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Study of consecutive mechanism of desorption with diffusion step under non-isothermal conditions

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Abstract

A mechanism of desorption consecutive with diffusion into the micropores of a solid phase is postulated. In the development of the consecutive model complex integrals were obtained; these are solved using the Gauss–Kronrod method of numerical integration. Theoretical temperature programmed desorption spectra (TDS) are calculated. The influence of diffusion parameters on the position and shape of the calculated TDS were investigated. Kinetic parameters calculated using methods based on the change of temperature of the peak maximum and those assumed in the calculation of theoretical spectra are compared.

INTRODUCTION

Desorption is one of the fundamental surface phenomena and has been a topic of experimental and theoretical investigations [1,2]. In spite of this, the complex mechanism of desorption is still not well understood. The overall process in the micropores of a solid phase always includes a diffusion step, although the desorption is usually considered as a first or second order reaction [3] or as a process limited by diffusion [4,5]. However, diffusion cannot simply be neglected, especially if the rate constants of the desorption and diffusion steps are close in value ($k_{des} \approx k_{diff}$). From the viewpoint of chemical kinetics and for the interpretation of thermal desorption results, this condition is very important.

For most gas–solid reactions, the activation energy of diffusion is close to activation energy of desorption for physisorbed species, whereas the activation energy of desorption for chemisorbed molecules is several times greater [6–8]. The pre-exponential factors for desorption are not strictly

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limited. Theoretically, the pre-exponential factor for desorption is about 10^{13} s^{-1} for monatomic species and could rise to 10^{15} s^{-1} for diatomic molecules [9,10]. Despite theoretical expectations, experimentally obtained values of the pre-exponential factor for the desorption process can cover ten orders of magnitude (10^5–10^{15} s^{-1}) [9]. In the case of porous solids, diffusion coefficients vary between 10^{-7} and 10^{-10} m^2 s^{-1} [11,12]. The expected pre-exponential factor for diffusion could vary over two or three orders of magnitude. Consequently, the rate constants could be close in value ($k_{des} \approx k_{diff}$) owing to compensation effects in both the desorption and the diffusion steps.

One way of investigation of the contribution of both surface processes and diffusion involves calculations of theoretical curves obtained with a previously postulated mechanism. In this work, a model of two consecutive steps, desorption and diffusion, is assumed, and theoretical temperature-programmed desorption spectra (TDS) are calculated. A certain critical intermediate state or precursor state (a loosely bonded intermediate able to migrate on the surface) already postulated by King and co-workers [13–15], has been accepted, and is introduced into the model. A numerical method for calculation of complex integrals has been established, and is used in the computation of theoretical TDS. It is shown that the influence of the diffusion step cannot be neglected in the interpretation of single and broad peak TDS.

MODEL AND NUMERICAL CALCULATIONS

The desorption process, considered as a reaction with two consecutive steps can be presented schematically

$$S \xrightarrow{k_1} P \xrightarrow{k_2} G \tag{1}$$

Here S denotes a molecule of adsorbate bonded with an active site on the surface, P is the precursor or intermediate state, and G denotes the free gas molecule; k_1 and k_2 are specific rate constants of the separate steps. In the case of such a mechanism, the desorption rate can be expressed by the following equation

$$v = dN_G/dt = k_2 p(t) \tag{2}$$

where p is the concentration or partial surface coverage of the intermediate state and N_G is the number of desorbed molecules.

In order to establish the dependence of concentration (partial surface coverage) of species P on time, a system of ordinary differential equations (ODEs) is developed. If the concentrations of substances S, P and G are s,

p and g respectively, and if first-order rate kinetics are assumed, the system of ODEs is given by

$$\frac{\mathrm{d}s(t)}{\mathrm{d}t} = -k_1 s(t) \tag{3}$$

$$\frac{\mathrm{d}p(t)}{\mathrm{d}t} = k_1 s(t) - k_2 p(t) \tag{4}$$

$$\frac{\mathrm{d}g(t)}{\mathrm{d}t} = k_2 p(t) \tag{5}$$

Non-isothermal conditions are given by the relationship between time and temperature

$$T = f(t) \tag{6}$$

$$\mathrm{d}T = f'(t)\,\mathrm{d}t \tag{7}$$

Let E_i be the activation energy for the two steps in eqn. (1), and A_i ($i = 1, 2$) the pre-exponential factors. Specific rate constants k_i ($i = 1, 2$), are connected with activation energies through the well known Arrhenius equation. Now, the system of ODEs becomes

