THERMAL DESORPTION UNDER CONDITIONS OF FREELY OCCURRING READSORPTION: A METHOD FOR EVALUATION OF THE EXPERIMENTAL DATA

Jan PAVLÍČEK

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

Received January 25th, 1983

A method is proposed which permits to determine the differential enthalpy, differential entropy and kinetic order of desorption from the thermal desorption experiments carried out under close-to-equilibrium conditions. The main preference of the proposed method can be seen in the possibility to use for evaluation the entire range of the desorption curve, as well as, in the unified description of the most frequently used types of heating. The approximations enabling such a unified description lead to deviations which are, in major, mutually eliminated and the resulting error is therefore negligible if compared with the accuracy of the experimental data.

The temperature-programmed desorption in the flow of inert gas is a frequently used experimental technique, applied *e.g.* in the studies of the properties of supported catalysts. In a course of these experiments, the temperature of the adsorbent is raised in a pre-set way and the concentration of desorbed gas in an inert gas flow is measured. Using a proper selection of experimental conditions (flow rate of the inert, heating rate), it is possible to perform two different types of experiments. In the first case, readsorption is negligible against the desorption while, in the second case, readsorption plays a significant role and experiment proceeds under practically equilibrium conditions.

In the case of negligible readsorption the experimental data can be evaluated by a number of methods[1-4] proposed for flash-desorption experiments, since both the above mentioned processes can be described with formally identical mathematical expressions. A more complicated case occurs if the experiments were performed under conditions of freely occurring readsorption In such a case, it is possible to apply a method which evaluates[5] the change in position of the maximum, in dependence on the heating rate and initial surface coverage. Unfortunately, this method requires to vary the experimental conditions in such a wide range that they can be fulfilled only with difficulty. Another possibility is represented by the iteration method[6], comparing the experimental and theoretical desorption curves. This method is, nonetheless, rather complicated and requires to carry out several numerical integrations in each step.

A theoretical analysis of experimental conditions under which the desorption is either negligible or connected with freely occurring readsorption was described recently in several papers[7-9]. The authors came to the conclusion that in the case of porous materials, it is not only very difficult, but practically impossible to perform experiments in which readsorption would be negligible[9]. The more important is therefore the task to find a simple method permitting evaluation of the thermal desorption spectra obtained under conditions of freely occurring readsorption.

It is the aim of the present paper to propose a method modifying the earlier procedure suggested for the experiments of the first type[4] and permitting to use the entire range of the experimental curve.

THEORETICAL

The rate of desorption for the case of freely occurring readsorption can be expressed, on basis of the Langmuir model, by the equation

$$-\frac{\mathrm{d}\Theta}{\mathrm{d}t} = k_\mathrm{D}\Theta^\mathrm{m} - k_\mathrm{A}C(1 - \Theta)^\mathrm{m} \tag{1}$$

where Θ is the coverage, t is the time, k_A and k_D are the rate constants of adsorption and desorption, C is the mole fraction of desorbed gas in the gas phase and m is the kinetic order of desorption and adsorption, respectively. The mass balance per a unit time is given by the following expression[5]

$$FC = M_\mathrm{S}n_\mathrm{A}[k_\mathrm{D}\Theta^\mathrm{m} - k_\mathrm{A}C(1 - \Theta)^\mathrm{m}]\,, \tag{2}$$

where M_S is the mass of the adsorbent, n_A is the amount of gas (in mol) adsorbed per a unit mass of the adsorbent at a unit coverage and F is the inert gas flow in mol per second.

