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Analysis of Second-Order Desorption Kinetics in Temperature-Programmed Desorption

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Following the lines of thought of R. J. Cvetanović and Y. Amenomiya [*in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 103. Academic Press, New York, 1967], a mathematical analysis of second-order temperature-programmed desorption (TPD) spectra in the case of freely occurring readsorption is presented. Some critical remarks are made about the use of equations relating the temperature of the peak maxima to the enthalpies of adsorption, both for first- and second-order desorption kinetics. The shapes of the theoretical lines describing second-order desorption at several values of enthalpy of adsorption and initial coverage are calculated.

INTRODUCTION

In the literature (*1–6*), several methods are presented for the analysis of desorption spectra obtained in temperature-programmed desorption (TPD). Most of these deal with first- and second-order desorption from monoenergetic surface sites *in the absence of readsorption*, an experimental situation often encountered in UHV studies on desorption of gases from metal films and well-defined crystallographic planes.

Cvetanović and Amenomiya (*3, 4*) designed an apparatus with which the TPD spectra of gases desorbing from oxides, metal powders, and supported catalysts are measured in a stream of inert carrier gas (helium or argon). The equations derived by these authors describe the desorption kinetics both when readsorption is absent and when *readsorption can occur freely*.

In the former case, the flow rate of the carrier gas is chosen so high that the partial pressure of the desorbing gas above the adsorbent is low enough to limit the rate of readsorption to so small a fraction of the rate of desorption that, in fact, pure desorption kinetics are studied. In the second case, the flow rate of the carrier gas is chosen so low as to render the rate of adsorption practically equal to the rate of desorption; in this situation, one, in fact, measures the rate at which the adsorption equilibrium shifts to the gas-phase side.

In studying hydrogen chemisorption on metals, the activation energy of adsorption is usually zero, and a simple preliminary calculation on the basis of Eyring's (7) reaction-rate theory shows that desorption without readsorption cannot be realized unless the flow rate of the carrier gas is set at 10^4 liters/g of sample/hr or more, which is hardly feasible. Therefore, in analyzing spectra of temperature-programmed hydrogen desorption from metals or metal-on-

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carrier catalysts, one should make allowance for the occurrence of readsorption.

In this article, we present a mathematical analysis of TPD spectra for *second-order* desorption attended by readsorption. The results will be compared with the equations published for the first-order case by Cvetanović and Amenomiya (*3*, *4*); further critical remarks will be made about the practical application of equations relating the temperature at the maximum of the desorption peak, T_M, to the enthalpy of adsorption. Finally, the so-called lineshape analysis of desorption peaks will be discussed.

THEORY FOR SECOND-ORDER TPD WITH FREELY OCCURRING READSORPTION

We proceed from the assumption that, as in most TPD studies, the heating schedules are linear with time. Then:

$$T = T_0 + \beta t, \tag{1}$$

where T is the temperature at time t, T_0 is the temperature at time zero (start of the desorption run), t is the time, and β is the heating rate coefficient, which is chosen between 1 and 30°C/min.

The rate of desorption of an adsorbate dissociatively adsorbed, under conditions in which the desorbed gas can readsorb freely, may be represented by:

$$-\frac{d\theta}{dt} = k_d\theta^2 - k_a\frac{p}{p_0}(1-\theta)^2, \tag{2}$$

where θ is the coverage of a certain adsorbed state, t is the time, k_d is the rate constant for desorption, k_a is the rate constant for adsorption, and p/p_0 is the pressure of the desorbing gas above the adsorbent divided by the total pressure (1 atm).

Equation (2) is valid only if the enthalpies and entropies of activation during the desorption process are constant, with the exception of the localization entropy, represented by the Langmuir terms θ^2 and $(1-\theta)^2$. Furthermore, there should be enough mobility in the adsorbed layer to bring the dissociatively adsorbed species together by means of an activated surface migration process, the kinetics of which should not be rate determining. The activation energy of surface migration being only about 10% of the activation energy of desorption, this will usually be the case. Lapujoulade and Neil (*8*) have shown that, in the case of hydrogen chemisorption on Ni (111), the partition function of activated migration of hydrogen atoms over the surface is about 1, which means that the translational entropy inherent in this migration is virtually 0.

