

The Kinetics of Adsorption on a Nonuniform Surface

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The Roginsky-Zeldovich-Elovich equations describing the rates of chemisorption of gases onto solid surfaces are adequately accounted for in the case of nondissociative adsorption by assuming a surface consisting of only three to five sets of sites, each set comprising about the same number of sites. The rate constants for the adsorption onto these sets must fall within certain limits but the variation permissible is sufficient to allow appreciable variation between the sets in the activation energy for adsorption. The model can be extended to include a desorption process.

The Roginsky-Zeldovich-Elovich (R.Z.E.) equations have found wide application in the description of rates of chemisorption of gases onto solid surfaces (1): They are usually tested in two forms:

$$dq/dt = a \exp(-bq) \quad (1)$$

and

$$q = (1/b)[\ln(t + t_0) - \ln t_0] \quad (2)$$

where q is the quantity adsorbed in time t , a and b are constants and

$$t_0 = 1/ab \quad (3)$$

Equation (1) is usually employed in the logarithmic form

$$\ln(dq/dt) = \ln(a) - bq. \quad (4)$$

Examination of the literature shows that in most of the cases where R.Z.E. kinetics are reported only Eq. (2) has been used,* and plots of q vs. $\log(t)$ or $\log(t + t_0)$ (where t_0 is "an arbitrary constant to linearize the plot at small t ") are often reasonably linear over two to four powers of 10 in t . Abrupt inflections are sometimes met with, and the reason for these, and the significance of changes in a and b (or b and t_0) as the temperature or pressure is changed

* For example, the results of Burwell and Taylor (5), used by Taylor and Thon (6) to illustrate the use of Eq. (2) are specifically stated by Burwell and Taylor *not* to obey Eq. (1).

continue to be the subject of much discussion.

Probably the most widely accepted explanation for the R.Z.E. equations is that in which the surface is treated as an array of sets of sites of different adsorption potential, x , each with an activation energy for adsorption, ϵ , where

$$\epsilon = rx \quad (0 < r < 1) \quad (5)$$

Halsey's equations (2), or similar ones derived by Brunauer, Love, and Keenan (3), can be integrated over the whole surface with certain simplifying assumptions (2, 4), to yield essentially Eqs. (1) and (2). Halsey describes his model as a continuously non-uniform surface and in fact any model in which sites become progressively filled as a result of the surmounting of a potential barrier which increases regularly with coverage will give the R.Z.E. equations. The model is physically not unreasonable but lacks definition since the mathematical manipulations imply a near-infinite range of sets of sites, each set associated with its own activation energy, although of course contributions to the adsorption process from sites above a certain ϵ_{\max} will be negligibly small.

From reading many original papers in which R.Z.E. kinetics of adsorption are reported and also a recent review article (1) the impression is obtained that observa-

tion of adherence to R.Z.E. kinetics exercises a strong inhibitory action upon most authors: Usually no detailed discussion of the surface geometry is attempted. This may well be because of the generally held belief that these kinetics imply a continuously nonuniform surface with an infinity, or at least a very large number, of sets of sites. In an attempt to remove this inhibition it is the purpose of this paper to demonstrate in the most general terms that a large number of sets of sites is not necessary, three to five sets being sufficient provided the ratios of the rates of adsorption on the sets fall within a certain range.

Most surfaces which have been studied (metal films or finely divided powders) would be expected to expose only a small number of different crystal faces to the gas phase, and on each we might expect only a small number of different types of adsorption site. Thus any surface would be expected to comprise less than say 20 different sets of sites (as determined by rates and activation energies of chemisorption). It is quite likely that the effective number of different sets will be much less than this.

Consider a surface of n sets of sites, each capable of adsorbing N molecules at saturation under the conditions of pressure and temperature used so that $N_1 = N_2 = N_3 = \dots = N_n = N$. Ignore for the moment desorption and assume no surface mobility between sets so that each set is effectively isolated from the others. Then on each set the rate of adsorption at any time, t , is

$$(d\theta_j/dt) = k_j(1 - \theta_j), \quad (6)$$

where θ_j is the fractional coverage at t and k_j includes the rate constant for the set and any normalization (pressure/volume) terms depending on the experimental conditions.

