Simulation of Composite Temperature-Programmed Desorption Curves. I. One Single Continuous Stirred Tank Reactor Approximation

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A theoretical analysis of the behaviour of temperature-programmed desorption curves (TPD) is given for an adsorption/desorption system where there are several distinct adsorbed states, some of them possibly being rather similar so that they mix into one desorption curve during an experiment. The analysis has been carried out for a model with no temperature or pressure gradients and for complete adsorption/desorption equilibrium. The Langmuir adsorption isotherm is valid.

Conditions for obtaining maximum information from desorption experiments have been found. Choosing low initial pressure or high initial temperatures entails the loss of information about the weakest sites, but the TPD curve for the stronger sites is not significantly influenced. The "sharpness" of the different TPD peaks and the possibility of obtaining separate peaks for different adsorption states increases with *decreasing* heating rate. The effect may be discussed in terms of a "sharpness factor" $Q/(\beta \cdot n_{0T})$, where Q is carrier flow rate, β is rate of temperature increase and n_{0T} is catalyst adsorption capacity.

Dedicated to Professor Otto Bastiansen on his 70th birthday

There has been a recent emphasis on "the theoretical" foundation of temperature-programmed desorption (TPD) on high surface area substances. A survey of the field and further references are found in the recent works by Demmin and Gorte,[1] and Rieck and Bell.[2]

The most important outcome of the recent efforts may be that it has been shown that readsorption in the catalyst bed cannot be eliminated and that the normal situation is that there is essentially adsorption equilibrium throughout the TPD. During these investigations the influence of carrier gas flow rate, particle size and bed depth were investigated.

Rieck and Bell[2] investigated the TPD for the case where the system can be approximated to consist of a single continuous stirred tank reactor (CSTR) as well as several such reactors in series. Demmin and Gorte[1] extended the multiple CSTR concept by establishing the differential equations which are valid for infinitely many CSTR's, i.e. for the plug-flow reactor (PFR) limit.[1]

It is however, remarkable that TPD from a sorbent with more than one set of (ad)sorbing sites has not been looked at. It is precisely for this case that temperature-programmed desorption is a superior investigation technique.

It is the purpose of this paper to describe more closely the properties of a TPD system with several distinct adsorbed states, some of them possibly rather similar so that they may mix into one desorption peak during the TPD experiment.

The aim of the work described here was to obtain information about the performance of TPD experiments in order to obtain maximum information in such cases.

The model

Like Rieck and Bell,[2] we shall assume that the experimental system behaves like a single CSTR

model or, in some cases, a multiple CSTR model (see their Fig. 1). The experimental layout to have in mind is, however, like Fig. 1 in Demmin and Gorte's paper.[1]

It is immaterial for the discussion which follows whether the sorbent consists of porous particles or not. A zero concentration gradient within each CSTR element is assumed. This corresponds to the limiting case of infinite diffusion coefficient, or the zero flow and rate of temperature rise limit. It has been shown in Refs. 1 and 2 that this limiting behaviour is easily obtained in experimental systems.

In cases in which the experiment is arranged so that the sorbent is filled in a long narrow tube, such as a chromatographic column, a model of multiple CSTR will have to be used. The situation will eventually, with increasing length-to-radius ratio, transform into a situation corresponding to a plug-flow reactor (PFR). The analysis will be carried out for a constant rate of temperature increase $(T = T_i + \beta \cdot t)$,* but any time-dependent temperature function could of course be used. The mathematical formulations take their simplest forms when $d(l/T)/dt$ is kept constant, but the ensuing simplification is of no importance for the handling of the equations.

