

ADSORPTION WITH MOBILE PRECURSOR – DETERMINATION OF THE KINETIC ORDER

Jan PAVLÍČEK

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received January 23rd, 1985

A method is proposed which makes possible a more reliable determination of the adsorption order from the dependence of coverage on exposition in the case of adsorption with a mobile precursor. It is pointed out that the evaluation of experiments carried out at a single temperature may lead to erroneous conclusions. The method is also advantageous for the more exact determination of the limiting coverage and the slope of the tangent at the origin of coordinates.

Data about the dependence of the surface coverage by adsorbed particles on the time of exposure are frequently obtained from experiments in the field of surface science. Their analysis gives information about the character of the adsorption kinetics, whether it proceeds by the molecular or dissociative mechanism, *etc.* Our aim is to show that the usual interpretation of experimental data may lead to results which are both qualitatively and quantitatively incorrect, especially in the rather frequent case where adsorption proceeds *via* weakly adsorbed mobile particles, so-called precursor. We shall deal with the model introduced by Kisliuk^{1,2}, which corresponds to the Langmuir model supplemented by the intermediate stage mentioned. The underlying assumptions are as follows: (1) No interactions between the chemisorbed particles take place. (2) The chemisorbed layer is in an equilibrium state. (3) The probability, α , of trapping into the state of a weakly adsorbed mobile precursor is independent of the coverage in the chemisorbed layer.

In the case of molecular adsorption (further denoted K_1), the model is uniquely defined by the above assumptions. For dissociative adsorption, two variants must be distinguished³: precursor existing above one adsorption center (variant K_{2_1}) and precursor existing above a couple of neighbouring adsorption centers (variant K_{2_2}). Equations for the dependence of coverage on exposition in each case will be derived below.

Adsorption Kinetics

The increment of the number of adsorbed particles (or occupied adsorption centers) can be expressed as⁴

$$dn = m\sigma dt, \quad (1)$$

where n denotes the number of occupied adsorption centers per unit surface area, m adsorption order (1 for molecular, 2 for dissociative adsorption), s sticking probability, σ number of impacts per unit surface area and unit time, and t time. If the adsorption proceeds at constant pressure, σ is constant. The coverage Θ is defined as the ratio of the number of occupied adsorption centers n to their maximum number n_M , hence Eq. (1) can be rewritten as

$$d\Theta = ms \frac{\sigma}{n_M} dt. \quad (2)$$

In order to integrate this equation, we need to know the dependence of the sticking probability on the coverage. On the basis of the model considered, there are several methods^{3,5-8} how to derive the desired dependence; if they are used correctly, they lead to identical results. Perhaps the most illustrative is the method used by Cassuto and King³, which describes the adsorption kinetics by means of the rate constants, k_D , k_M , and k_A , of the elementary steps (desorption, migration, and chemisorption) of the mobile precursor. Considering the above model, we can express their results as follows:

$$(K1) \quad s/s_0 = (1 - \Theta)/(1 - D_1 D_2 \Theta), \quad (3a)$$

$$(K2_1) \quad s/s_0 = \frac{(1 - \Theta)^2}{1 - D_1 \Theta - D_1 D_2 \Theta (1 - \Theta)}, \quad (3b)$$

$$(K2_2) \quad s/s_0 = \left[1 + (1 - D_1 D_2) \left(\frac{1}{(1 - \Theta)^2} - 1 \right) \right]^{-1}. \quad (3c)$$

The constant D_1 can be expressed as the ratio of the sticking probability, s_0 , at zero coverage to the probability of trapping α

$$D_1 = s_0/\alpha \quad (4a)$$

and the constant D_2 can be expressed as

$$D_2 = k_M/(k_D + k_M). \quad (4b)$$

The constants D_1 and D_2 are in the range from 0 to 1. Zero value of D_2 ($k_M = 0$) means that the precursor is immobile, in which case the variants K1 and K2₂ become identical with the Langmuir model of the first or second order.

With regard to the form of equations (3a-c), it is convenient to write equation (2) in the form

$$\frac{s_0}{s} d\Theta = ms_0 \frac{\sigma}{n_M} dt. \quad (5)$$

Equations (3a-c) can now be introduced into (5) and integrated to give

$$(K1) \quad (D_1 D_2 - 1) \ln(1 - \Theta) + D_1 D_2 \Theta = s_0 \frac{\sigma}{n_M} t, \quad (6a)$$

$$(K2_1) \quad (1 - D_1) \frac{\Theta}{1 - \Theta} + (D_1 D_2 - D_1) \ln(1 - \Theta) + D_1 D_2 \Theta = 2s_0 \frac{\sigma}{n_M} t, \quad (6b)$$

$$(K2_2) \quad (1 - D_1 D_2) \frac{\Theta}{1 - \Theta} + D_1 D_2 \Theta = 2s_0 \frac{\sigma}{n_M} t. \quad (6c)$$