Then

$$1 - \theta_j = \exp(-k_j t) \quad (7)$$

Over the whole surface

$$\frac{d\theta_s}{dt} = \frac{1}{n} \sum_1^n \left(\frac{d\theta_j}{dt} \right) = \frac{1}{n} \sum_1^n k_j \exp(-k_j t) \quad (8)$$

and

$$\theta_s = \frac{1}{n} \sum_1^n \theta_j = 1 - \frac{1}{n} \sum_1^n \exp(-k_j t) \quad (9)$$

The extension of these equations to the case when the number of sites in each set is different is obvious. The problem is then to determine whether, on this model, for small n and any reasonable choice of k_j , values of $d\theta_s/dt$ and θ_s from Eqs. (8) and (9) satisfy Eqs. (1)–(4): Clearly under the conditions stated θ_s can be written for q in these equations.

The matter does not appear to be susceptible to analytic treatment, so that a few simple cases have been examined by direct computation. For ease of calculation the rates k_j have been taken to be e or simple fractions of e . Since we are effectively concerned only with the ratios between the various k_j , the conclusions are perfectly general.

Consider first the case of a uniform surface, i.e. one with one set of sites, adsorbing according to Eq. (6). Figure 1 shows plots of $\log(d\theta/dt)$ vs. θ and $\log(\text{time})$ vs. θ where $k = 2.3$; also shown is the plot of $\log(\text{time} + 0.1)$ vs. θ , i.e. Eq. (2) with $t_0 = 0.1$. This latter plot is adequately linear from $\theta = 0.02$ to $\theta = 0.9$ over $t = 0.01$ to $t = 1.0$ and we conclude that Eq. (2) by itself is not an adequate test of the R.Z.E. relationship unless it is obeyed over a variation of 10^3 or more in time. It is also evident from the figure that the $\log(\text{rate})$ vs. θ plot is approximately linear up to $\theta \approx 0.7$, by which time the rate has fallen to about one-third of its initial value: Thus in this case also care is needed when considering linear $\log(\text{rate})$ vs. θ plots, particularly when the rate of adsorption does not change very much during the period of observation.

Figure 2 shows plots of Eq. (2) and Eq. (4) calculated by means of Eq. (8) and (9) with $t_0 = 0$, for a surface of three sets of sites with $k_1 = e$, $k_2 = e/30$ and $k_3 = e/1000$. The plot of Eq. (4) clearly reveals the presence of the three sets but the plot of Eq. (2) with t_0 is satisfactorily linear over nearly 10^4 in t . The correction of t by using $t_0 = 0.1$ [cf. Eq. (2)] will extend the linear range by another power of 10 and bring the first point at

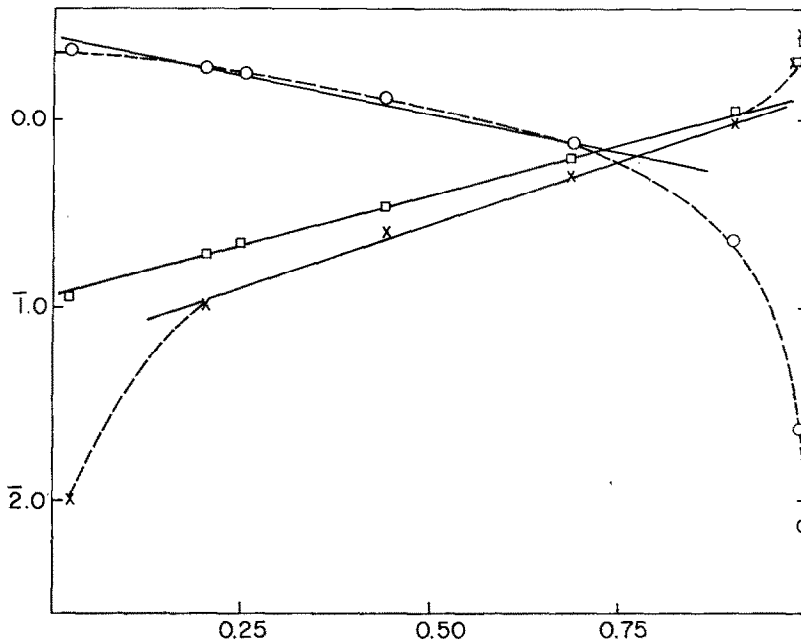


FIG. 1. Adsorption according to Eq. (6), \odot , $\log(d\theta/dt)$ vs. θ ; \times , $\log(t)$ vs. θ ; \square , $\log(t + 0.1)$ vs. θ .