Combining expressions (*1*) and (*2*), we obtain a relation between the rate of desorption $-(\mathrm{d}\Theta/\mathrm{d}t)$ and the measured quantity C

$$-\frac{\mathrm{d}\Theta}{\mathrm{d}t} = \frac{F}{M_\mathrm{S}n_\mathrm{A}}C\,. \tag{3}$$

Substituting this relation into (*1*), we get for C

$$C = \frac{M_\mathrm{S}n_\mathrm{A}k_\mathrm{D}\Theta^\mathrm{m}}{F + M_\mathrm{S}n_\mathrm{A}k_\mathrm{A}(1 - \Theta)^\mathrm{m}}\,. \tag{4}$$

For the case of close-to-equilibrium desorption, it must hold[5] that $FC \ll M_\mathrm{S}n_\mathrm{A}k_\mathrm{A}C\,.\,(1 - \Theta)^\mathrm{m}$, so that the expression (*4*) can be transformed into

$$C = K\left(\frac{\Theta}{1 - \Theta}\right)^\mathrm{m}, \tag{5}$$

where

$$K \equiv \frac{k_D}{k_A} = \exp\left(\Delta S/\boldsymbol{R}\right) \exp\left(-\Delta H/\boldsymbol{R}T\right) \tag{6}$$

is the reciprocal value of the equilibrium constant of adsorption, ΔS is the differential entropy and ΔH the differential enthalpy of adsorption. After introduction of the symbols

$$A^* = \exp\left(\Delta S/\boldsymbol{R}\right) \tag{7a}$$

and

$$\varepsilon = \Delta H/\boldsymbol{R}T, \tag{7b}$$

we can write expression (5) in the form

$$C = A^* e^{-\varepsilon} \left(\frac{\Theta}{1 - \Theta}\right)^m \tag{8}$$

which, along with the equation

$$-\frac{d\Theta}{dt} = \frac{F}{n_A M_S} A^* e^{-\varepsilon} \left(\frac{\Theta}{1 - \Theta}\right)^m, \tag{9}$$

permits one to obtain the theoretical desorption curves.

It is convenient to write the heating rate in the following way[2]:

$$\beta \equiv \frac{dT}{dt} = aT^{2-x}, \quad a = \text{const.}, \; x = 0, 1, 2\,. \tag{10}$$

Using this relation, we can express in a unified way not only the most commonly applied linear type of heating ($x = 2$), but also the hyperbolic ($x = 0$) and exponential type ($x = 1$) of heating which can be both, in certain aspects, more easily subjected to theoretical analysis[10]. Integrating equation (9), we find

$$\frac{FA^*}{n_A M_S a} \left[\frac{E_x(\varepsilon)}{T^{1-x}} - \frac{E_x(\varepsilon_0)}{T_0^{1-x}}\right] = N_m(\Theta), \tag{11}$$

where

$$N_m(\Theta) = -\int_{\Theta_0}^{\Theta} \left(\frac{1 - \Theta}{\Theta}\right)^m d\Theta, \tag{12}$$

and[10]

$$E_x(\varepsilon) = \int_1^{\infty} u^{-x} e^{-\varepsilon u} \, du \,. \tag{13}$$

Index 0 in the preceding relations signifies the initial values of the coverage, temperature and parameter ε. Integral $N_m(\Theta)$ can be expressed in the analytical form while integral $E_x(\Theta)$ can be formulated analytically only for the case $x = 0$. In other cases, it has to be approximated by means of a series[2]

$$E_x(\varepsilon) = \frac{e^{-\varepsilon}}{\varepsilon + x}\left[1 + \frac{x}{(\varepsilon + x)^2} + \frac{x(x - 2\varepsilon)}{(\varepsilon + x)^4} + \ldots\right]. \tag{14}$$

If one is using only the first term of expansion, the maximum error does not exceed 3·5%, for $\varepsilon \geqq 5$ (ref.[10]). It can be also shown[10] that under usual experimental conditions, $E_x(\varepsilon_0) \ll E_x(\varepsilon)$ and it can be therefore omitted in expression (*11*). The expression has then a form

$$N_m(\Theta) = \frac{F}{n_A M_S} \frac{A^*}{a} \frac{e^{-\varepsilon}}{\varepsilon + x} T^{x-1} \,. \tag{15}$$

In the next step, we shall introduce function C^+ defined as

$$C^+ \equiv C T^x = A^* T^x e^{-\varepsilon} \left(\frac{\Theta}{1 - \Theta}\right)^m . \tag{16}$$