$$\frac{\mathrm{d}s(T)}{\mathrm{d}T} = \frac{A_1}{f'(t)}\exp\left(-\frac{E_1}{RT}\right)s(T) \tag{8}$$

$$\frac{\mathrm{d}p(T)}{\mathrm{d}T} = -\frac{A_1}{f'(t)}\exp\left(-\frac{E_1}{RT}\right)s(T) - \frac{A_2}{f'(t)}\exp\left(-\frac{E_2}{RT}\right)p(T) \tag{9}$$

$$\frac{\mathrm{d}g(T)}{\mathrm{d}T} = \frac{A_2}{f'(t)}\exp\left(-\frac{E_2}{RT}\right)p(T) \tag{10}$$

Integration is performed from the point $T = T_0$ (corresponding to the beginning of the time scale, $t = 0$). The following notation was introduced

$$I_i(u) = \int_{T_0}^{u} \frac{1}{f'(t)}\exp\left(-\frac{E_i}{RT}\right)\mathrm{d}T \qquad i = 1, 2 \tag{11}$$

were u is a final temperature in the process of integration.

Equation (8) can be easily solved as an equation with separation of variables. Using notation (11), a particular solution which satisfies the initial condition $s(T_0) = (s)_0$ is

$$s(u) = (s)_0 \exp[-A_1 I_1(u)] \tag{12}$$

In order to obtain the relationship between the concentration of substance P and temperature, the substitution of eqn. (12) into eqn. (9) is necessary, and leads to the linear first-order ODE

$$\frac{\mathrm{d}p(T)}{\mathrm{d}T} = \frac{A_1}{f'(t)}(s)_0 \exp\left[-\frac{E_1}{RT} - A_1 I_1(T)\right] - \frac{A_2}{f'(t)}\exp\left(-\frac{E_2}{RT}\right)p(T) \tag{13}$$

A particular solution satisfying the initial condition $p(T_0) = (p)_0$ is

$$p(u) = \exp[-A_2 I_2(u)][(p)_0 + A_1(s)_0 L(u)] \tag{14}$$

where

$$L(u) = \int_{T_0}^{u} \frac{1}{f'(t)} \exp\left[-\frac{E_1}{RT} - A_1 I_1(T) + A_2 I_2(T)\right] \mathrm{d}T \tag{15}$$

It is not necessary to find a particular solution of eqn. (10) because $g(T)$ can be calculated from the mass conservation law. Moreover, the desorption rate in the case of non-isothermal conditions can be derived knowing only the concentration of intermediate state P.

It is assumed that in the second step of scheme (1) only diffusion takes place. A solution of Fick's law can be used. In the case of spherical particles with radius r_0 the following expression is valid [16]

$$\frac{M_\mathrm{t}}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{r_0^2}\right) \tag{16}$$

where M_t is the amount of gas desorbed up to time t; M_∞ is the amount desorbed up to equilibrium conditions, and D is the diffusion coefficient related to the coefficient D_0 and activation energy for the diffusion process E_diff with a relation of Arrhenius type.

Usually, only the first term of the sum in eqn. (16) is considered [4]

$$\frac{M_\mathrm{t}}{M_\infty} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{D\pi^2 t}{r_0^2}\right) \tag{17}$$

After rearrangement of the previous equation, we get a well known equation for first-order rate kinetics

$$\ln\left(\frac{M_\infty - M_\mathrm{t}}{M_\infty}\right) = \left(\frac{D\pi^2}{r_0^2}\right) \ln\left(\frac{6}{\pi^2}\right) t \tag{18}$$

Evidently the rate constant can be expressed by

$$k_2 = \left(\frac{D_0\pi^2}{r_0^2}\right) \ln\left(\frac{6}{\pi^2}\right) \exp\left(-\frac{E_\mathrm{diff}}{RT}\right) \tag{19}$$

Therefore a pre-exponential factor for the second step in eqn. (1) can be calculated using

$$A_\mathrm{diff} = \frac{D_0\pi^2}{r_0^2} \ln\left(\frac{6}{\pi^2}\right) \tag{20}$$

Finally, a simulation of the TDS could be calculated by introducing the value for $p(t)$, and thus for $p(T)$, into eqn. (2). In this work, only the case of linear heating rate was considered, and thus

$$\frac{\mathrm{d}T}{\mathrm{d}t} = f'(t) = \text{const} = \beta \tag{21}$$

A simultaneous change of all kinetic parameters in the developed model gives a complex multi-dimensional problem. In this paper the kinetic analysis is performed by a step by step procedure; one particular parameter is changed within appropriate limits while the others are kept constant; in this way, families of spectra arise. As only the case of linear heating rate has been examined, the problem is reduced to three dimensions (temperature, kinetic parameter, rate of desorption).