$t \approx 0.01$ onto the line without altering the linearity of the rest of the plot. Even though Fig. 2 shows the presence of the three sets the relationship is approximately linear from $\theta = 0.15$ to $\theta = 0.95$, the greatest deviation from the line drawn occurring around $\theta = 0.70$ where the rate from Eq. (4) is about 0.5 that required for a linear relationship. Experimentally such a deviation would be missed if no measurements happened to be taken between $\theta = 0.67$ and 0.77 : The rather smaller deviation around $\theta = 0.40$ might well be within the normal experimental error since accurate measurements of rates of adsorption (which should ideally be taken under constant pressure) are difficult to obtain.

Figure 3 shows a similar plot of the same data with the addition of two more zones, with $k_4 = e/5$ and $k_5 = e/160$. The plot of Eq. (4) is now reasonably linear from $\theta \approx 0.2$ to 0.85 while the linearity of Eq. (2) has been if anything further improved; again a small value of t_0 will bring the first point on to a linear plot without affecting the remainder.

With suitable choice of the ratios k_1/k_2 , k_2/k_3 both Eq. (2) and Eq. (4) give plots of

adequate linearity for a surface of three zones; thus the use of $k_1 = e$, $k_2 = e/10$, $k_3 = e/100$ gives a plot of $\log(\text{rate})$ vs. θ which is reasonably linear from $\theta = 0.2$ to 0.85 and a $\log(\text{time})$ vs. θ plot (with $t_0 = 0$) linear from $t \approx 0.1$ to 40 . In general it appears that the $\log(\text{time})$ vs. θ plots are linear except for the very first stages of the adsorption, over a range of time equal to about 10 times the ratio k_1/k_n where k_1 is the fastest rate and k_n the slowest; use of a small value of t_0 will extend this linearity by at least another power of 10. In this model it is evident that both Eq. (2) and Eq. (4) will fail to hold during the final stages of the adsorption when the last sites on the slowest zone will be filling up. No model which assumes a small number of sets of sites and adsorption according to Eq. (6) can avoid this. It is also to be noted that with a finite number of sets of sites, and finite values of k_j the extrapolation of the $\log(\text{rate})$ vs. θ plot to $\theta = 0$ will always give initial rates of adsorption greater than the true initial rate, which is equal to