From the condition for the maximum of this function, $dC^+/dT = 0$, we get

$$\frac{F}{n_A M_S} A^* = a T_M^{1-x} (\varepsilon_M + x) \, e^{\varepsilon_M} \frac{(1 - \Theta_M)^{m+1}}{m \Theta_M^{m-1}} \,, \tag{17}$$

where index M relates to values of the variables at maximum of the function C^+. Substituting Eq. (*17*) into (*15*) we obtain

$$N_m(\Theta) = \frac{\varepsilon_M + x}{\varepsilon + x} \frac{T_M}{T} e^{\varepsilon_M - \varepsilon} \left(\frac{T}{T_M}\right)^x \frac{(1 - \Theta_M)^{m+1}}{m \Theta_M^{m-1}} \tag{18}$$

which is for $\Theta = \Theta_M$ simplified into a form

$$N_m(\Theta_M) = \frac{(1 - \Theta_M)^{m+1}}{m \Theta_M^{m-1}} \,. \tag{19}$$

We can see from Eqs (*12*) and (*19*) that Θ_M is for the given order only a function of Θ_0. This property is preserved in the original function C only in the case of hyperbolic type of heating ($x = 0$), where $C^+ \equiv C$. For all other types of heating, the coverage at the maximum of experimental curve C depends also on the parameter ε.

Next, we shall defined a dimensionless function R, in the form

$$R \equiv \frac{C^+}{C^+_M} = \left(\frac{T}{T_M}\right)^x e^{\varepsilon_M - \varepsilon} \left[\frac{\Theta(1 - \Theta_M)}{\Theta_M(1 - \Theta)}\right]^m \qquad (20)$$

denoting

$$D = \frac{\varepsilon_M + x}{\varepsilon + x} \frac{T_M}{T} \qquad (21)$$

and

$$s = \varepsilon_M - \varepsilon + x \ln \frac{T_M}{T}\,. \qquad (22)$$

Using these symbols, we can write Eqs (*18*) and (*20*) in the form

$$N_m(\Theta) = De^s \frac{(1 - \Theta_M)^{m+1}}{m\Theta_M^{m-1}} \qquad (23)$$

and

$$R = e^s \left[\frac{\Theta(1 - \Theta_M)}{\Theta_M(1 - \Theta)}\right]^m. \qquad (24)$$

Applying the approximation

$$\frac{\varepsilon_M + x}{\varepsilon + x} \approx \frac{T}{T_M} \qquad (25)$$

which is valid for $x \ll \min(\varepsilon_M, \varepsilon)$, we get $D = 1$. From Eqs (*19*), (*23*) and (*24*) it is then evident that for a given Θ_0 and m, the coverage Θ as well as function R depend only on the variable s.

The adsorption enthalpy can be found from two known values of the variable s, in the following way: First, we transform equation (*22*) into a form

$$\left[s_i + x \ln \frac{T_M}{T_i}\right] \frac{R}{\Delta H} = \frac{1}{T_M} - \frac{1}{T_i}\,. \qquad (26)$$

The value of ΔH can be then evaluated from two different values s_i and s_j and the corresponding temperatures, from the expression

$$\frac{\Delta H}{R} = \left[s_j - s_i + x \ln \frac{T_i}{T_j}\right] \frac{T_i T_j}{T_j - T_i} \, . \tag{27}$$

Assuming that we know the order m, temperature T_M and the corresponding value C_M, we can evaluate ΔH and A^* by using the following procedure: *1*) We calculate a set of values R_i from the experimental data; $R_i = C_i T_i^x / C^M T_M^x$. *2*) Using expressions (*19*), (*23*) and (*24*), we plot for a given Θ_0, the theoretical curve $R = R(s)$. *3*) From this theoretical curve, we find the values of the variable s_i corresponding to the value R_i. *4*) Using an arbitrary pair s_i and s_j and the corresponding temperatures T_i and T_j, we find the value of ΔH. *5*) From the condition for a maximum and using the known experimental values F, M_S and n_A, we evaluate A^*. The above described procedure permits to apply for the evaluation of ΔH and A^*, the entire range of the experimental curve. The question of validity of the used approximations and of the determination of the desorption order and temperature T_M will be discussed in the next section.

