

DETERMINATION OF THE ACTIVATION ENERGY IN TPD EXPERIMENTS. I. A NEW METHOD FOR HOMOGENEOUS SURFACES

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ABSTRACT

The principles of the temperature programmed desorption method are discussed. Some errors which occur in the evaluation of the activation energy are analyzed. A new method to estimate the activation energy is proposed, and the drawbacks of this method are discussed.

INTRODUCTION

Temperature programmed desorption (TPD) is often used to characterize the interactions which occur in solid–gas systems. These interactions are described by the kinetic parameters which appear in the general equation of the desorption rate [1]

$$-\frac{d\theta}{dt} = A\theta^n \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where θ is the degree of coverage of the surface, t is the time, A the pre-exponential factor, n the order of desorption, E the activation energy, R the gas constant and T the temperature (K).

In the case of homogeneous surfaces, for which

$$\frac{dE}{d\theta} = 0 \quad (2)$$

one has to determine the values of the order of desorption, the pre-exponential factor and the activation energy. For the case of heterogeneous surfaces where

$$\frac{dE}{d\theta} \neq 0 \quad (3)$$

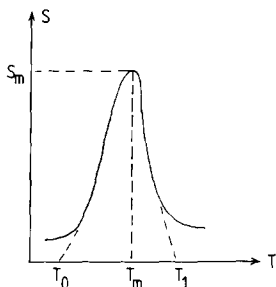


Fig. 1. The usual shape of a thermogram. T_m is the value of the temperature for which the signal, S , is maximum. T_0 and T_1 are the temperatures for which S begins to increase and finishes decreasing, respectively.

i.e., E is a function of θ , one has to determine the values of all the above-mentioned parameters as well as the analytical form of the function $E(\theta)$.

The evaluation of the kinetic parameters is carried out starting from the thermogram (Fig. 1), eqn. (1), and the fact that the sample is heated in one of the following ways

$$\text{linear [2,3]} \quad T = T_0 + \beta t \quad (4a)$$

$$\text{hyperbolic [2,3]} \quad 1/T = (1/T_0) - \beta t \quad (4b)$$

$$\text{exponential [4]} \quad T = T_0 \exp(\beta t) \quad (4c)$$

(where β is the heating rate) or in other ways [5]. One also takes into account that the signal, S , which is recorded in thermograms versus temperature, is proportional [1] to the rate of desorption.

A linear heating programme (eqn. 4a) is often used for experimental reasons although many mathematical difficulties arise in the integration of eqn. (1), which would be eliminated by a hyperbolic programme. Special emphasis is usually given to the determination of the activation energy, perhaps because this parameter seems to have a structural meaning, whereas

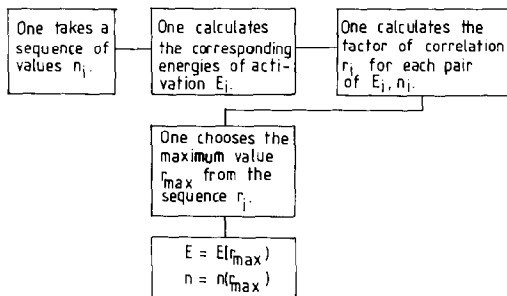


Fig. 2. The algorithm of determination of the kinetic parameters.

the evaluation of the order of desorption is often neglected although it has a deeper chemical meaning. Our opinion is that the parameters n and E should be determined together, in the manner shown in Fig. 2, where one can see the algorithm of such a determination.

Although, for the reasons given above, special emphasis has been given in the literature to the determination of the activation energy, often, one also forgets to estimate the errors of the corresponding methods. There are methods which calculate E with significant errors. One of these is the method which uses the shift of the maximum desorption rate ("the shift method") on changing the heating rate. Actually, this method was introduced to non-isothermal kinetics by Kissinger [6].

Using the shift method to evaluate the activation energies from our own TPD results we obtained very scattered values and consequently we analyzed the reasons in detail. In this paper we discuss the errors of this method and then we propose a new one.

ERRORS OF THE SHIFT METHOD

The shift method starts from the equation

$$\ln \frac{T_m^2}{\beta} = \frac{E}{RT_m} + \ln \frac{E}{AR} \quad (5)$$

which can be derived from eqns. (1) and (4a) with $n = 1$. The index m means that the temperature corresponds to the maximum of the desorption rate. If one carries out at least three TPD experiments with different heating rates and plots $\ln(T_m^2/\beta)$ versus $1/T_m$, one can easily determine the activation energy and the pre-exponential factor.

Mathematically speaking, this method is very good and it is not difficult to calculate the activation energy in this way. This is why we can find the shift method in many papers. Moreover, one of these (Lord and Kittelberger [7]) shows that this method can be used without significant errors even if the order of desorption, n , is 2. They came to this conclusion on the basis of their calculated thermograms for $n = 2$. Starting from these thermograms and using eqn. (5) they obtained activation energies with errors of less than 1.5%.