It is appropriate to choose the pressure divided by 1 atm as a variable in Eq. (2). Then, k_d and k_a in Eq. (2) both have the dimension seconds^{-1}, so that, in the equation describing the adsorption equilibrium:

$$K = k_d/k_a = \exp(\Delta S/R) \times \exp(-\Delta H/RT), \tag{3}$$

K, the reciprocal adsorption equilibrium constant, becomes a dimensionless number, just like $\exp(\Delta S/R)$ and $\exp(-\Delta H/RT)$. In Eq. (3), ΔS is the differential entropy of adsorption, and ΔH is the differential enthalpy of adsorption.

Equation (2) may be written in the form of a material balance by equating the amount of gas detected in the carrier gas stream per unit time to the amount of gas desorbing per unit time:

$$FC = -V_s v_m(d\theta/dt) = v_m V_s k_d\theta^2 - v_m V_s k_a C(1-\theta)^2. \tag{4}$$

In Eq. (4), V_s is the volume of the solid phase in the catalyst bed, v_m is the amount of gas adsorbed at full coverage per unit volume of the solid phase in a certain adsorbed state, F is the carrier gas flow rate, and C is the mole fraction of the desorbing gas in the 1-atm carrier gas stream and, hence, equal to the hydrogen pressure divided by 1 atm.

Cvetanović and Amenomiya (3), in presenting the first-order analog of Eq. (4), made a mistake in that they omitted v_m in the second right-hand term of their Eqs. (3) and (4).

Combining Eqs. (1) and (4), we obtain:

$$-v_m\beta(d\theta/dT) = v_m k_d \theta^2 - v_m k_a C(1-\theta)^2. \quad (5)$$

From Eqs. (4) and (5) it follows that

$$C = -(v_s v_m \beta/F)(d\theta/dT), \quad (6)$$

and, from Eq. (4):

$$C = V_s v_m k_d \theta^2/[F + V_s v_m k_a (1-\theta)^2]. \quad (7)$$

When readsorption occurs freely, the net amount of desorbing gas per unit time, FC, is much less than the amount readsorbing per unit time, $V_s v_m k_a C(1-\theta)^2$; Eq. (7) then reduces to

$$C = \frac{k_d\theta^2}{k_a(1-\theta)^2} = K\frac{\theta^2}{(1-\theta)^2}, \quad (8)$$

where K, defined by Eq. (3), is the reciprocal value of the conventional equilibrium constant of adsorption, or

$$K = A^* \exp(-\Delta H/RT), \quad (9)$$

with A^* standing for $\exp(\Delta S/R)$. From Eqs. (6) and (8) it follows that:

$$-\frac{d\theta}{dT} = \frac{FK}{v_m V_s \beta}\frac{\theta^2}{(1-\theta)^2} = \frac{F\theta^2}{v_m V_s \beta (1-\theta)^2} \times A^* \exp(-\Delta H/RT). \quad (10)$$

At the peak maximum $dC/dT \equiv 0$; from Eqs. (8) and (10), therefore we obtain:

$$K_M = \frac{v_m V_s \beta}{F}\frac{(1-\theta_M)^3}{2\theta_M}\frac{\Delta H}{RT^2{}_M} = A^* \exp(-\Delta H/RT_M), \quad (11)$$

where K_M is the value of K at $T = T_M$, the temperature at the peak maximum, and θ_M is the coverage at $T = T_M$.

Equation (11) may be written in the logarithmic form:

$$2\log T_M - \log\beta = \frac{\Delta H}{2.303RT_M} + \log\left[\frac{(1-\theta_M)^3 V_s v_m \Delta H}{2\theta_M F A^* R}\right]. \quad (12)$$

For *first-order* desorption with freely occurring readsorption, Cvetanović and Amenomiya (3) arrived at:

$$2\log T_M - \log\beta = \frac{\Delta H}{2.303RT_M} + \log\left[\frac{(1-\theta_M)^2 V_s \Delta H}{FA^*R}\right]. \quad (13)$$

Recalculation showed this equation to be correct, except for omission of the factor v_m in the second term on the right-hand side of Eq. (13).

Application of Eqs. (12) and (13) to the Determination of ΔH

Measuring TPD spectra in the range of freely occurring readsorption has the advantage that the heat of adsorption, ΔH, can, under favorable experimental conditions, be directly derived from the peak maximum by means of Eqs. (12) or (13). Measurements in the absence of readsorption are more difficult to perform and, moreover, provide a less characteristic adsorption parameter, viz., the activation energy of desorption, which is equal to the heat of adsorption only if the adsorption is nonactivated.