$$\frac{1}{n} \sum_{j=1}^n k_j$$

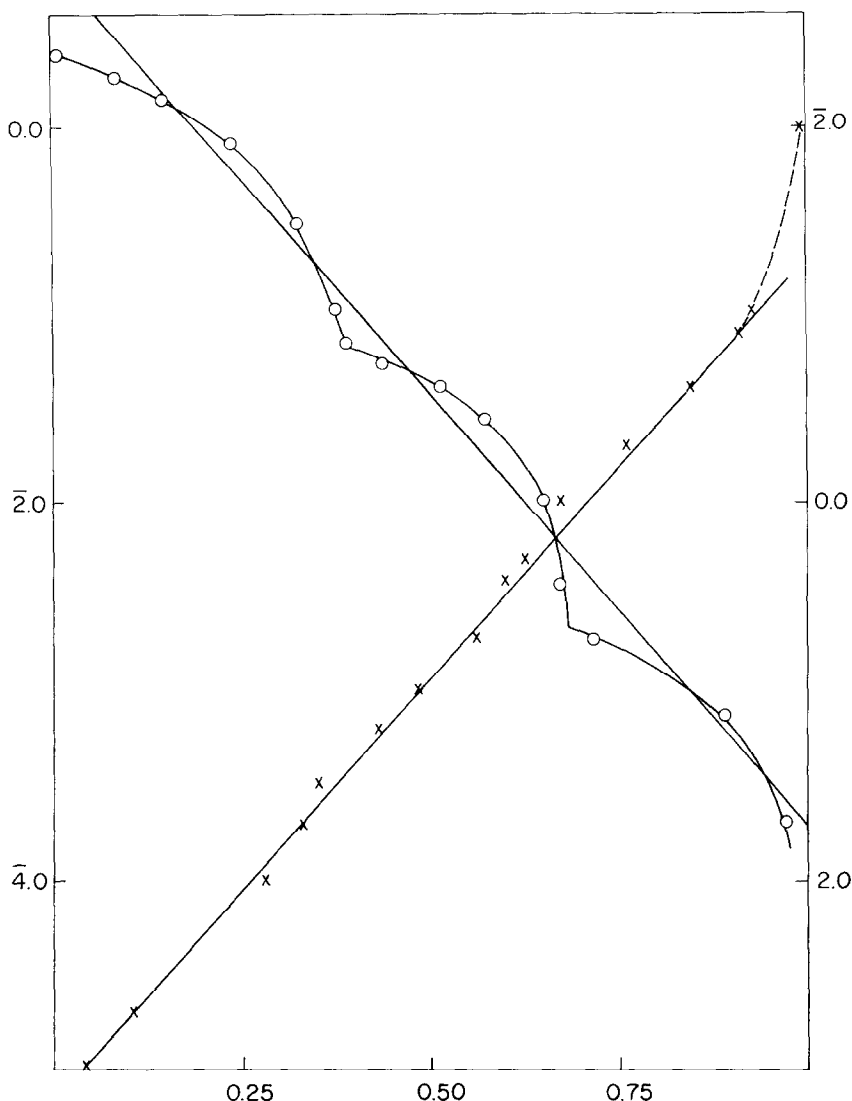


FIG. 2. Plots of Eqs. (2) and (4); \odot , $\log(d\theta/dt)$ vs. θ ; \times , $\log(t)$ vs. θ .

This is evident from the form of Eqs. (6)–(9) and the weight given to the rates at higher values of θ when drawing the best straight line through the $\log(\text{rate})$ vs. θ data. The discrepancy is evident in Figs. 2 and 3.

The model can be extended to include the adsorption of the first portion of gas immeasurably rapidly, i.e. by adding another set of sites, which we will call the zero set, and putting $k_0 = \infty$. This was tested for the case $k_1 = e$, $k_2 = e/10$, $k_3 = e/100$, retaining the assumption that the number of sites in each set is equal. The instantaneous adsorption

to $\theta = 0.25$ alters the slopes of the $\log(\text{rate})$ vs. θ and $\log(\text{time})$ vs. θ plots (and also the value of t_0) but the data still conform to Eqs. (2) and (4) although since the observable range of Eq. (4) (with $\theta = q$) is reduced from $\theta = 0-1$ to $\theta = 0.25-1$ some contraction in range is inevitable. Both plots of Eq. (4) showed a satisfactory linear relationship from $\log(\text{rate}) = 0.2$ to $\log(\text{rate}) = 3.8$. It is not even necessary to keep the restriction that $N_1 = N_2 = N_3$, etc., although it is clear that for a given choice of the constants k_j not too wide a variation in N_j is permis-