We note that Lord and Kittelberger obtained such a good precision for the determination of the activation energy because they used the calculated values of T_m and they assumed that the heating rate varies so greatly that the ratio of the maximum to the minimum rate is 1000:1. To use calculated values for T_m means that T_m must be measured without errors, and to vary β so greatly means that the straight line drawn among the plotted data must be of a higher precision than when β varies in a smaller range.

To show that the errors of the shift method are significant even when $n = 1$, we assume that the temperature is measured with errors of about $5\text{--}10^\circ$, which are not excessively large [8], and that the ratio of the maximum to minimum heating rates is $16:1$, as in our own TPD experiments. We varied the heating rate in the range corresponding to this ratio, but not in a larger one because higher values of $\beta_{\max}/\beta_{\min}$ would involve a significant change in the kinetics of the desorption.

Before calculating the errors of the shift method let us analyze eqn. (5) to find two mathematical results which will allow us to calculate these errors easily.

By carrying out two TPD experiments with different heating rates, β_1 and β_2 , we shall record the two maxima of the desorption rate at two different temperatures, $T_{m,1}$ and $T_{m,2}$. Consequently, we can write eqn. (5) twice: first for $\beta_1, T_{m,1}$ and second for $\beta_2, T_{m,2}$. Subtracting the two equations we readily find that

$$\frac{E}{R} \left(\frac{1}{T_{m,1}} - \frac{1}{T_{m,2}} \right) + 2 \ln \frac{T_{m,2}}{T_{m,1}} = \ln \frac{\beta_2}{\beta_1} \quad (6)$$

We shall use this equation to calculate a new position of the maximum as a function of the old value, the activation energy and the ratio β_2/β_1 . As one can see, the variation, ΔT_m , of the position of the maximum temperature depends only on the ratio β_2/β_1 and not on the separate values of the heating rates.

Starting again from eqn. (5) after several algebraic calculations we find that

$$\beta = \frac{ART_m^2}{E} / \exp\left(\frac{E}{RT_m}\right)$$

This result allows us to state that for any value of E there is a value of β for which the maximum is recorded at a given value of the temperature, T_m .

Consequently, we can assume that for any value of E we have used the corresponding value of the heating rate, β_E^0 , such that the maximum was registered at the temperature $T_m^0 = 370$ K. This, of course, means that for the all values of E we registered the corresponding maxima at the same temperature, 370 K.

Starting from this assumption and using eqn. (6) we calculated, for several values of E , the other values of T_m when the heating rate is twice or four times as high or low as β_E^0 . The results of these computations are shown in Table 1. Using this table one may calculate the corresponding values of ΔT_m .

As one can see from Table 1 for the same variation of β the values of ΔT_m decrease when E increases. One can also see that when E is higher than a certain value, the variations ΔT_m , obtained when the heating rate increases or decreases twice, become smaller than the errors of the temperature measurements. This result, of course, suggests that the values of the activa-

TABLE 1

The position of the maximum temperature, T_m (K) as a function of the heating rate and the activation energy

E (kcal mol ⁻¹)	T_m at a heating rate of:				
	$\beta_0/4$	$\beta_0/2$	β_0	$2\beta_0$	$4\beta_0$
2.5	292	327	370	420	490
5.0	319	343	370	402	438
10.0	340	355	370	388	406
15.0	349	359	370	382	395
20.0	354	362	370	379	389
25.0	357	364	370	378	385
30.0	359	365	370	377	383

tion energies could be inaccurately estimated on account of the errors of the temperature measurements.

In Table 2 we give the values of the errors of E values as a function of the values of E and of the errors of the temperature measurements: (a) 5° and (b) 10°. The values from Table 2 were calculated from Table 1 values. Assuming that we measured the temperature with an error of 5 or 10° we calculated the corresponding values of $\Delta(\ln T_m^2/\beta)$ and $\Delta(1/T_m)$ for each pair $(\ln T_m^2/\beta, 1/T_m)$. Plotting these results we could draw, for each row of Table 1 (a given value of E), two straight lines from which we calculated two different values, E_1 and E_2 , for the activation energy. We calculated the error $\Delta E/E$ by dividing the difference $E_1 - E_2$ by the true value of E , used to determine the values from Table 1.

Taking into account Table 2 and considering that an error of 10% is not excessively large, one can state that the shift method is good for determining activation energies with values smaller than 10 kcal mol⁻¹, when T is measured with an error smaller than 5°. For values higher than 10 kcal mol⁻¹, the errors become significant and this method is not reliable.

In the following we shall put forward the basis of a new method to determine the activation energy. As it will be shown, the errors of this new method are sufficiently small.

