Journal of Thermal Analysis, Vol. 14 (1978) 53—77

METHODS FOR THE DETERMINATION OF HEATS OF ADSORPTION

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(Received September 15, 1977)

Various methods can be utilized for the determination of heats of adsorption, either directly by means of calorimeters or indirectly by application of the Clausius-Clapeyron equation to equilibrium data.

The determination of equilibrium data in the case of adsorption phenomena is discussed in the first part of this review. Gas-chromatographic methods and a method based upon the measurement of the equilibrium pressure of oxygen over metal oxides are, in particular, described.

When adsorption is performed under non-equilibrium conditions, the use of the Clausius-Clapeyron equation is precluded. A brief description of the applications of kinetic methods for the determination of activation energies of desorption is presented in the second part of the review.

The third part of the review is devoted to a survey of the calorimetric methods available for adsorption and heterogeneous catalysis studies. Recent technological improvements such as the use of continuous or semi-continuous procedures or the deconvolution of calorimetric curves are described.

Physical adsorption, like any phase-change, and chemical adsorption, like any chemical reaction, are basically manipulations of energy. They can therefore be characterized by variations of the fundamental thermodynamic functions: Gibbs energy, enthalpy, entropy, etc. [1].The methods used for the experimental determination of these quantities do not differ in principle from those utilized in classical thermodynamics and are essentially based upon calorimetric and *pv* data.

However, a casual glance at the literature reveals that an extremely large number of direct or indirect methods have been proposed and that the same systems are repeatedly reinvestigated (hydrogen on nickel is a good example) [2]. The discrepancy between the apparent simplicity of the problem and the amount of work which has been devoted to its solution in practical cases can be explained by the three following reasons:

i) Adsorption can occur in an extremely broad temperature range, covering practically the whole temperature scale, and it can be detected in an extended pressure range. Moreover, since any molecule, in the gaseous or liquid state, may adsorb, when some experimental conditions are satisfied, on the surface of any solid or liquid, it is clear that a large number of experimental techniques will be required to investigate all the aspects of such a universal phenomenon.

ii) In contrast with their analogues for phase changes or chemical reactions, molar thermodynamic quantities in adsorption are not intensive: they change with the quantity of material involved. It is a well-known fact that in a large number of cases the (e.g.) differential molar energy of adsorption decreases with increasing surface coverage. Changes of differential thermodynamic quantities with increasing surface coverage can be explained by a number of reasons related to a preexisting or induced surface heterogeneity. Their determination, however, complicates the experimental study of adsorption. Moreover, the biographical heterogeneity of the adsorbent very often varies markedly with the sample preparation or pretreatment, and the experimentalist is thus compelled to reinvestigate similar systems.

iii) Depending upon the final aim of the proposed thermodynamic study and considering the features of adsorption collected in i) and ii), it is clear that the experimentalist will have to face different constraints. Ultra-high vacuum studies with oriented single-crystal planes, for instance, must be developed to determine data that theoreticians can use in their calculations. High-temperature studies of industrial catalysts will be needed in other cases. The multiplicity of the investigated systems and their variability certainly justifies the number of methods which have been proposed.

In this review, the discussion will be limited almost exclusively to the determination of "heats of adsorption". This term is commonly, but somewhat loosely, used to qualify the following derivative thermodynamics functions [3] and their integrals:

– the differential energy of adsorption defined by:

$$\Delta_a \dot{u} = \dot{u}^a - u^g \tag{1}$$

where $\dot{u}^a$ and u^g are the differential molar energies of the adsorptive in, respectively, the adsorbed and gaseous state, at a constant temperature and volume. It is related to the calorimetric differential heat $\left(\frac{\partial Q_{ex}}{\partial n^a}\right)_{T,A}$ by

$$\Delta_a \dot{u} - RT = \left(\frac{\partial Q_{ex}}{\partial n^a}\right)_{T,A} + V_B \left(\frac{\partial p}{\partial n^a}\right)_{T,A} \tag{2}$$

where V_B is the volume of the calorimeter vessel and p, the adsorptive pressure.

– the differential enthalpy of adsorption, defined by

$$\Delta_a \dot{h} = \dot{h}^a - h^g \tag{3}$$

where $\dot{h}^a$ and h^g are the differential molar enthalpies of the adsorptive in, respectively, the adsorbed and gaseous state, at a constant temperature and pressure. It is also called the isosteric heat (or preferably, enthalpy) [1] of adsorption, q_{st}:

$$q_{st} = \dot{u}^a - u^g - RT = \dot{u}^a - h^g = \dot{h}^a - h^g \tag{4}$$

since, in the Gibbs model, the adsorbate volume is equal to zero.