The model analyzed here is based on the validity of the Langmuir isotherm for each set of sites in, generally, multi-site cases. Since the desorption model investigated here is based upon assumed complete equilibrium, and diffusion is effectively assumed to be infinitely fast, eqn. (1) is obviously valid for multi-site Langmuir adsorption.

$$n = \sum_i n_i = \sum_i \frac{n_{0i} \cdot K_i \cdot p}{1 + K_i \cdot p} \qquad (1)$$

From this equation the following equation is easily deduced by simple mass balance considerations.[3]

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*The following symbols are employed:

n, n_0: molar quantities; $K = \exp((\Delta H^0 - T\Delta S^0)/RT)$: the adsorption constant; p: partial pressure of adsorbate/desorbate; Q: Volume flow rate of carrier gas + desorbate at prevailing pressure, measured at temperature T_0 (contribution of desorbate to gas flow is neglected); R: gas constant; t: time; β: temperaure increase per unit time; ΔH^0, ΔS^0: Enthalpy and entropy of adsorption in standard state; T: absolute temperature.

$$p \cdot (Q/RT_0) = - \sum_i \frac{n_{0i} \cdot K_i}{(1 + K_i \cdot p)^2}$$

$$\times \left(\frac{dp}{dt} + p \cdot \beta \cdot \frac{\Delta H_i^0}{R \cdot T^2} \right) \qquad (2)$$

In order to treat the differential equation, e.g. for carrying out simulation computations, it is appropriate to rearrange it so that dp/dt is an explicit function of $T(t)$ and p. The following result is then obtained:

$$\frac{dp}{dt} = - \frac{p \cdot (Q/RT_0) + p \cdot \beta \cdot (1/R \cdot T^2) \cdot \sum_i L_i \cdot \Delta H_i^0}{\sum_i L_i} \qquad (3)$$

where $\quad L_i = \dfrac{n_{0i} \cdot K_i}{(1 + K_i \cdot p)^2}$

It should be kept in mind that the equilibrium constant, K, is a function of temperature, T, which is again a function of time, t.

Eqn. (3) is valid for a single CSTR. It can easily be extended to comply with multiple CSTR. This will be described in a subsequent paper.[4]

Eqn. (3) is an ordinary differential equation of the first order. It cannot be solved in terms of elementary functions, but its numerical solution does not pose any particular problems. The remainder of this paper will concentrate on simulating various "experimental" situations by means of eqn. (3). In doing this, information is obtained on the behaviour of systems behaving according to the model outlined above, and also on how actual experiments should be carried out in order to obtain maximum information from them.

Experimental

There are no real experiments to be reported, but a short discussion of the simulated "experimental conditions" chosen for the simulations may be warranted. Furthermore, a few words about the computer and the computational method seem appropriate.

Emphasis has been put on choosing parameters in eqn. (3) which are centered around experimentally attainable values. This has been done in

the hope that the results may be directly transferred to experimental reality.

Carrier gas flow rate. A value of 30 ml min^{-1} at room temperature (atmospheric pressure) has been used throughout.

Adsorption capacity. n_0 on site i, i.e. n_{0i}, has been given values in the range 0.1 to 0.25 mmol (2 to 5 ml at STP). These are reasonable values for 10 to 1000 mg of sorbent.

Since the case of a single set of adsorbing sites has been investigated in depth by others,[1,2] all cases considered here involve at least two sets of sorbing sites.

Rate of temperature increase, β. A main point is to investigate the influence of this parameter, and values ranging from 0.02 K min^{-1} to 100 K min^{-1} have been investigated.

Pressure. The desorbent pressure during a TPD will depend upon the choice of the other parameters. However, the initial pressure depends on how a given experiment is carried out, and it is therefore a parameter determined by the experimenter. A range of initial pressures from 10^{-8} mbar to about 1 mbar have been investigated.

The fundamental parameters of an adsorbent/adsorbate system, i.e. enthalpy and entropy of adsorption, are not influenced by the experimenter. Essentially all computations have been carried out for a single standard entropy of adsorption which was chosen to be $\Delta S^0 = -200$ J mol^{-1} K^{-1} for a standard state of the gas at 1 mbar and of the adsorbed state at a coverage $\theta = \frac{1}{2}$ for a given set of adsorbing sites. The stipulated value for the adsorption entropy is quite close to the translational entropy of small molecules at 1 mbar. Thus, if a molecule loses its translational freedom upon adsorption and this loss is the dominant contribution to the adsorption entropy, the choice is a reasonable one. The enthalpies of adsorption have been chosen in the range -75 kJ mol^{-1} to -155 kJ mol^{-1}. This is a range quite often met in real systems.