Evidently, the explicit calculations of concentrations s and p, given by eqns. (12) and (14), leads to a need for calculation of complex integrals. A wide use of the well known function $p(x)$ [17] ($x = E/RT$) in the evaluation of integral (11) [in the case of linear heating rate, $f'(t) = \beta$] is evident from the literature. However, the accuracy of this approach is limited.

In addition, in this work, a problem arises in the estimation of integral (15) [which function is clearly more complicated than integral (11)]. In this case the use of the $p(x)$ function is not possible. The simplest approach based upon polynomial approximation is not recommended, because of the complex functional dependences between a number of terms in the polynomial approximation and a wide range of parameters.

Therefore we decided to calculate integrals (11) and (15) employing methods of numerical integration. The main idea behind numerical evaluation of definite integrals is the following equality

$$\int_a^b F(x)\,\mathrm{d}x = \sum_{k=1}^{n} a_k F(x_k) + \text{EPS} \tag{22}$$

Here, n is the number of points used for function evaluations, a_k are weights obtained from the approximation of function F, and x_k are points at which the function F is evaluated. EPS is an error term which can be neglected within the required accuracy.

There exists a variety of formulae (22) depending on the choice of approximation for function F. Today, the best choice is based on the Gauss–Kronrod pair of formulae, which gives the value of the integral together with the accuracy of estimation. In comparison with other methods of numerical integration, the accuracy of this method is high. In this paper we used a Gauss–Kronrod integration routine named QK15 [18]. The high accuracy of the results obtained strongly supports the theoretical basis for this method.

All calculations are performed on a PC AT computer with an MS FORTRAN 4.10 compiler. A program for computations of theoretical TDS, written in FORTRAN 77 language, is available on request.

RESULTS AND DISCUSSION

A series of desorption spectra is computed using eqn. (2) [after substitution of eqn. (14) into it] for selected ranges of values of the relevant kinetic parameters. The following series of desorption spectra are computed from the initial condition of saturation in the chemisorbed overlayer, i.e. $(s)_0 = 1$.

As a result of evaluation of the postulated kinetic model, a reaction rate dependent on four kinetic parameters and the heating rate arises. Generally one can assign any values to the parameters but in the case of surface processes they are limited to appropriate domains.

Usually, E_{diff} is an order of magnitude less than the activation energy for desorption of chemisorbed species [6–8]. Here, TDS were calculated with energies whose ratio was varied in the following range: $1 < E_1/E_{\text{diff}} < 10$.

Experimentally obtained values of the pre-exponential factor for desorption processes, A_1, fall in the range of a few orders of magnitude [9] and consequently in this paper parameter A_1 varies between 10^5 and 10^{13} s^{-1}. Meanwhile, the pre-exponential factor A_{diff} is limited by diffusion coefficients (10^{-7}–10^{-10} m^2 s^{-1}) [11,12], see eqn. (20). Therefore, kinetic parameter A_{diff} (calculated for a spherical particle with a mean radius equal to 10 μm) varies in a narrow range (1–100 s^{-1}).

In order to investigate the influence of the desorption step on the shape and position of the TDS, parameters E_1 and A_1 are varied while diffusion parameters E_{diff} and A_{diff} are kept constant. Figure 1 presents a typical series of TDS obtained for the change of E_1 from 60 kJ mol^{-1} to 160 kJ mol^{-1}, and with a pre-exponential factor for desorption similar to that theoretically expected ($A_1 = 10^{12}$ s^{-1}). Broad curves, in almost the same