DISCUSSION

The Effect of the Used Approximations

In the described procedure, we have applied in total three approximations when omitting the integral $E_x(\varepsilon_0)$, by substituting the integral $E_x(\varepsilon)$ with the first term in the series (*14*) and by using equation (*25*). It is known that the approximation of the first type is fully justified under common experimental conditions[10]. The influence of the second and third type of approximation will be discussed in the following part.

Taking into account also the higher-order terms in the series (*14*), we obtained integral $E_x(\varepsilon)$ in the form

$$E_x(\varepsilon) = \frac{e^{-\varepsilon}}{\varepsilon + x} I \, , \tag{28}$$

where $I = I(\varepsilon, x)$ and $I \geqq 1$. Using the above expression, we can write equations (*19*) and (*23*) in the form

$$N_m(\Theta_M) = I_M \frac{(1 - \Theta_M)^{m+1}}{m \Theta_M^{m-1}} \tag{29}$$

and

$$N_m(\Theta) = I D e^{s} \frac{(1 - \Theta_M)^{m+1}}{m \Theta_M^{m-1}} \, . \tag{30}$$

It is evident from equation (*29*) that in this last, more precise formulation, the coverage Θ_M depends on parameters ε and x. Only in the case of the hyperbolic type of heating ($x = 0$) (for which relations $D = 1$ and $I = 1$ hold exactly), Θ_M is only a function of Θ_0.

Fig. 1 illustrates curve R calculated for the parameters $m = 1$, $\varepsilon_M = 10$, $x = 2$ and $\Theta_0 = 1$. The errors in the calculated values of R caused by the individual types of approximations are given in Fig. 2. It is possible to see that both types of approximations lead to errors which are comparable in size, but of opposite signs, so that they compensate to large extent each other.

The resulting error is then practically negligible when compared with the accuracy of the experiment and with the increasing values of parameter ε it becomes even smaller.

Evaluation of Temperature T_M

In the previous section it was assumed that the temperature T_M is known. This value is needed for the calculation of function R from the experimental data. Basically, it is possible to plot the values of function C^+ and evaluate the temperature T_M graphically but one can also use another method. From the definition of the function C^+, we can easily see that

$$X \equiv T_p/T_M \leqq 1\,, \tag{31}$$

where T_p denotes the temperature corresponding to the maximum of the experimental curve C. From the condition for this maximum, we can derive the following relations

$$A^* \frac{F}{n_A M_S} = a T_p^{1-x} \varepsilon_p e^{\varepsilon_p} \frac{(1 - \Theta_p)^{m+1}}{m \Theta_p^{m-1}} \tag{32}$$

and

$$N_m(\Theta_p) = \frac{\varepsilon_p}{\varepsilon_p + x} \frac{(1 - \Theta_p)^{m+1}}{m \Theta_p^{m-1}}\,, \tag{33}$$

in which index p denotes the quantities corresponding to the maximum on the experimental curve C. From Eq. (*33*), it follows that Θ_p is, for $x \neq 0$, not only the function of Θ_0 but also of ε_p and ε_M, respectively. This dependence is illustrated in Fig. 3 for $\Theta_0 = 1$ and $x = 2$.

Combining equations (*32*) and (*17*), we find for $X = T_p/T_M$ a following relation

$$X^{x-1} \frac{\varepsilon_p X + x}{\varepsilon_p} e^{\varepsilon_p (X-1)} \left(\frac{1 - \Theta_M}{1 - \Theta_p}\right)^{m+1} \left(\frac{\Theta_p}{\Theta_M}\right)^{m-1} - 1 = 0 \tag{34}$$

Solving this relation, we get X as a function of ε_p or ε_M. This dependence is plotted in Fig. 4 for the case of linear heating. The values of T_p and T_M quite evidently differ, especially at the lower values of ε_M. It is impossible to use, in such a case, the earlier described procedure in which, in first approximation, the temperature T_M

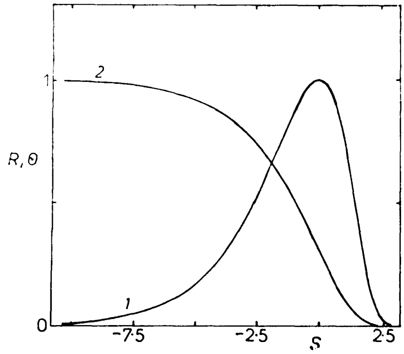

FIG. 1

Function R *1* and function Θ *2*, calculated for the parameters $m = 1$, $\varepsilon_M = 10$ and $x = 2$