Temperature and temperature range. Like the starting pressure, the choice of initial temperature affects the desorption curve which might be obtained. High initial temperatures and low pressures remove adsorbate from the weaker sites, and thus also information about them.

The larger part of the simulations was carried out using 285 or 335 K as initial temperature. The temperature was mostly varied over a 650 K interval, which was sufficient to desorb all adsorbate in most cases.

The computations were carried out on an Epson QX-10 microcomputer, programming in BASIC. The computations reported here were mostly carried out in the seven-digit single precision mode, but tests have been carried out to ascertain that changing to 16 digit precision accuracy would not change the results.

The most commonly used method for numerical solution of differential equations is the Runge-Kutta method, which is one of the fastest computational methods. In the present case it was decided that computational speed was not very important (it was fast enough); there was thus no incentive to spend time on programming, and a more easily programmed method was chosen (Euler's method), care being taken to ensure sufficient computational accuracy. The Epson QX-10 has a 640×400 high resolution graphic screen, the content of which may be reproduced directly on paper by a matrix printer. The curves presented here are copies of such curves.

Results and discussion

Suppose a given experiment has given the TPD curve shown in Fig. 1. Such a curve will be obtained provided the model is valid (Langmuir adsorption, 1 CSTR) when the sorbent/gas interaction results in 5 sites with the properties given in Table 1, and the experiment is carried out according to the "experimental conditions" given in the figure text. This adsorption system will form the basis for the discussion in this paper. The guiding principle for the choice of sorbing system and simulated experimental conditions can be summarized as follows:

Five sets of sites were chosen in order to pack a lot of information into one figure. The first peak of the curve in Fig. 1 is due to coalescence of the peaks from the first two sites. The following three peaks are from the remaining three sites. They exhibit increasing separation in accord with the increasing difference, absolute and relative, between the adsorption enthalpies. The adsorption
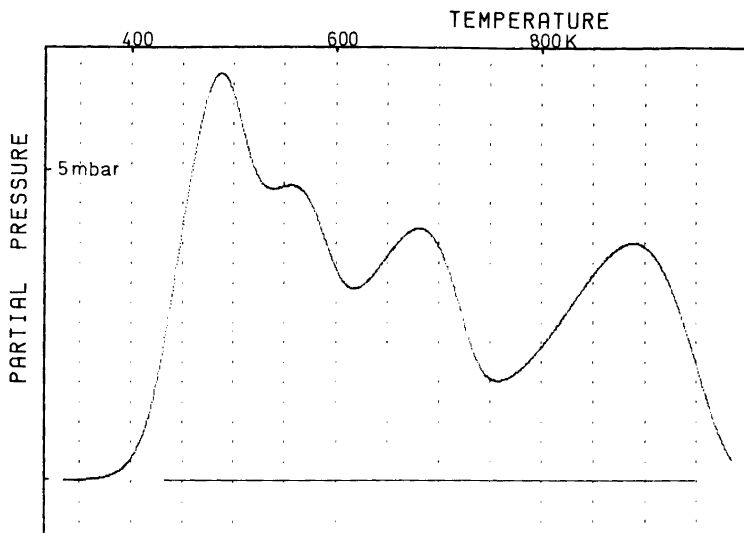
Fig. 1. Simulated desorption curve for adsorbent with 5 sets of sites having the adsorption capacities and adsorption enthalpies given in Table 1. Carrier gas flow 30 ml min^{-1}, start temperature 285 K, start pressure 0.001 mbar. Heating rate 3 K min^{-1}. The first peak is attributable to sites 1 and 2. Their energy difference is so small that the peak is not separated.

entropy represents a fair estimate of the loss of entropy of a gas molecule when it is losing essentially all freedom of motion upon being adsorbed (standard state in gas phase 1 mbar). The exact value of this adsorption entropy does not significantly influence the following discussion. The n_0 values have been chosen to represent values which might be met in experimental reality. The relative values of n_{0i} were chosen so that each peak could be of the same height.

The "experimental conditions" correspond to a physically feasible experiment (except perhaps the initial pressure, which at 0.001 mbar is lower than most experimenters' patience would permit).