Since, as will be shown later, θ_M varies very slightly with large variations of ΔH, the slope of the plot of $2\log T_M - \log\beta$ against $1/T_M$ should give the enthalpy of adsorption, at constant F and at constant θ_i. The coverage θ_i is the initial surface coverage which is highly determinative for the value of θ_M.

Similarly, variation of θ_M at constant F and β or variation of F at constant θ_M and β provides a means of determining ΔH from the shift in the position of the peak maximum T_M.

Some critical remarks have to be made with respect to the above methods of ΔH determination. First, θ_M and F appear in Eqs. (12) and (13) as logarithms, so that an experimental variation of these terms by a factor of at least 100 is required to determine ΔH with reasonable accuracy; in practice, however, such large variations are difficult to realize. Second, in the derivation of Eqs. (12) and (13), it was tacitly assumed that $A^* = \exp(\Delta S/R)$ and, hence, ΔS are temperature independent, but this does not hold in many cases. This point will be discussed further in the Results.

An alternate method for calculating ΔH from the position of the peak maximum is simply to fill in all measurable quantities, β, T_M, θ_M, V_s, v_m, and F, in Eq. (12) or (13) and to calculate A^* from the differential adsorption entropy at temperature T_M. Of course, this can only be done if the differential adsorption entropy is known with reasonable accuracy. Further, θ_M has to be calculated from the integrated peak surface area up to $T = T_M$, divided by the total peak surface area at $\theta_i = 1$. In the succeeding paper (*9*) we shall deal with the application of this procedure to a TPD study of hydrogen adsorption on palladium.

TABLE 1

Values of Surface Coverages at Peak Maximum (θ_M) for Second-Order Desorption with Freely Occurring Readsorption at Various Initial Coverages (θ_i)

ϵ^*_M	θ_M			
	$\theta_i = 1.0$	$\theta_i = 0.75$	$\theta_i = 0.50$	$\theta_i = 0.25$
10	0.6006	0.5018	0.3185	0.1512
20	0.4959	0.4430	0.2935	0.1412
33.33	0.4537	0.4143	0.2812	0.1365
40	0.4430	0.4066	0.2779	0.1353
50	0.4324	0.3988	0.2745	0.1340
66.67	0.4217	0.3908	0.2709	0.1326
100	0.4110	0.3827	0.2672	0.1312

The Theoretical Lineshape in Second-Order Desorption

Instead of determining ΔH from the position of the peak maximum, it can also be found by comparing the theoretical lineshapes for various values of ΔH with the measured lineshapes. As will be explained below, this can be done without knowledge of the adsorption entropy, provided this entropy is temperature independent. Furthermore, theoretical line shapes may serve as a tool in establishing whether the desorption is first or second order in coverage, or whether we are dealing with a single adsorption state or with a combination of states desorbing simultaneously.

First, it is necessary to evaluate θ_M, the coverage of an adsorbed state at $T = T_M$, as a function of θ_i and ΔH. Let us write $\epsilon^* = \Delta H/RT$ and $\epsilon^*_M = \Delta H/RT_M$ and introduce the following normalized quantities: $C_n = C/C_M$, where C_M is the mole fraction of the desorbing gas at the peak maximum; $T_n = T/T_M$, where T_M is the temperature when $dC/dT = 0$. We can then transform Eq. (10) into:

$$-\frac{d\theta}{dT_n} = \frac{\theta^2}{(1-\theta)^2}\,\frac{F}{v_m V_s \beta}\,T_M A^* \times \exp(-\epsilon^*_M/T_n), \qquad (14)$$

and, on substituting the value $(F/V_s v_m \beta)$ from Eq. (11), into:

$$-\frac{d\theta}{dT_n} = \frac{\theta^2}{(1-\theta)^2}\,\frac{(1-\theta_M)^3}{2\theta_M}\,\epsilon^*_M \times \exp(\epsilon^*_M)\exp(-\epsilon^*_M/T_n). \qquad (15)$$

It is important to note that the latter substitution causes A^* in Eq. (11) and A^* in Eq. (14) to cancel each other out, *so that all following equations, including the* *equation describing the line shape, are entropy independent.* However, this statement is valid only if A^* in Eq. (14) is temperature independent, since A^* in Eq. (11) is exclusively related to the entropy at the peak maximum T_M.