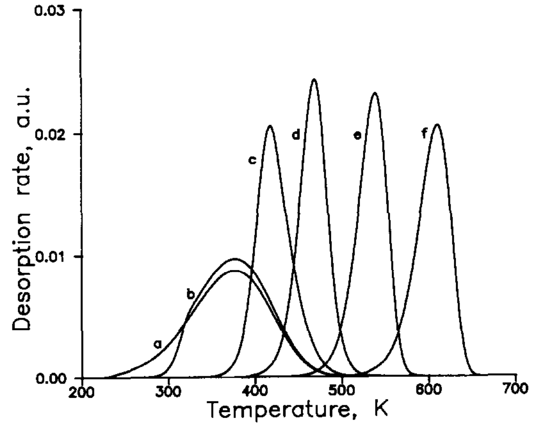

Fig. 1. The set of TDS calculated using common parameters: $A_1 = 10^{12}$ s^{-1}, $E_{\text{diff}} = 23$ kJ mol^{-1}, $A_{\text{diff}} = 10$ s^{-1}; and varying parameter E_1: a, $E_1 = 60$ kJ mol^{-1}; b, $E_1 = 80$ kJ mol^{-1}; c, $E_1 = 100$ kJ mol^{-1}; d, $E_1 = 120$ kJ mol^{-1}; e, $E_1 = 140$ kJ mol^{-1}; f, $E_1 = 160$ kJ mol^{-1}.

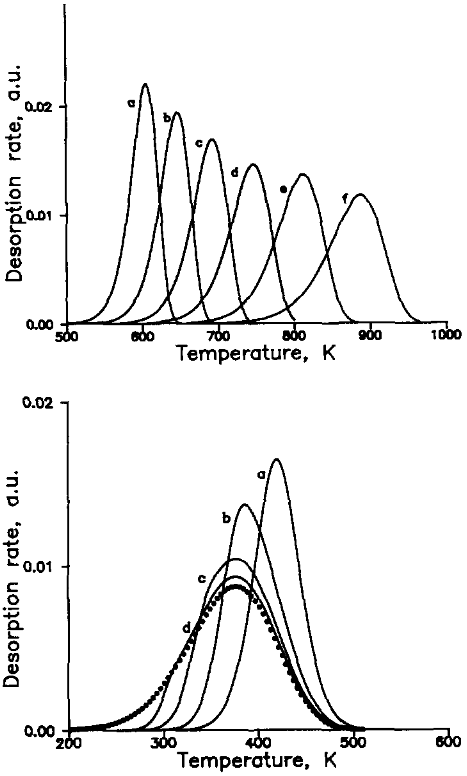

Fig. 2. (top) The series of calculated TDS obtained by varying parameter A_1. The set of TDS calculated using common parameters: $E_1 = 170$ kJ mol^{-1}, $E_{\mathrm{diff}} = 23$ kJ mol^{-1}, $A_{\mathrm{diff}} = 10$ s^{-1}; and varying parameter A_1: a, $A_1 = 10^{13}$ s^{-1}; b, $A_1 = 10^{12}$ s^{-1}; c, $A_1 = 10^{11}$ s^{-1}; d, $A_1 = 10^{10}$ s^{-1}; e, $A_1 = 10^{9}$ s^{-1}; f, $A_1 = 10^{8}$ s^{-1}. (bottom) The set of TDS calculated using common parameters: $E_1 = 60$ kJ mol^{-1}, $E_{\mathrm{diff}} = 23$ kJ mol^{-1}, $A_{\mathrm{diff}} = 10$ s^{-1}; and varying parameter A_{diff}: a, $A_{\mathrm{diff}} = 10^{6}$ s^{-1}; b, $A_{\mathrm{diff}} = 10^{7}$ s^{-1}; c, $A_{\mathrm{diff}} = 10^{8}$ s^{-1}; d, $A_{\mathrm{diff}} = 10^{9}$ s^{-1}. Spectra marked by ● were calculated using parameters: $E_{\mathrm{diff}} = 23$ kJ mol^{-1}, $A_{\mathrm{diff}} = 10$ s^{-1}.

position, are obtained when small energies are applied (spectra calculated for $E_1 = 60$ kJ mol^{-1} and $E_1 = 80$ kJ mol^{-1}). With further increase of the activation energy for desorption (above 120 kJ mol^{-1}) narrow curves are obtained. In this case, a peak shift towards high temperatures is visible; this is a well known effect in non-isothermal kinetics. The existence of broad curves in the domain of small values of E_1 could be interpreted as a result of diffusion controlled reaction.