As stated above, the case $D_2 = 0$ leads to the Langmuir model of the first and second order, to which equations (6a) and (6c) are reduced. These equations represent the dependence of the coverage on the time or exposition corresponding to the given model, and can be compared with experimental data, as usual. It is convenient for further discussion to introduce the generalized time variable

$$\varepsilon = ms_0 \frac{\sigma}{n_M} t. \quad (7)$$

In this way, all curves with the same constant D_1 and D_2 regardless of the values of s_0 , σ , and n_M fuse together. Typical dependences of Θ on ε are shown in Fig. 1, where curve 1 corresponds to constant sticking probability, curves 2 and 3 correspond

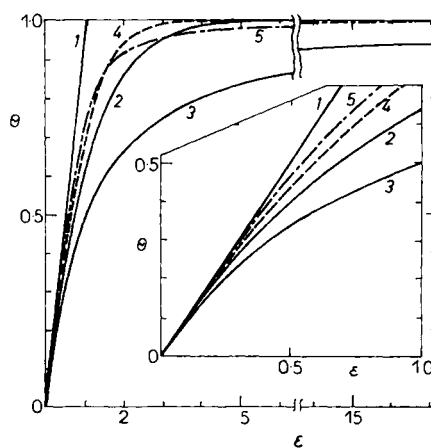


FIG. 1

Dependence of coverage on ε (proportional to exposition). 1 Constant sticking probability; 2 Langmuir model of first order; 3 Langmuir model of second order; 4 Kisliuk model of first order (K1), $D_1 D_2 = 0.5$; 5 Kisliuk model of second order (K2₁), $D_1 = 0.9$, $D_2 = 1$

to the Langmuir model of the first and second order. All curves for the Kisiulik model of the first order lie in the region delimited by curves 1 and 2. In the case of both variants of the second-order model, the situation is more complicated. The curves can either lie in the region between curves 2 and 3, or, at low expositions, between curves 1 and 2 and with increasing exposition they may intersect curve 2 and pass into the region between curves 2 and 3. It can be seen from Fig. 1 that the dependences for the first and second order are similar in certain cases (curves 4 and 5). With regard to possible errors in the determination of the total coverage (*i.e.* exposition time at which the surface is saturated), it is possible that the experimental data can be fitted by curves of the first and second order equally well. A method for elimination of this ambiguity is proposed below.

Treatment of Experimental Data

It is apparent from equation (2) that the slope $d\theta/dt$ in the limit for zero coverage (or time) is equal to the multiplier standing before t in Eq. (7) for the generalized time variable. The construction of a tangent to the experimental curve (graphically or numerically) may be problematical, although in the given case the dependence of θ on t for low expositions is nearly linear. To eliminate possible errors, we proceed as follows. We introduce new coordinates

$$Y = \frac{-t}{\ln(1-\theta)}, \quad X = \frac{-\theta}{\ln(1-\theta)}. \quad (8a,b)$$

The variable X is equal to 1 for $\theta = 0$ and 0 for $\theta = 1$. Equations (6a-c) thus acquire the form

$$(K1) \quad s_0 \frac{\sigma}{n_M} Y = 1 - D_1 D_2 + D_1 D_2 X, \quad (9a)$$

$$(K2_1) \quad 2s_0 \frac{\sigma}{n_M} Y = D_1 - D_1 D_2 + \left(D_1 D_2 + \frac{1 - D_1}{1 - \theta} \right) X, \quad (9b)$$

$$(K2_2) \quad 2s_0 \frac{\sigma}{n_M} Y = \left(D_1 D_2 + \frac{1 - D_1 D_2}{1 - \theta} \right) X. \quad (9c)$$

It is apparent that the variable Y has for $X = 1$ (*i.e.* $\theta = 0$) in all three cases the same value $Y_0 = n_M/m\sigma s_0$. The dependence of Y on X is, however, different for different adsorption orders. In the case of the first order, the dependence is linear and attains a finite value of $Y = (1 - D_1 D_2) n_M/m\sigma s_0$ for $X = 0$ ($\theta = 1$), as apparent from Eq. (9a). For both variants in the case of the second order, Y increases to infinity in this limit (Fig. 2). A plot of Y against X , based on experimental data,

leads to the determination of the multiplier $ms_0\sigma/n_M$ and enables one to estimate the adsorption order. In the case of adsorption of the first order, which gives a linear plot of Y vs X , the product of D_1D_2 can also be determined. In the case of dissociative adsorption, however, the decision between the two possible variants is difficult. For their distinguishing, it is convenient to introduce the following transformation of coordinates:

$$R = \frac{1}{\Theta} - \varepsilon \frac{1 - \Theta}{\Theta^2}, \tag{10a}$$

$$Z = \frac{1}{\Theta} + \frac{1 - \Theta}{\Theta^2} \ln(1 - \Theta). \tag{10b}$$