Integration of Eq. (15) between the limits θ_i and θ_M and between the corresponding temperature limits $T = 0$ and $T_n = T/T_M = 1$ gives:

$$\frac{2\theta_M}{(1-\theta_M)^3}\int_{\theta_i}^{\theta_M}\frac{(1-\theta)^2}{\theta^2}\,d\theta = \epsilon^*_M \exp(\epsilon^*_M) \times \int_0^1 \exp(-\epsilon^*_M/T_n)\,dT_n, \quad (16)$$

or

$$\frac{2\theta_M}{(1-\theta_M)^3}\left[\left(\frac{1}{\theta_M}-\frac{1}{\theta_i}\right) + \ln\left(\frac{\theta_M}{\theta_i}\right)^2 - (\theta_M-\theta_i)\right] = \epsilon^*_M \exp(\epsilon^*_M \cdot I_{(1)}), \quad (17)$$

where $I_{(1)}$ is the definite integral

$$\int_0^1 \exp(\epsilon^*_M/T_n)\,dT_n.$$

The values of the definite integral $I_{(1)}$ have been computed for $\epsilon^*_M = 10$, 20, 33.33, 40, 50, 66.67, and 100. For each of these ϵ^*_M values, θ_M has been evaluated from Eq. (17) for four different initial surface coverages ($\theta_i = 1$, 0.75, 0.50, and 0.25). The results are listed in Table 1.

If θ_M is known, Eq. (15) can be solved for θ as a function of ϵ^*_M, θ_i, and T_n. Via the transformation $x = \epsilon^*_M(1 - 1/T_n)$, we find:

$$-\frac{d\theta}{dx} = \frac{\theta^2}{(1-\theta)^2} \times \frac{(1-\theta_M)^3}{2\theta_M}\,\frac{\exp(x)}{(1-x/\epsilon^*_M)^2}, \quad (18)$$

where $\theta = \theta_M$ at $x = 0$.

Integration of Eq. (18) between the limits θ_M and θ and between the corresponding temperature limits $x = 0$ (for $T_n = 1$ and hence $T = T_M$) and x yields:

$$\theta - \frac{1}{\theta} - 2\ln\theta = \theta_M - \frac{1}{\theta_M} - 2\ln\theta_M - \frac{(1-\theta_M)^3}{2\theta_M}\int_0^x \frac{\exp(x)}{(1-x/\epsilon^*_M)^2}\,dx. \quad (19)$$

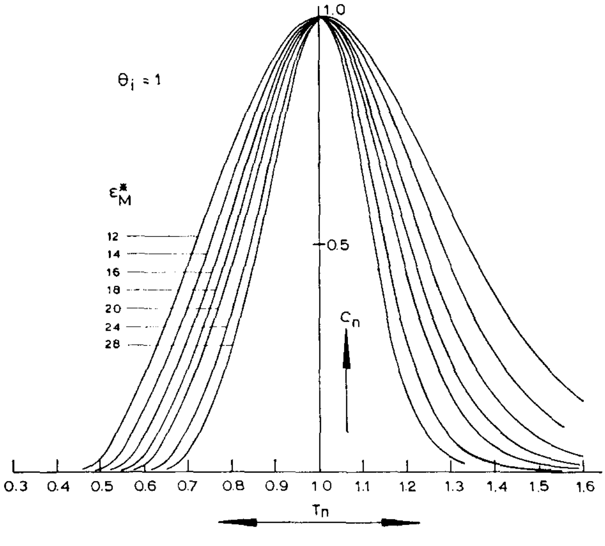

FIG. 1. Concentration of desorbing gas as a function of temperature (time), for second-order desorption with freely occurring readsorption. Normalized peak shapes are presented for various values of ϵ^*_M. Initial coverage $\theta_i = 1$.