The influence of the pre-exponential factor for the desorption step, A_1, is investigated in the domains of strongly (Fig. 2(top)) and weakly bonded (Fig. 2(bottom)) molecules. In both cases the same diffusion parameters ($E_{\mathrm{diff}} = 23$ kJ mol^{-1}, $A_{\mathrm{diff}} = 10$ s^{-1}) are applied. The variation of parameter A_1 from 10^7 to 10^{13} s^{-1} leads to changes in the profile and the position of the TDS. For high values of parameter E_1, the TDS become broader and shift towards high temperature as parameter A_1 decreases (Fig. 2(top)). Interesting results are obtained in simulation of the overall reaction in the domain of low values of parameter E_1. In Fig. 2(bottom), the overall reaction (1) and the diffusion are compared. In the domain of small activation energies for desorption, an increase of parameter A_1 reduces the overall process (1) to diffusion as the rate limiting step. Specifically, all spectra (obtained with A_1 increase) from the series in Fig. 2(bottom) shift to the curve marked with open circles, presenting a diffusion process with the same parameters as in the family of curves from a to d. Obviously, a decisive influence of the diffusion step on the TDS profile could be expected in the case of weakly bonded molecules.

The effect of diffusion on the shape and position of the TDS is examined in the case of a small value of the ratio E_1/E_{diff} ($E_1/E_{\text{diff}} < 3$). Figure 3

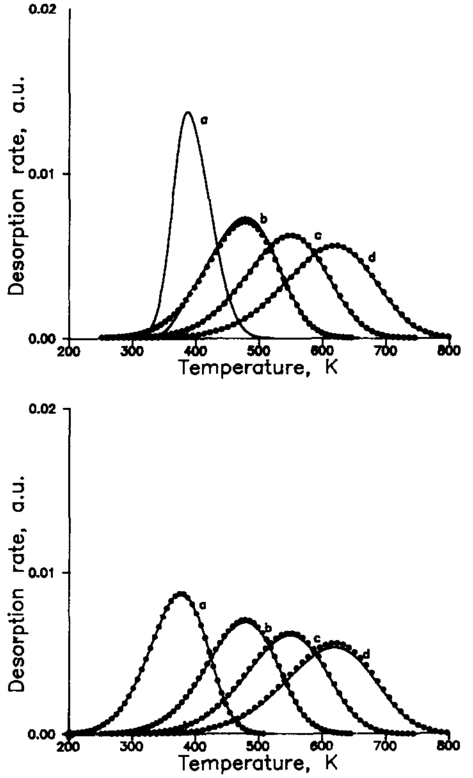

Fig. 3. (top) The series of calculated TDS obtained by varying parameter E_{diff}. The set of TDS calculated using common parameters: $E_1 = 60$ kJ mol^{-1}, $A_1 = 10^{12}$ s^{-1}, $A_{\text{diff}} = 10$ s^{-1}; and varying parameter E_{diff}: a, $E_{\text{diff}} = 23$ kJ mol^{-1}; b, $E_{\text{diff}} = 30$ kJ mol^{-1}; c, $E_{\text{diff}} = 35$ kJ mol^{-1}; d, $E_{\text{diff}} = 40$ kJ mol^{-1}. (bottom) The set of TDS calculated using common parameters: $E_1 = 60$ kJ mol^{-1}, $A_1 = 10^7$ s^{-1}, $A_{\text{diff}} = 10$ s^{-1}; and varying parameter E_{diff}: a, $E_{\text{diff}} = 23$ kJ mol^{-1}; b, $E_{\text{diff}} = 30$ kJ mol^{-1}; c, $E_{\text{diff}} = 35$ kJ mol^{-1}; d, $E_{\text{diff}} = 40$ kJ mol^{-1}.