In this way, equations (6a-c) acquire the form

$$(K1) \quad R = D_1D_2 + (1 - D_1D_2)Z, \tag{11a}$$

$$(K2_1) \quad R = D_1D_2 + (D_1 - D_1D_2)Z, \tag{11b}$$

$$(K2_2) \quad R = D_1D_2. \tag{11c}$$

Thus, the nonlinear dependence of Θ on ε is linearized for all three variants of our model. Typical dependences are shown in Fig. 3. The constants D_1 and D_2 can be determined either from the limiting values of R or from the slope of the dependences of R on Z . The variable Z lies in the interval $\langle 0.5, 1 \rangle$ for $\Theta \in \langle 0, 1 \rangle$.

In the case of adsorption of the first order, we have $R = 1$ for $Z = 1$ regardless of the values of D_1 and D_2 . For $Z = 0.5$, $R = (1 + D_1D_2)/2$. For adsorption of the

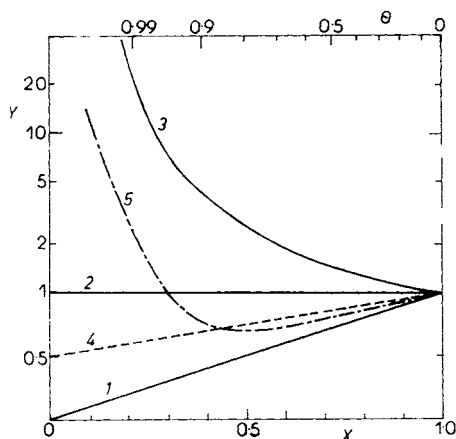


FIG. 2
 Dependence of Y on X (first transformation).
 Multiplying factor $n_M/ms_0 = 1$. 1 Constant sticking probability; 2 Langmuir model of first order; 3 Langmuir model of second order; 4 Kisliuk model of first order ($K1$), $D_1D_2 = 0.5$; 5 Kisliuk model of second order ($K2_1$), $D_1 = 0.9$, $D_2 = 1$

second order with a precursor above one adsorption center ($K2_1$), we have $R = (D_1 + D_1 D_2)/2$ for $Z = 0.5$, and $R = D_1$ for $Z = 1$. In the case of adsorption of the second order with a precursor above two neighbouring centers, R is constant in the whole interval. Limiting cases $R = 1$, $R = Z$, and $R = 0$ correspond to constant sticking probability and Langmuir model of the first and second order. If the experimental data are plotted in the Z, R coordinates, the adsorption order and the constants D_1 and D_2 can be reliably determined. Difficulties may occur if (a) for variant ($K2_1$) the constant $D_1 \approx 1$; this variant can then hardly be distinguished from ($K1$); (b) for variant ($K2_1$) the constant $D_2 \approx 1$, leading to difficult distinction from variant ($K2_2$).

To overcome these difficulties, the constants D_1 and D_2 must be examined more closely. The first of them can be expressed as

$$D_1 = (1 + k_D/k_A)^{-1}. \quad (12)$$

If we use the rate constants in the usual form

$$k_i = v_i \exp(-E_i/RT) \quad (13)$$

and assume that $E_D > E_A$, then $1 > D_1 > (1 + v_D/v_A)^{-1}$ for $0 < T < \infty$. Analogously, the constant D_2 (for $k_M > 0$)

$$D_2 = (1 + k_D/k_M)^{-1} \quad (14)$$

obeys the inequality $1 > D_2 > (1 + v_D/v_M)^{-1}$ for $E_D > E_M$ in the same temperature interval. It is apparent that both D_1 and D_2 depend markedly on the temperature.

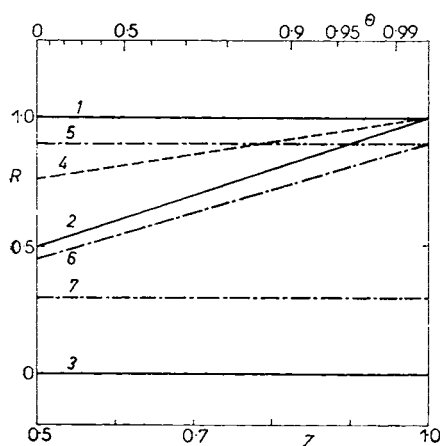


FIG. 3

Dependence of R on Z (second transformation). 1 Constant sticking probability; 2 Langmuir model of first order; 3 Langmuir model of second order; 4 Kisliuk model of first order ($K1$), $D_1 D_2 = 0.5$; 5 Kisliuk model of second order ($K2_1$), $D_1 = 0.9$, $D_2 = 1$; 6 as 5, but $D_2 = 0$; 7 Kisliuk model of second order ($K2_2$), $D_1 D_2 = 0.3$

Hence, the mentioned difficulties in distinguishing the variants can be overcome by studying adsorption at several different temperatures.