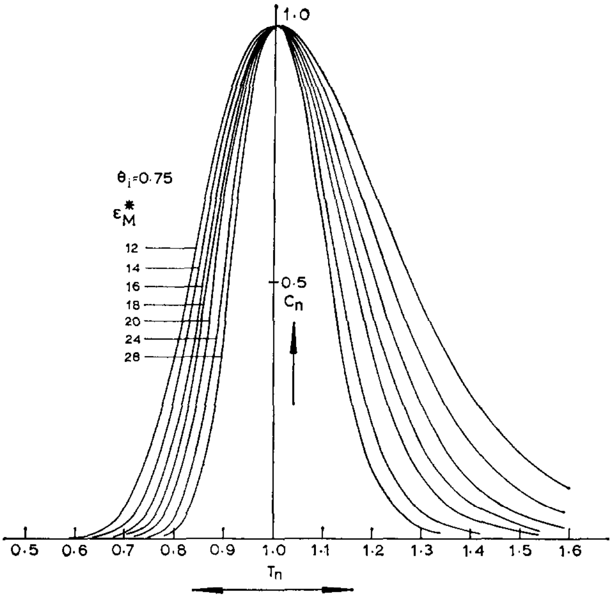

FIG. 2. As Fig. 1, except $\theta_i = 0.75$.

Equation (19) was used for computing the values of θ.

From Eq. (8), we can derive (with $C_n = C/C_M$):

$$C_n = \frac{\theta^2}{(1-\theta)^2} \frac{(1-\theta_M)^2}{\theta^2_M} \exp(x). \quad (20)$$

Now, C_n can be calculated as a function of T_n for chosen values of ϵ^*_M and θ_i.

RESULTS

Figure 1 shows the normalized peak shapes for second-order desorption with freely occurring readsorption, computed

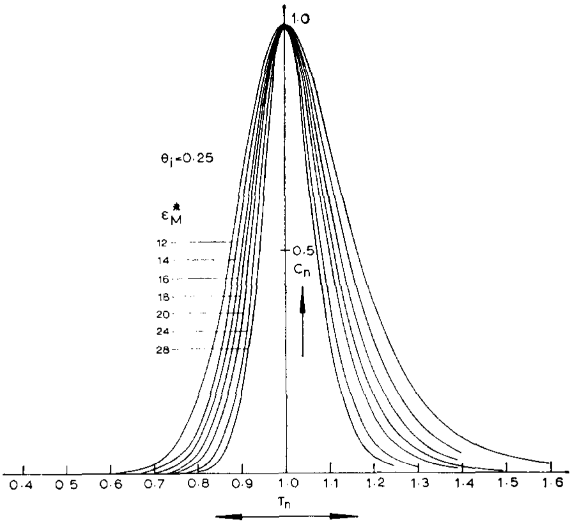

FIG. 3. As Fig. 1, except $\theta_i = 0.25$.

as indicated above for different values of ϵ^*_M, but for $\theta_i = 1$ in all cases. Similarly, Figs. 2 and 3 give the results for $\theta_i = 0.75$ and 0.25, respectively. It is interesting to compare our second-order results with those presented by Cvetanović and Amenomiya (*3*) for first-order desorption with freely occurring readsorption. This is done by plotting the half-value peak width (i.e., the width of the peaks at $C_n = 0.5$, in T/T_M units) as a function of the initial coverage θ_i, as shown in Fig. 4 for both first- and second-order desorption. It is seen that second-order peaks are appreciably broader than first-order peaks and that, even if the initial coverage is known with a rather low accuracy, a comparison between measured and theoretical peak shapes enables us to distinguish between first- and second-order desorption.

We wish to emphasize here that Figs. 1, 2, and 3 describe the peak shapes only if the enthalpy *and* entropy of adsorption are independent of coverage and temperature. This also holds for the line shapes presented by Cvetanović and Amenomiya (*3*) for first-order desorption with freely occurring readsorption. Constancy of adsorption entropy was not mentioned as a requirement by these authors.

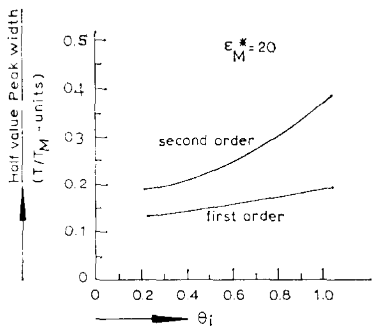

FIG. 4. Half-value peak width, as a function of initial coverage, for first- and second-order theoretical lineshapes, at $\epsilon^*_M = 20$. The first-order half-value peak widths are taken from Ref. (*3*).