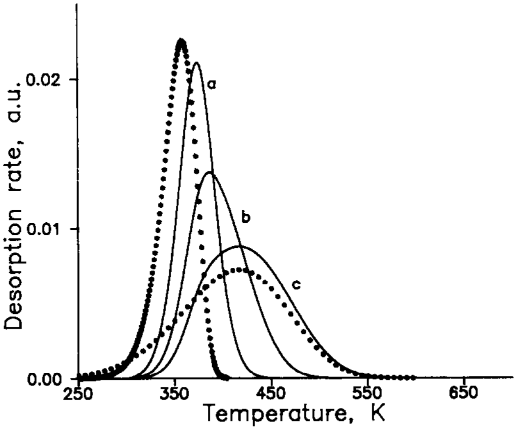

Fig. 4. The set of TDS calculated using common parameters: $E_1 = 60$ kJ mol^{-1}, $A_1 = 10^7$ s^{-1}, $E_{\text{diff}} = 23$ kJ mol^{-1}; and varying parameter A_{diff}: a, $A_{\text{diff}} = 30$ s^{-1}; b, $A_{\text{diff}} = 10$ s^{-1}; c, $A_{\text{diff}} = 4$ s^{-1}. Spectra marked by $*$ were computed with desorption parameters: $E_1 = 60$ kJ mol^{-1}, $A_1 = 10^7$ s^{-1}. Spectra marked with ● were computed with diffusion parameters: $E_{\text{diff}} = 23$ kJ mol^{-1}, $A_{\text{diff}} = 10$ s^{-1}.

demonstrates the typical series of TDS obtained with increasing parameter E_{diff}. The overall reaction rate is strongly dependent on this parameter. The spectra presented in Fig. 3 obtained by using the consecutive mechanism are identical with those calculated for the appropriate diffusion parameters only (all marked with open circles). In the whole series, only curve (a) (Fig. 3(top)) presents a process which is not controlled by diffusion, while diffusion becomes the rate limiting step with a small change of the parameter E_{diff} (curves (b)–(d)). Also, diffusion is the rate limiting step when the pre-exponential factor of desorption A_1 has high values (see Fig. 3(bottom)).

Now let us see the results of varying parameter A_{diff} when the activation energy for desorption has a small value. We observe (Fig. 4) a shift of T_M toward higher temperatures and broadening of the spectra with a small decrease in A_{diff}. The pre-exponential factor $A_1 = 10^7$ s^{-1} is applied. It is evident from Fig. 2(b) that the curve calculated for $A_{\text{diff}} = 10$ s^{-1} is in the domain of influence of both desorption and diffusion. However, Fig. 4 illustrates both possible boundary cases, the first with desorption ($*$) and the second with diffusion (●) as the rate limiting step. Therefore, as a result of A_{diff} change, a family of TDS placed between two boundary curves is obtained.

When the ratio of activation energies is on the upper limit ($E_1/E_{\text{diff}} > 5$), the desorption step becomes important in the overall process. Typical results are shown in Fig. 5. The resulting family of spectra (Fig. 5(top)) shows the result of changing the pre-exponential factor A_{diff}. As a result of variation of the diffusion coefficients from 10^{-8} to 10^{-10} m^2 s^{-1} (i.e. the