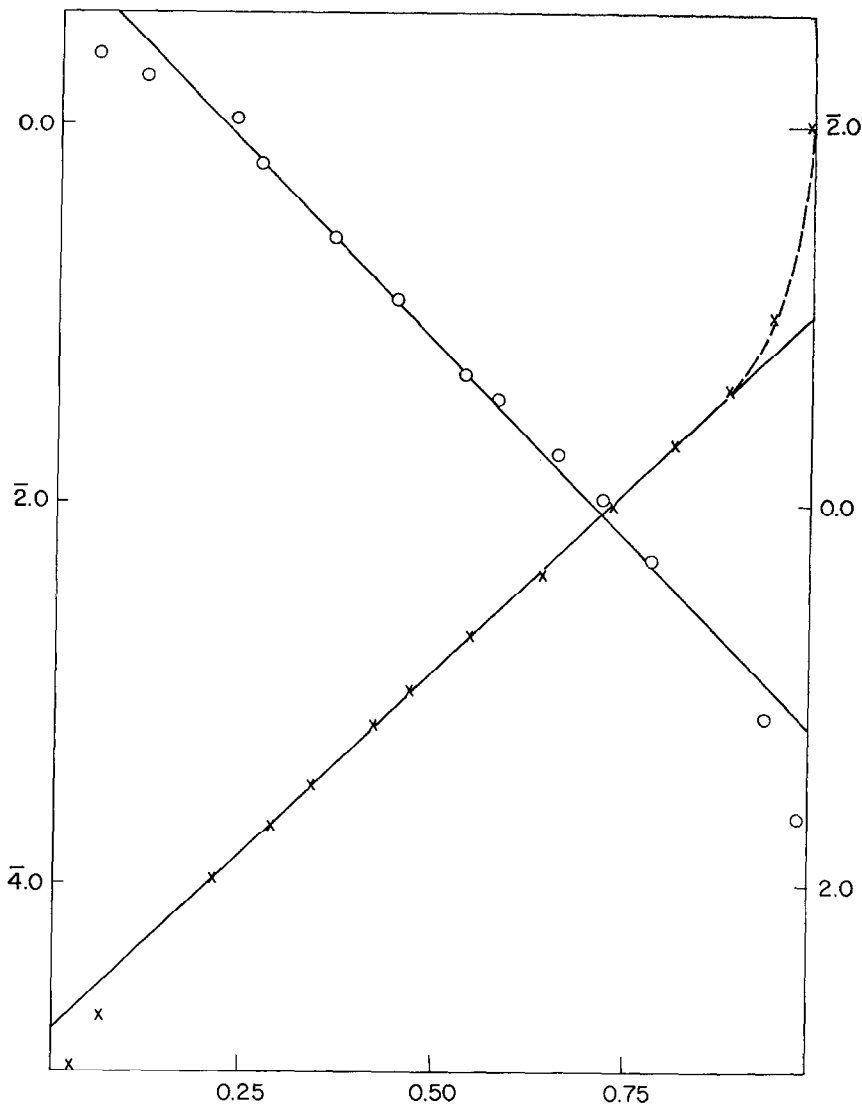


FIG. 3. Data of Fig. 2 with two zones added; \circ , $\log(d\theta/dt)$ vs. θ ; \times , $\log(t)$ vs. θ .

sible. Proper examination of this point by direct calculation over a wide range of k_j is tedious but might perhaps be a suitable subject for examination by computer.

It is to be noted that on the model proposed, when the k_j are so chosen that Eqs. (2) and (4) are obeyed, the values of b obtained from the slopes of the plots of these two equations are equal, so that the model is consistent with both these equations—an essential requirement if it is to provide a satisfactory explanation of the R.Z.E. relationship. Thus from Fig. 3, $b = 2.05e$ from

the plot of Eq. (4) and $1.99e$ from Eq. (2) with $t_0 = 0$; similarly the three-zone case discussed in the last two paragraphs gives $b = 3.24e$ and $= 3.14e$, respectively. Even in the case of one zone (a uniform surface with $k = e$) $b = 0.8e$ from Eq. (2) and $1.08e$ from Eq. (4) with $t_0 = 0.1$. The values of b bear no simple relationship to $\sum_1^n k_j$ which is equal to $1.24e$ in the first case, $1.11e$ in the second, and $1.0e$ in the third. In the three- or five-zone models considered the value of t_0 is too small and its choice too arbitrary—depending on the degree of fit

it is required to achieve to Eq. (2) at very small t —to make it worthwhile to discuss the evaluation of [Eqs. (1) and (3)] from Eq. (2) and (3). It has been noted earlier that the extrapolation of Eq. (4) to $\theta = 0$ will always give incorrect values of a , the discrepancy increasing with increase in the slope of the plot of Eq. (4). For these reasons we attach little significance to values of a which have been reported in the literature; they may on occasion bear some relationship to the initial rate of adsorption, but this is uncertain.