The characteristic feature of the method described is the considerable sensitivity of the transformations to the determination of the instant of surface saturation and the limiting value Y_0 . As can be seen from Fig. 1, the coverage in the case of adsorption with a mobile precursor attains rapidly a value around 95% and further changes only slowly. It is therefore rather difficult to find out at which exposition the limiting coverage is attained, and the experimental curve may be normalized by using a not too accurate value. The influence of such inaccuracy on the Y - X and R - Z dependences is shown in Figs 4 and 5.

In the case of the Y - X dependence (Fig. 4), an error in the determination of the limiting coverage causes the same error in the determination of the multiplying factor. However, it has a considerable influence on the character of the dependence and can cause confusion of the molecular with the dissociative mechanism, if no other representation is used.

In the case of the R - Z dependence, the deviations are notable especially in the boundary regions. Overestimation of the coverage (*i.e.* attributing the value of $\theta = 1$ to a not quite saturated surface) leads only to slight errors, whereas under-

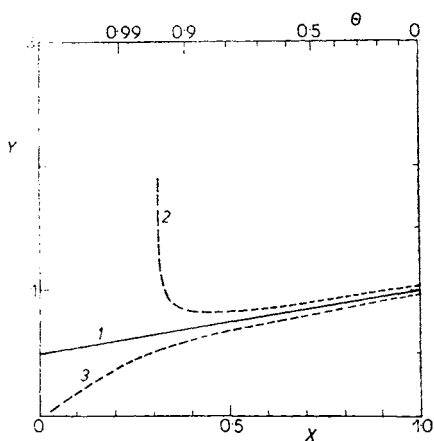


FIG. 4

Dependence of Y on X — influence of incorrect determination of limiting coverage. Multiplying factor $n_M/m\sigma s_0 = 1$. 1 Kisliuk model of first order (K1), $D_1 D_2 = 0.5$; 2 coverage overestimated by 5%; 3 coverage underestimated by 5% (experiment finished prematurely)

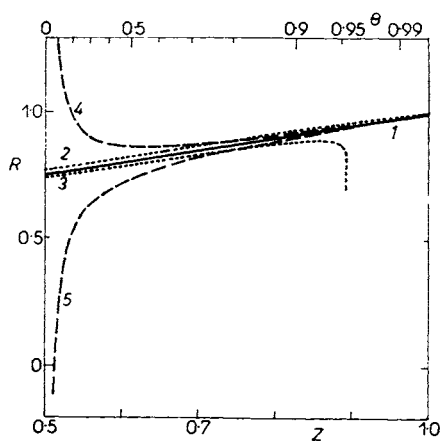


FIG. 5

Dependence of R on Z — influence of incorrect determination of limiting coverage and Y_0 . 1 Kisliuk model of first order (K1), $D_1 D_2 = 0.5$; 2 coverage overestimated by 5% (experiment finished prematurely); 3 coverage underestimated by 5%; 4, 5 $\pm 5\%$ error in the determination of Y_0

estimation leads to nonlinearity for $Z \rightarrow 1$. An error in the value of Y_0 leads to large deviations for $Z \rightarrow 0.5$. Nonlinearity in this representation indicates that either the limiting coverage or the value of Y_0 was incorrectly determined. If changes of these values in the range of a few per cent do not lead to linearization of the R - Z dependence, it can be assumed that the real situation does not correspond to the assumptions inherent in the model used, which is therefore unsuitable for the description of the experimental data.

REFERENCES

1. Kisliuk P.: J. Phys. Chem. Solids 3, 95 (1957).
2. Kisliuk P.: J. Phys. Chem. Solids 5, 78 (1958).
3. Cassuto A., King D. A.: Surface Sci. 102, 388 (1981).
4. Hayward D. O., Trapnell B. M. W.: *Chemisorption*, p. 87. Butterworths, London 1964.
5. King D. A., Wells M. G.: Proc. Roy. Soc. (London) A 339, 245 (1974).
6. Kohrt C., Gomer R.: J. Chem. Phys. 52, 3283 (1970).
7. Kohrt C., Gomer R.: Surface Sci. 40, 71 (1973).
8. Schönhammer K.: Surface Sci. 83, L 633 (1979).

Translated by K. Micka.