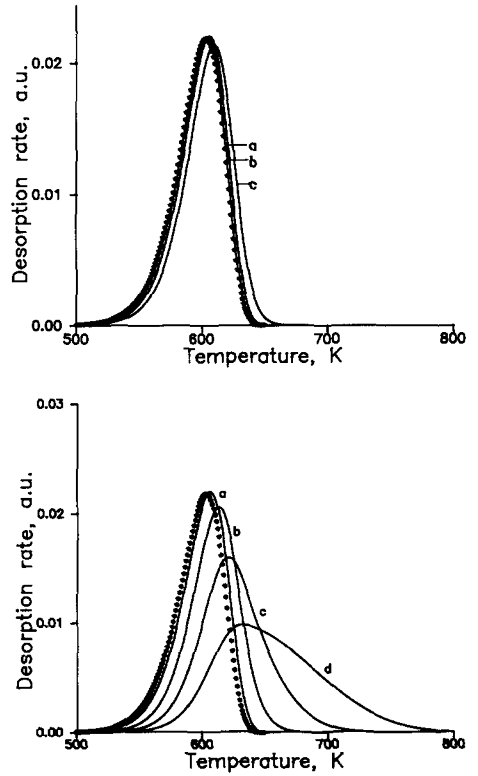

Fig. 5. The series of calculated TDS obtained by varying parameter A_{diff}. (top) The set of TDS calculated using common parameters: $E_1 = 170$ kJ mol^{-1}, $A_1 = 10^{13}$ s^{-1}, $E_{\mathrm{diff}} = 23$ kJ mol^{-1}; and varying parameter A_{diff}: a, $A_{\mathrm{diff}} = 30$ s^{-1}; b, $A_{\mathrm{diff}} = 10$ s^{-1}; c, $A_{\mathrm{diff}} = 4$ s^{-1}. Spectra marked b * were computed with desorption parameters: $E_1 = 170$ kJ mol^{-1}, $A_1 = 10^{13}$ s^{-1}. (bottom) The set of calculated TDS using common parameters: $E_1 = 170$ kJ mol^{-1}, $A_1 = 10^{13}$ s^{-1}, $A_{\mathrm{diff}} = 10$ s^{-1}; and varying parameter E_{diff}: a, $E_{\mathrm{diff}} = 23$ kJ mol^{-1}; b, $E_{\mathrm{diff}} = 30$ kJ mol^{-1}; c, $E_{\mathrm{diff}} = 35$ kJ mol^{-1}; d, $E_{\mathrm{diff}} = 40$ kJ mol^{-1}.

variation of parameter A_{diff} from 1 to 100 s^{-1}; eqn. 20), T_{M} shifts only a few degrees. Further increase of the diffusion coefficients (A_{diff}) reduces the consecutive mechanism to a first-order rate reaction, in fact, desorption becomes the rate limiting step (*).

Figure 5(bottom) presents a set of TDS obtained with different values of E_{diff}. T_{M} is very close to that calculated for the desorption step only (*). Obviously, in the case of chemisorbed molecules, the variation of both diffusion parameters (A_{diff}, E_{diff}) produces an insignificant influence on the position of the TDS. Broadening of spectra is observed with an increase of E_{diff} only, although this effect is not so significant as in Fig. 3, in spite of the same values of parameter E_{diff}.

As a result of variation of the relevant kinetic parameters in the postulated consecutive model, several trends are observed.

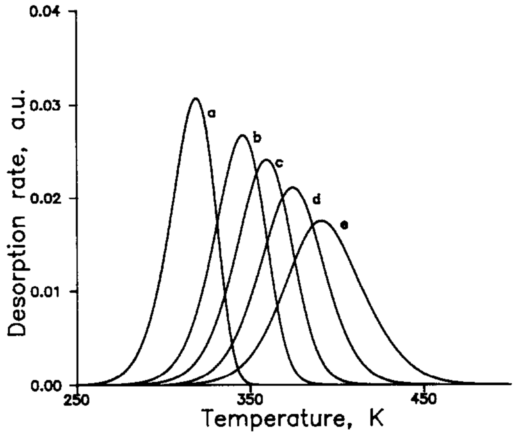

Fig. 6. The series obtained using common parameters: $E_1 = 60$ kJ mol^{-1}, $A_1 = 10^7$ s^{-1}, $E_{\text{diff}} = 23$ kJ mol^{-1}, $A_{\text{diff}} = 30$ s^{-1}; and varying heating rate β: a, $\beta = 1$ °C min^{-1}; b, $\beta = 5$ °C min^{-1}; c, $\beta = 10$ °C min^{-1}; d, $\beta = 20$ °C min^{-1}; e, $\beta = 40$ °C min^{-1}.

Generally, increasing influence of diffusion (increase of activation energy for diffusion and decrease of pre-exponential factor A_{diff}) leads to broadening of the calculated TDS and shift of the temperature of the peak maximum (T_M) toward higher values. A strong influence of both diffusion parameters on the overall reaction rate is observed in the case of small values of activation energy for desorption E_1. However, the effect of A_{diff} decrease (in the relevant range of values) is almost insignificant in the case of high energies E_1; an increase in E_{diff} produces considerably smaller consequences than that for small values of E_1. Therefore, if reaction takes place inside a pore of solid substance, the overall reaction rate could be influenced by the diffusion process, especially if the molecules are weakly bonded.

The result of variation of the heating rate (with all kinetic parameters kept constant) is represented by a typical set of TDS in Fig. 6. As usual, with increasing heating rate, the peaks shift towards higher temperatures and the curves become broader.

Generally, as a result of a reaction mechanism consisting of two consecutive steps, desorption and diffusion, under non-isothermal conditions, spectra with a single peak are obtained. Consequently, experimental resolution of the desorption and diffusion processes is not possible. In addition, problems of interpretation of single peak TDS and of calculation of kinetic parameters appear.