The k_j will usually be temperature dependent, and a plot of $\log(d\theta/dt)$ at constant θ vs. $1/T$ will give the variation of the activation energy for adsorption, E_θ at various θ : A plot of E_θ vs. θ yields by extrapolation values of E at $\theta = 0$ and 1. It is normal for E_θ so determined to increase more or less linearly with increasing θ , giving a positive value of ΔE , often lying between 1 or 2 and say 15 kcal mole⁻¹ where

$$\Delta E = E_{\theta=1} - E_{\theta=0} \quad (10)$$

and indeed this (or some equivalent variation) appears as an essential part of almost all theories so far proposed which lead to the R.Z.E. kinetics. When we consider only a small number of sets of sites however, it is clear that, particularly over a restricted temperature interval, there is no reason why ΔE should not be negative, i.e. E may decrease as θ increases.

As an indication of the ability of the three-five-set surface to accommodate appreciable values of ΔE consider the case when $E_{\theta=0}$ is zero and ΔE is 10 kcal mole⁻¹. Then if we begin with a surface of three sets with rates at 300°K proportional to e , $e/10$, and $e/100$, those with a linear variation of E become e , $e/30$, $e/1000$ approximately at 260°K (or at 350°K if ΔE is negative). As we have seen, a three-set surface with these rate constants does not give an entirely satisfactory plot of Eq. (4) but the addition of one or two more sets of intermediate rates, $e/5$ and $e/150$, will do so: Inclusion of two similar intermediate sets in the surface at 300°K will not affect the linearity of the plot of Eq. (2) and (4) at that temperature. Obviously if the value of ΔE is decreased the temperature range may be increased accordingly.

The effect of the inclusion of a desorption process may be written for the simplest case of nondissociative adsorption

$$d\theta_j/dt = k_j(1 - \theta_j) - k'_j\theta_j \quad (11)$$

$$= k_j(1 - m\theta_j), \quad (12)$$

where

$$m = (k_j + k'_j)/k_j \quad (13)$$

On integration

$$\begin{aligned} 1 - m\theta_j &= \exp(-mk_jt) \\ &= \exp[-(k_j + k'_j)t] \end{aligned} \quad (14)$$

Since at equilibrium $d\theta_j/dt$ is zero we see from Eq. (11) that addition of a desorption process reduces the value of N_j for the set to N_j/m ; The weighted values of $d\theta_j/dt$ and of θ_j to be used in Eqs. (8) and (9) must be similarly reduced. Thus if only one set is subject to desorption the net effect is to reduce the importance of this set relative to the others. If desorption is an activated process that set will normally drop out of the picture as the temperature is raised. Such a progressive elimination of sets, coupled with the gradual appearance of desorption in the remaining sets and parallel introduction of new sets, less accessible energetically, would in the case of positive ΔE allow the extension of the restricted set model to activated adsorption/desorption processes over a much wider temperature range than that envisaged above without ever considering more than three or four sets at any one temperature.

Dissociative adsorption yields expressions which are too complicated for the simple treatment adopted here; calculations are tedious but indicate that the effect is in general similar to that of the simpler case discussed in the previous paragraph.

REFERENCES

1. LOW, M. J. D., *Chem. Rev.* **60**, 267 (1960).
2. HALSEY, G. D., *J. Phys. Chem.* **55**, 21 (1951).
3. BRUNAUBER, S., LOVE, K. S., AND KEENAN, R. G., *J. Am. Chem. Soc.* **64**, 751 (1942).
4. PORTER, A. S., AND TOMPKINS, F. C., *Proc. Roy. Soc.* **A217**, 529 (1953).
5. BURWELL, R. L., AND TAYLOR, H. S., *J. Am. Chem. Soc.* **58**, 697 (1936).
6. TAYLOR, H. A., AND THON, N., *J. Am. Chem. Soc.* **74**, 4169 (1952).