TABLE 2

The errors, $\Delta E/E$ (%), of the determination of E as a function of the values of E and of the errors of the temperature measurements: (a) 5° and (b) 10°

E (kcal mol ⁻¹)	2.5	5.0	10.0	15.0	20.0	25.0	30.0
$\Delta E/E$ (a)	9	11	18	25	34	44	53
$\Delta E/E$ (b)	18	23	39	59	92	158	288

THEORETICAL

As a basis of the method which we shall propose, we must start from the general equation of the desorption rate. Taking into account eqn. (4a), relationship (1) becomes

$$\left(-\frac{d\theta}{dT}\right) = \frac{A}{\beta} \theta^n \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Taking into account that the value of $(-d\theta/dT)$ is maximum when

$$\frac{d^2\theta}{dT^2} = 0 \quad (8)$$

one can write

$$-\left(\frac{d^2\theta}{dT^2}\right)_m = \frac{A}{\beta} \left[n\theta_m^{n-1} \left(\frac{d\theta}{dT}\right)_m - \frac{E}{RT_m} \theta_m^n \right] \exp\left(-\frac{E}{RT_m}\right) = 0 \quad (9)$$

and, consequently, one can readily find that

$$E = nRT_m^2 \left(-\frac{d\theta}{dT}\right)_m / \theta_m \quad (10)$$

where the index m means that the respective parameters have values relating to the maximum of the desorption rate (see Fig. 1). This is the relationship that we propose to use in the new method. We note that formula (10) is used in non-isothermal kinetics for the evaluation of the activation energy [9].

To determine the value of E with relationship (10) we must be able to calculate the ratio $(-d\theta/dT)_m/\theta_m$ using the recorded thermogram. In order to do that, we assume that the signal S , which is recorded in the thermogram, versus temperature, is proportional [1] to the desorption rate and, consequently, to $(-d\theta/dT)$. Thus, we can write

$$\left(-\frac{d\theta}{dT}\right) = kS \quad (11)$$

Supposing that at the temperature T_0 (see Fig. 1), the degree of coverage is θ_0 , at T_m the degree of coverage is θ_m and that at T_1 we have $\theta_1 = 0$, integrating eqn. (11) between the limits T_0 and T_1 and then between T_m and T_1 , it turns out that

$$\theta_0 = k \int_{T_0}^{T_1} S dT \quad (12)$$

and, respectively

$$\theta_m = k \int_{T_m}^{T_1} S dT \quad (13)$$

Thus, from eqns. (11) and (12) we find that

$$\left(-\frac{d\theta}{dT}\right)_m = \theta_0 S_m / \int_{T_0}^{T_1} S dT \quad (14)$$

and, from eqns. (12) and (13), that

$$\theta_m = \theta_0 \int_{T_m}^{T_1} S dT / \int_{T_0}^{T_1} S dT \quad (15)$$

Taking into account eqns. (14) and (15), the ratio $(-d\theta/dT)_m/\theta_m$ will be given by

$$\left(-\frac{d\theta}{dT}\right)_m/\theta_m = S_m / \int_{T_m}^{T_1} S dT \quad (16)$$

Before using this expression in formula (10) we must say that we assumed that $\theta_1 = 0$. In fact, this is not rigorously true, but we shall see that relation (16) remains the same, in a good approximation, even if $\theta_1 \neq 0$.

If $\theta_1 \neq 0$, one can show, in the manner used before, that the ratio $(-d\theta/dT)_m/\theta_m$ is given by

$$\left(-\frac{d\theta}{dT}\right)_m/\theta_m = \frac{S_m}{\frac{\theta_1}{\theta_0 - \theta_1} \int_{T_0}^{T_1} S dT + \int_{T_m}^{T_1} S dT} \quad (17)$$

Taking into account that from our own computed thermograms we find that the ratio θ_1/θ_0 is smaller than 10^{-3} and that, consequently, $\theta_1/(\theta_0 - \theta_1) \ll 1$, in formula (17) we can neglect

$$\frac{\theta_1}{\theta_0 - \theta_1} \int_{T_0}^{T_1} S dT$$

because it is much smaller than the other term. Thus, on account of the reasons given above, formula (17) is, in fact, with a good approximation, equivalent to formula (16).

Using, now, eqns. (10) and (16) we find the relationship

$$E = nRT_m^2 S_m / \int_{T_m}^{T_1} S dT \quad (18)$$

This is the relationship that we propose for evaluating the activation energies in TPD experiments.

DISCUSSION

As one can see from eqn. (18), to determine the value of the activation energy one needs to estimate the order of desorption, n , and to determine the values of T_m , S_m , T_1 and I from the recorded thermogram, where

$$I = \int_{T_m}^{T_1} S dT$$

To determine T_m , S_m and T_1 is, of course, quite easy and I can be calculated from the thermogram by numerical integration. In a way, it is

more difficult to estimate the true value of the order of desorption, but one can do this in the manner shown in Fig. 2 or one can assume its value a priori because desorption is usually an elementary reaction.

To estimate the errors of this method we calculated the values of E using the various computed thermograms. Assuming that the temperature is measured with an error of 10° , we found errors smaller than 5%.

When we simultaneously computed E and n in the manner shown in Fig. 2, the errors depended on the chosen values of the sequence n_i . They were smaller than 8% when we varied n with steps of 0.1.

We must also note that for $n = 1$ this method is similar to Chen's method [10]. According to Chen, the activation can be determined by the help of the formula

$$E = 2.52 RT_m^2/\omega - 2 RT_m \quad (19)$$

where ω is the half-width of the TPD curve.

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