There are several methods for determination of kinetic parameters based on changes of T_M position. From consideration of previous results, it is clear that the diffusion step can change the profile of TDS. A well known method for determination of kinetic parameters is that based on T_M shift

TABLE 1

The comparison of kinetic parameters predicted in calculation of theoretical TDS and those obtained using Redhead's equation (pseudokinetic parameters)

Parameters used in consecutive model				Pseudokinetic parameters	
E_1 (kJ mol^{-1})	A_1 (s^{-1})	E_{diff} (kJ mol^{-1})	A_{diff} (s^{-1})	E_{pseudo} (kJ mol^{-1})	A_{pseudo} (s^{-1})
60	10^{9}	23	10	22.3	7.8
60	10^{7}	40	10	40.1	10.3
60	10^{12}	23	10	23.1	10.3
60	10^{7}	23	4	27.3	17
60	10^{6}	23	10	45.7	5×10^{3}
60	10^{7}	23	30	46.2	4×10^{4}
105	10^{12}	23	10	75.6	5×10^{7}
170	10^{13}	40	10	113.7	2.8×10^{7}
170	10^{13}	30	10	134	3.7×10^{9}
170	10^{13}	23	10	151	2×10^{11}
160	10^{12}	23	10	156.8	5×10^{11}

obtained for different linear heating rates [19,20]. In Table 1, kinetic parameters assumed in the consecutive model and those evaluated using Redhead's equation [19] (pseudokinetic parameters) are compared.

The results presented in Table 1 show that pseudokinetic parameters are close in values to kinetic parameters of the corresponding steps only in the cases where diffusion (rows 1–4 in Table 1) or desorption (row 11) is the rate limiting step. However, in the cases where both steps consecutively have an influence on reaction rate, pseudokinetic parameters between those for desorption and diffusion are obtained (rows 5–10 in Table 1). Obviously, the values of kinetic parameters obtained using the method based on the assumption of a simple surface reaction can be erroneous if in reality the reaction mechanism is complex. Theoretically, the pre-exponential factor for desorption has a value near the frequency of vibration of adsorbed molecules, i.e. 10^{13} s^{-1}. However, experimentally obtained values, published in the literature [9] are often considerably smaller. It should be noted from Table 1 that the values of pseudopre-exponential factors are smaller than those theoretically expected in all cases where the diffusion step is important for the overall reaction rate. Evidently, experimentally obtained low values of pre-exponential factors can arise from the contribution of a diffusion step in a surface process.

REFERENCES

1 G. Comsa and R. David, Surf. Sci. Rep., 5 (1985) 145.
2 M. Grunze, Springer Ser. Surf. Sci., 5 (1986) 197.
3 F.M. Lord and J.S. Kittelberger, Surf. Sci., 43 (1974) 173.

4 D. Fraenkel and A. Levy, J. Chem. Soc. Faraday Trans. 1, 84 (1988) 1817.
5 Y.C. Chan and R.B. Anderson, J. Catal., 50 (1977) 319.
6 K. Christmann, Surf. Sci. Rep., 9 (1988) 1.
7 I.M. Campbell, Catalysis at Surfaces, Chapman and Hall, London, 1988.
8 N.D. Hoyle, P.H. Newbatt, K. Rollins, P.A. Sermon and A.T. Wurie, J. Chem. Soc. Faraday Trans. 1, 81 (1985) 2605.
9 E.G. Seebauer, A.C.F. Kong and L.D. Schmidt, Surf. Sci., 193 (1988) 417.
10 J.M. Soler and N. Garcia, Surf. Sci., 124 (1983) 563.
11 D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, 1974.
12 R.M. Barrer, Zeolites and Clay Minerals as Solids and Molecular Sieves, Academic Press, London, 1978.
13 D.A. King, Surf. Sci., 64 (1977) 43.
14 A. Cassuto and D.A. King, Surf. Sci., 102 (1981) 388.
15 M. Alnot and A. Cassuto, Surf. Sci., 112 (1981) 325.
16 J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, 1956.
17 J. Šesták, Thermochim. Acta, 3 (1971) 150.
18 D. Kahaner, C. Nolez and S. Nash, Numerical Methods and Software, Prentice-Hall International, Englewood Cliffs, NJ, 1989.
19 A.P. Redhead, Vacuum, 12 (1962) 245.
20 Y. Amenomiya, Chemtech, 6 (1976) 128.