Table 1. Physical properties of adsorption system. These data were used for the simulated TPD curves shown in the figures.

n_{0i} / mmol	ΔH_i^0/kJ mol^{-1}	ΔS_i^0/J mol^{-1} K^{-1}
0.120	− 75	−200
0.134	− 80	"
0.151	− 95	"
0.184	−117	"
0.245	−155	"

When running a TPD experiment there are several experimental parameters which can be changed, viz. carrier gas flow, mass of sorbent, start temperature, heating rate, and start pressure. We shall here investigate the influence of changing start pressure, start temperature and heating rate. The effect of changing the heating rate is the same as could be obtained by changing flow rate or sorbent mass. This can be seen from eqn. (3), and is discussed in detail below.

Start pressure. The first experimental parameter to be changed is the initial pressure, p_{start}. A series of computations using different initial pressures have been carried out. Resulting TPD curves from some of the computations are shown in Fig. 2. Other "experimental conditions" are the same as for Fig. 1 apart from the somewhat higher starting temperature, T_i, which was set at 335 K.

The effect of gradually going down from the relatively high start pressure of 0.1 mbar to 1×10^{-8} mbar in different simulated experiments is seen to be quite dramatic as far as the low-temperature end of the curves is concerned. On the other hand, it should be noted that all peaks on the high-temperature side of the one "under
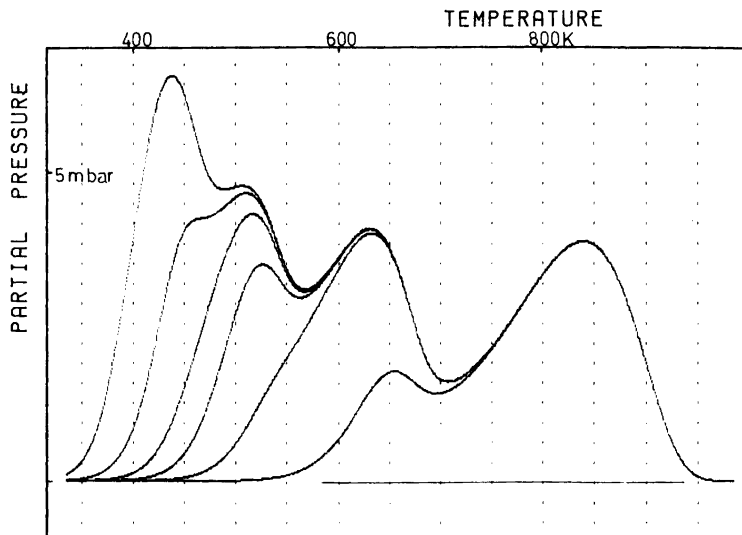
Fig. 2. Simulated desorption curves for various start pressures. The desorption system is the same as in Fig. 1, apart from the initial temperature which has been chosen at 335 K. The start pressures are, from left to right, 1×10^{-1}, 1×10^{-2}, 1×10^{-3}, 1×10^{-4}, 1×10^{-5} and 1×10^{-8} mbar.
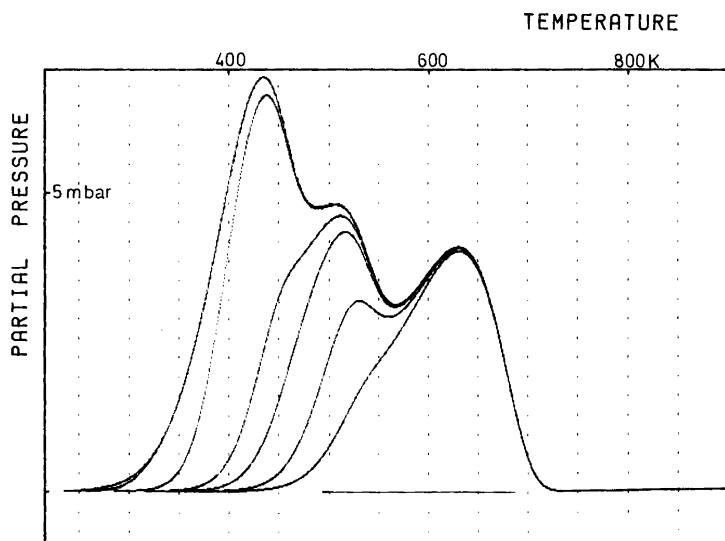