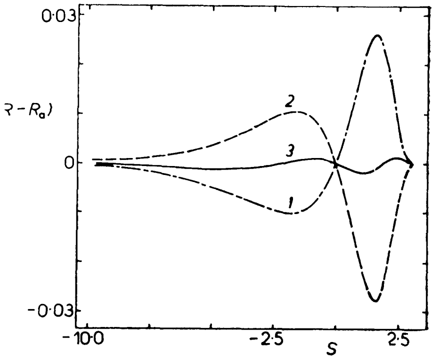

FIG. 2

Deviations of the function R resulting from the used approximations (for parameters $m = 1$, $\varepsilon_M = 10$ and $x = 2$); *1* $D = 1$, *2* $I = 1$, *3* $I = 1, D = 1$

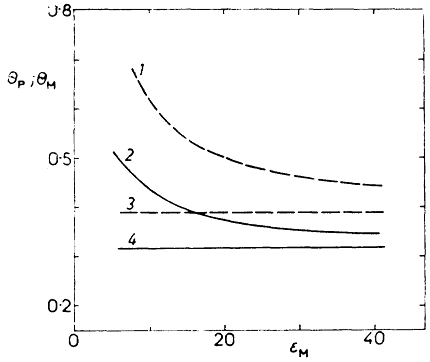

FIG. 3

The dependence of the Θ_p at the maximum of curve C and of the coverage Θ_M at the maximum of curve R — on the parameter ε_M — for the linear type of heating: *1* $\Theta_p = \Theta_p(\varepsilon_M)$, m = 2; *2* $\Theta_p = \Theta_p(\varepsilon_M)$, $m = 1$; *3* Θ_M, $m = 2$, $D = 1$, $I = 1$; *4* Θ_M, $m = 1$, $D = 1$, $I = 1$

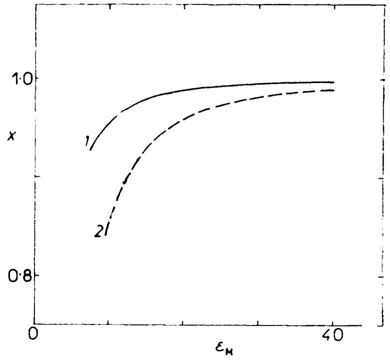

FIG. 4

The dependence of the ratio $X = T_p/T_M$ on ε_M, for the linear type of heating. *1* $m = 1$; *2* $m = 2$

was substituted with temperature T_p (ref.[4]). Temperature T_M can be estimated in the following way: We assume that curve C is in the neighborhood of the maximum roughly symmetrical and we find at the descending part of the curve the point at which $C_p^+ = C_{p'}^+$. The values of T'_M can be estimated from the following equation

$$T'_M = \frac{T_p + T_{p'}}{2}, \tag{35}$$

where $T_{p'}$ corresponds to the value $C_{p'}^+$. The error of this estimation is given by the expression

$$\Delta = \frac{T_M - T'_m}{T_M} 100 \tag{36}$$

and it is shown in Table I as a function of ε_M. The magnitude of this error is in the whole range within the experimental error.

Determination of the Kinetic Order

A number of methods has been proposed for determination of the desorption order. In the case of the temperature-programmed desorption with freely occurring readsorption, one can use *e.g.* the method[7] evaluating the desorption order from the ratio of the slopes of tangents drawn at the inflection points of the experimental curves. A parameter defined in this way permits to distinquish very well between the desorption orders in the cases of initial coverage $\Theta_0 \geqq 0{\cdot}8$, where the second-order parameter is much larger. With decreasing initial coverage, the values for both orders

TABLE I

The dependence of the error Δ in estimation of the temperature T_M and of the parameter $\chi_{1/2}$ — on ε_M — for the linear type of heating ($x = 2$), at a unit coverage ($\Theta_0 = 1$)

