous surface, things are not as simple as above, but r_a and r_d are already separated, so that their plots against surface coverage will be useful for obtaining the type of surface energy distribution.

Figure 4 shows the application of the present method to the results of Burwell

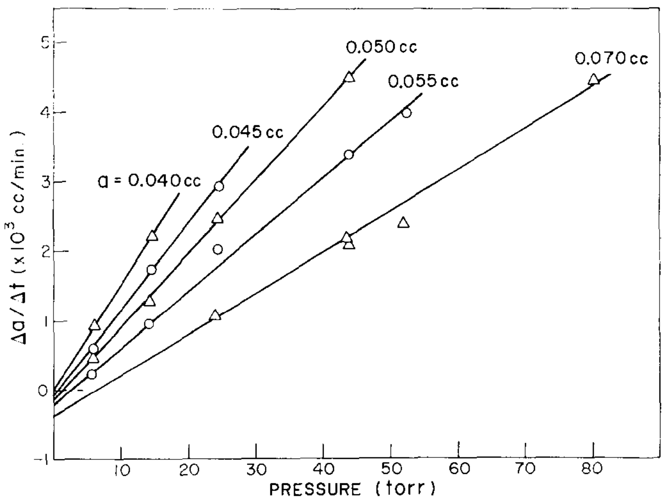

FIG. 3. Plot of $\Delta a/\Delta t$ against pressure for hydrogen on alumina. Catalyst weight 0 747 g, adsorption temperature 25°.

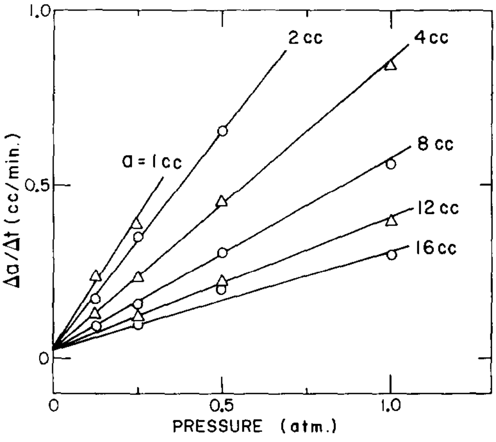

FIG. 4. Plot of $\Delta a/\Delta t$ against pressure for hydrogen on chromia (*2*). Catalyst weight 16 g, temperature 457°K.

and Taylor on the adsorption of hydrogen on chromia gel (*2*), in which again good linearity against pressure is seen. Although the intercepts are slightly positive, they are close to zero, suggesting that the adsorption is so strong that the desorption rate is negligible. The plot of log r thus obtained against the adsorbed amount gave two straight lines: one from 1 to 4 cc with a large slope; the other from 4 to 16 cc with a smaller slope. Taylor and Thon also indicated that Burwell's results fitted the Elvoich equation up to 2 cc (*3*).

As described above, the present treatment is not only useful for obtaining net rates of adsorption and desorption, but also is applicable to heterogeneous surfaces, since $\Delta a/\Delta t$ is taken at the same surface coverage. Furthermore, when r_a and r_d are separately obtained as functions of p and a [the detailed forms of $g(\theta)$ and $h(\theta)$ are not necessary], the isotherm can be predicted. It is also clear that the method is not limited to adsorption, but, in principle, is applicable to general reactions if suitable data are available.

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NOTES

Classification of Oxidation Catalysts According to the Type of Metal–Oxygen Bond*

INTRODUCTION

In recent years, many correlations have been made between the strength of the metal–oxygen bond of oxidation catalysts and their activity in the oxidation of several types of molecules (*1–4*).

It is known from organic and inorganic chemistry that the reactivity of a bond not only depends on its strength but also on its type.

In a previous article (*5*) we drew attention to the relationship existing between the activity in NH_3 and C_3H_6 oxidation of a series of molybdates studied by us and the presence of a metal–oxygen bond having double-bond character. No hypotheses were put forward on how such a metal–oxygen

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