Fig. 3. Stimulated desorption curves for various start temperatures. The desorption system is the same as in Fig. 1 [but the high energy site (site 5) is taken away because the adsorption constant K_5 is so large at the lowest temperatures that the maximum treated by the BASIC (10^{38}) is exceeded. For the start temperatures used, the site 5 peak would not be influenced). The start temperatures (from left to right) are 235, 255, 285, 315, 335, 365 and 385 K. Start temperatures 235 and 255 K both lead to curve I.

attack", for a given set of conditions, are unaffected. Even the peak under attack appears, although much smaller, at only slightly higher temperature.

The conclusion to be drawn from these computations is that loosely bonded sorbate, lost before the TDP, will not compromise the information to be obtained about the more strongly held molecules.

Start temperature. Another parameter the experimenter can, in principle, choose at will is the start temperature.

Not surprisingly, the effect of going from low to high start temperature at constant start pressure is the same as going from high to low start pressures at constant start temperature. Peaks due to weak adsorption are lost, but the remainder of the TPD curve is hardly influenced. The outcome of a series of computations is shown in Fig. 3. Experimentally, the temperature is usually the more easily controlled property. The situation most often met is that information about the whole adsorption function is wanted. In that case, the TPD would be run from as low a start temperature as feasible.

The result that the position of a desorption peak is not significantly influenced by desorption taking place from weaker sites is self-evident when there is no readsorption taking place. The result presented here shows that it is valid, as a very good approximation, also for the case of complete adsorption equilibrium.

Heating rate. From the foregoing discussion it is clear that although the TPD curves at first sight are completely altered when the prehistory of the adsorption system is changed, the transformation is in a sense a superficial one; the remaining peaks are essentially unchanged. The changes induced by changing the heating rates are, however, much more profound.

The effect on a given adsorption system of choosing different heating rates, as treated above, is seen clearly from Fig. 4. All "experiments" were started at 285 K and a start pressure of 0.001 mbar. The heating rate ranges from 0.025 K min^{-1} to 50 K min^{-1}. TPD experiments will often be run at 5 K min^{-1} heating rate. The curve obtained for this heating rate may be considered a "Standard" TPD curve for this system.
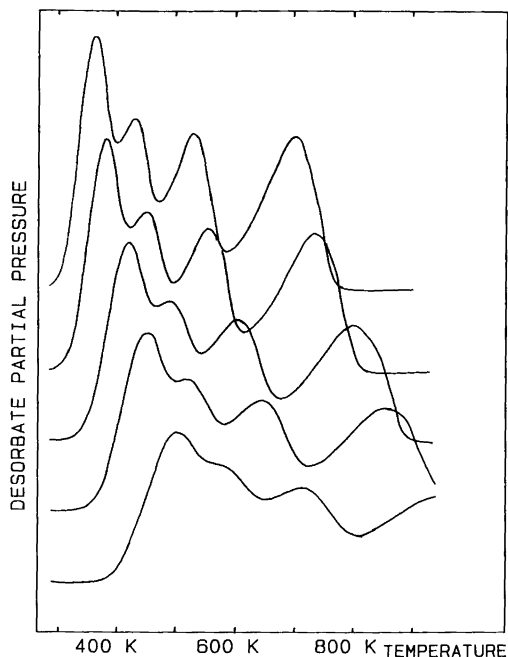
Increasing heating rates from 5 to 20 and fi-

Fig. 4. Stimulated desorption curves in the same system as in Fig. 1. All parameters but the heating rates are the same; they are 0.025, 0.1, 1, 5 and 50 K min^{-1}, respectively, from the top curve downwards. The ordinate scales have been chosen so that the areas below the curves are equal.

nally to 50 K min^{-1} move peaks to higher temperatures, and they increase in height approximately proportionally with the heating rate. Not seen in the figure is the fact that the ordinate scale for each curve is inversely proportional to heating rate.