ε_M	Δ %		$\chi_{1/2}$	
	$m = 1$	$m = 2$	$m = 1$	$m = 2$
10	0·166	−0·801	0·2946	0·1936
15	0·072	−0·053	0·2884	0·1814
20	0·035	0·022	0·2859	0·1765
25	0·020	0·027	0·2846	0·1741
30	0·012	0·022	0·2839	0·1727
35	0·008	0·017	0·2834	0·1718
40	0·005	0·013	0·2831	0·1712

of this parameter approach each other and at $\Theta_0 < 0{\cdot}6$ they are so near that considering the accuracy of the experimental data, the evaluation of the desorption order becomes extremely difficult. It is therefore more convenient to use for this purpose the parameter χ which has been introduced earlier[4] and defined as

$$\chi_{1/2} = \left(\frac{1}{T_R} + \frac{1}{T_L} - \frac{2}{T_M}\right) \Big/ \left(\frac{1}{T_L} - \frac{1}{T_R}\right). \tag{37}$$

Temperatures T_L and T_R relate to the points at the curve R for which $T_L < T_M < T_R$ and $R_L = R_R = 0{\cdot}5$. For the parameter $\chi_{1/2}$ defined in the above way, it is also possible to find, using Eq. (*26*), an equivalent expression

$$\chi_{1/2} = \left[-s_R - s_L + x \ln \frac{T_R T_L}{T_M^2}\right] \Big/ \left[s_R - s_L + x \ln \frac{T_L}{T_R}\right]. \tag{38}$$

By means of this relation, it is possible to show that parameter $\chi_{1/2}$ depends, for $x = 0$, only on the initial coverage Θ_0 while for the other types of heating, it is to lesser extent also a function of ε_M. The dependence of parameter $\chi_{1/2}$ on initial coverage is illustrated, for $x = 0$, in Fig. 5. The dependence of the same parameter on ε_M is given in Table I, for $x = 2$ and $\Theta_0 = 1$. It is obvious from both dependences that parameter $\chi_{1/2}$ has inside the whole range of variables Θ_0 and ε_M much higher values for the first order case than for the second order so that there should be no problem in determination of the kinetic order.

The presented discussion leads to the conclusion that the above described procedure can be applied, along with the method proposed for estimation of the kinetic order and temperature T_M, for evaluation of the thermal desorption experiments carried out under conditions of freely occurring readsorption.

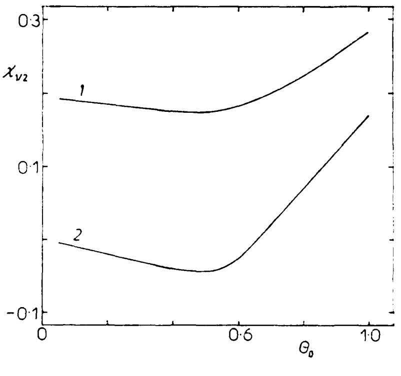

FIG. 5

The dependence of the parameter $\chi_{1/2}$ on Θ_0, for the hyperbolic type of heating. *1* $m = 1$; *2* $m = 2$

REFERENCES

1. Redhead P. A.: Vacuum *12*, 203 (1962).
2. Smutek M.: Vacuum *24*, 173 (1974).
3. Chan C.-M., Aris R., Weinberg W. H.: Appl. Surface Sci. *1*, 360 (1978).
4. Pavlíček J.: Appl. Surface Sci. *8*, 412 (1981).
5. Cvetanovič J., Amenomiya Y.: Catal. Rev. *8*, 21 (1972).
6. Konvalinka J. A., Scholten J. J. F., Rasser J. C.: J. Catal. *48*, 365 (1977).
7. Ibok E. E., Ollis D. F.: J. Catal. *66*, 391 (1980).
8. Herz R. K., Kiela J. B., Marin S. P.: J. Catal. *73*, 66 (1982).
9. Gorte R. J.: J. Catal. *75*, 164 (1982).
10. Smutek M., Černý S., Buzek F.: Advan. Catal. Relat. Subj. *24*, 243 (1972).

Translated by Z. Dolejšek.