Influence of the Temperature Dependence of the Entropy on the Theoretical Lineshape

In the case of dissociative adsorption of, e.g., hydrogen, on metals like nickel, palladium, and platinum, the total entropy of the hydrogen gas is lost on adsorption, the gas being adsorbed to immobility (*10, 11*), with the consequence that the adsorption entropy equals the entropy of the hydrogen gas at the reduced pressure. The statistical thermodynamic expression for A^* then reads [see Ref. (*7*)]:

$$A^* = \exp(S_{\mathrm{H}_2}/R) = \frac{(2\pi mkT)^{1.5}\cdot b_g}{h^3} \times \frac{8\pi^2 IkT}{h^2}\, g_{\mathrm{el}}\cdot g_{\mathrm{nuc}}, \quad (21)$$

and the temperature dependence of A^* can simply be written as:

$$A^* = \text{constant}\cdot T^{2.5}. \quad (22)$$

It is evident from this that, if the enthalpy of adsorption is determined from the shift in the position of the peak maximum T_M, a serious mistake can be made, because the left-hand side of Eq. (12) now reads $4.5 \log T_M - \log \beta$, instead of $2 \log T_M - \log \beta$. The influence that the temperature

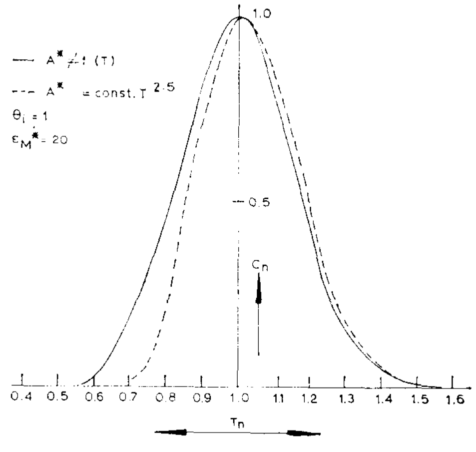

FIG. 5. Comparison of the lineshapes at $\epsilon^*_M = 20$ with (dashed line) and without (solid line) taking into account the temperature dependence of the adsorption entropy.

dependence of the entropy may have on the theoretical lineshapes is illustrated in Fig. 5, where the lineshape for $\epsilon^*_M = 20$ and $\theta_i = 1$, taken from Fig. 1 and valid for a temperature-independent adsorption entropy, is compared with the lineshape found when the entropy is temperature dependent, as is the case for dissociative hydrogen adsorption to total immobility. In the calculation of the lineshape, it is assumed that the adsorption entropy equals the experimentally determined entropy of the gas, in this case, hydrogen (*12*):

°K	S^0_T (e.u.)
300	31.00
400	32.98
500	34.53
600	35.79

These standard entropies obey Eqs. (21) and (22).

The temperature dependence of A^* changes the definite integral $I_{(1)}$ in Eq. (17) into:

$$I_{(1)} = \int_{0}^{1} \exp(-\epsilon^*_M/T_n) \cdot T^{2.5}_n dT_n. \quad (23)$$

From the revised Eq. (23), new values of θ_M can be derived.

The definite integral in Eq. (19) now reads:

$$\int_0^x \frac{\exp(x)}{(1 - x/\epsilon^*_M)^{4.5}} dx. \quad (24)$$

Numerical solution of this definite integral and introduction of a new value of θ_M into Eq. (19) allows one to compute values of θ as a function of x. Now, calculation of C_n is straightforward. The results are plotted in Fig. 5.

It is seen that, *in normalized coordinates*, the falling branch of the peak remains practically unchanged. However, a marked influence on the rising part of the peak is observed. The half-value peak width does not change appreciably.

A more detailed discussion of the consequences of a temperature-dependent adsorption entropy will be published elsewhere.

DISCUSSION

Temperature-programmed desorption with freely occurring readsorption in a stream of inert gas has various advantages. The method seems to lend itself very well for studying chemisorption on industrial samples, such as finely divided metals on oxide carriers or on metal blacks or sponges. As explained in this article, it is possible, in theory at least, to determine, for each adsorbed state, the population, the order of the desorption process, and the enthalpy of adsorption.

An important aspect of peak-shape analysis is that deviations from the ideal peak shape may point to nonvalidity of the suppositions made, i.e., constancy of the enthalpy and entropy as functions of coverage and temperature. Further, peak-shape analysis can assist in the proper separation of composite desorption peaks.

In the succeeding paper (*9*), we demonstrate the application of the mathematical analysis presented in this article in the study of hydrogen chemisorption on palladium and palladium-on-carrier catalysts.

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