The important effect of increasing the heating rate is that the curves are smeared out. The 5 K min^{-1} curve shows a reasonably well separated "spectrum". The second peak is defined by a barely perceptible maximum at 5 K min^{-1}; at 20 and 50 K min^{-1} it is only present as a broad shoulder. Turning the other way, we may see how the TPD curves develop when we try 1, 0.1 and finally 0.025 K min^{-1}. The peak maxima are shifted towards lower temperatures, as is to be expected. However, above all, the sharpness of the peaks increases markedly. The first and second peaks become very distinct, and they would undoubtedly also be separated in the case of a

considerably smaller adsorption enthalpy difference than that used in the computations.

Peak No. 1 is known to be attributable to two sets of sites with adsorption enthalpies of -75 and -80 kJ mol^{-1}. Peaks with such small energy differences apparently cannot be separated by a TPD technique.

The most widely used technique for estimating activation energies of desorption (when it is assumed that there is no readsorption) or enthalpies of adsorption (when allowing for readsorption) is to make runs at different heating rates, e.g. 3–50 K min^{-1}. The temperature of peak maximum at each heating rate is recorded. From these data the activation energy, E_a, or adsorption enthalpy, ΔH, is computed.[2,5] The results presented here show that the technique of using high heating rates leads to loss of information from the TPD curves. Rather, one should strive to use the lowest feasible heating rates.

Low heating rates conduce to low desorbate concentrations. This must not be compensated for by increasing sorbent quantity or decreasing carrier flow rate, as this will nullify the effect of a low heating rate. Indeed, as shown below, there is, within this model, only one experimental parameter the experimenter can adjust, namely the factor $Q/(n_{0T}\cdot\beta)$ which should, for maximum TPD spectrum sharpness, be as large as possible. It may thus be termed a "sharpness factor".

In order to show in detail that there is in fact a single sharpness factor which governs the behaviour of a given adsorption system, we shall go back to eqn. (3):

The adsorption capacity of each set of sites is given by n_{0i}. Clearly, we can write

$$n_{0i} = n_{0T}\cdot x_{0i}$$

where n_{0T} is the total adsorption capacity of the sorbent, and x_{0i} is the mole fraction capacity on each set of sites. Let L_i in eqn. (3) be replaced by a corresponding normalized quantity

$$L_i' = \frac{x_{0i}\cdot K_i}{(1 + K_i\cdot p)^2} \tag{4}$$

so that

$$L_i = n_{0T}\cdot L_i' \tag{5}$$

Let us furthermore make use of the linear heating rate, $T = T_i + \beta t$, from which it follows that

$$\frac{d}{dt} = \frac{d}{dT}\cdot\frac{dT}{dt} = \beta\cdot\frac{d}{dT} \tag{6}$$

Substituting from eqns. (5) and (6) into (3), and carrying out a slight rearrangement, the result given by eqn. (7) is obtained. The experimental parameters carrier flow (Q), adsorption capacity (n_{0T}) and heating rate (β) are seen to appear only in the expression $(Q/(n_{0T}\cdot\beta)$.

Clearly the TPD spectrum sharpness depends upon the magnitude of this sharpness factor, and not on flow rate, catalyst adsorption capacity (proportional to catalyst mass) or heating rate in particular.

It has now been shown that for the model upon which this paper is based, the decisive experimental parameter is the sharpness factor $Q/(n_{0T}\cdot\beta)$, which should be as large as possible. The extent to which the model is applicable is, however, not independent of which property is forcing the sharpness factor to a large value. Large values of Q, for instance, will result in an experiment taking place in a short time, and the assumption of zero concentration gradients will not be very realistic. These aspects have been analyzed in considerable detail by Gorte[1,6] and by Rieck and Bell.[2]

The consequences of carrying out the experiment in such a way that the single CSTR model breaks down for peak separation ability will be examined later.[4]

$$\frac{dp}{dT} = -\frac{p\cdot\dfrac{1}{RT_0}\cdot\left(\dfrac{Q}{n_{0T}\cdot\beta}\right) + p\cdot\dfrac{1}{RT^2}\cdot\displaystyle\sum_i L_i'\cdot\Delta H_i^0}{\Sigma L_i'} \tag{7}$$

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