Determination of heats of adsorption from equilibrium data

Adsorption isotherms (coverage, θ, versus pressure at a constant temperature) can be used to calculate heats of adsorption. It is probably pertinent to recall at this point that all data should correspond to a *reversible equilibrium* of the system, in the thermodynamic sense. The calculations of adsorption heats, in the case of systems which have not been *proved* to be reversible, may lead to serious errors. In this respect, the distinction between physical and chemical adsorptions is pointless. However, it is true that physical adsorptions are usually reversible, whereas many chemisorptions are studied at pressures and temperatures where they are not reversible.

When the relation between θ-p data and thermodynamic quantities is known, it is possible to calculate these quantities, and their variation with coverage, from a single isotherm. For instance, De Boer and Broekhoff have calculated, in this manner, the heats of adsorption of krypton, nitrogen and ethyl chloride on graphitized carbon, by assuming a two-dimensional condensation of the adsorbate [4]. This is not a purely experimental method for the determination of thermodynamic quantities, since a theoretical adsorption model must be assumed. It will not therefore be described any further in this review.

All experimental determinations of adsorption heats are based upon the use of the Clausius-Clapeyron equation:

$$q_{\mathrm{st}} = RT^2 \left(\frac{\partial \mathrm{Ln}\, p}{\partial T} \right)_\theta . \tag{5}$$

The underlying assumptions are that the partial molar volume of the adsorptive far exceeds that of the adsorbate and that the perfect gas approximation is justified.

Figure 1 shows, schematically, adsorption isotherms for two temperatures T_1 and T_2 ($T_1 > T_2$). If $q_{1\mathrm{st}}$ represents the isosteric heat of adsorption at a fractional coverage θ_1, then from Eq. (5):

$$\mathrm{Ln} \left(\frac{p_1}{p_2} \right) = \frac{q_{1\mathrm{st}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] . \tag{6}$$

The dependence of the isosteric heat on coverage can readily be evaluated by drawing a series of horizontal lines across the diagram in Fig. 1, reading off the corresponding values of pressure at the respective temperatures and substituting in Eq. (6).

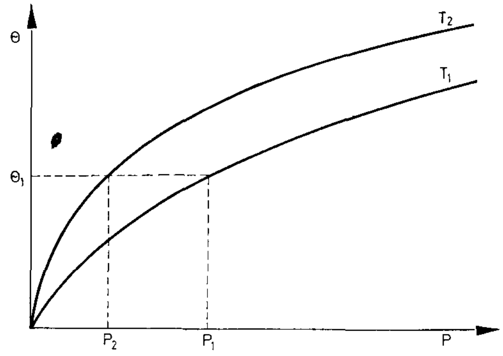

Fig. 1. Schematic diagram of adsorption isotherms at two temperature T_1 and T_2

It is important to note that isosteric heats are a function of temperature, cacording to Kirchhoff's law,

$$q_{st} = q_{0\,st} + \int_{0}^{T} \Delta Cp \, dT \tag{7}$$

ΔCp being the difference in the molar heat capacities of the adsorptive and of the adsorbate at a constant pressure. The temperature range of the isotherms used for the calculation of isosteric heats should therefore be reasonably narrow. Furthermore, if, in the temperature range investigated, another cause of variation of q_{st} with temperature exists (if the nature of the adsorption bond or the structure of the adsorbed layer change, for instance) it is evident, but still worth mentioning, that isosteric heats should not be calculated.

Volumetric and gravimetric adsorption methods

The different methods, either gravimetric or volumetric, for the determination of adsorption isotherms have been described in comprehensive treatises on adsorption or heterogeneous catalysis, e.g. [5] (for a review on volumetric measurements, see [6]; for recent gravimetric measurements, see [7, 8].

One of the difficulties in these measurements comes from the fact that the equilibrium pressure of the adsorbate is measured in a part of the adsorption line where the temperature is different from that of the adsorbent. Corrections for transpiration effects or thermomolecular flow must be carefully made. This often limits the precision of the measurements in the low-pressure range. However, the possibility of the volumetric determination of adsorption isotherms extending from ultra-high vacuum (relative pressure: 10^{-13} torr) [9] to saturation vapor pressure has been clearly demonstrated [10]. In gravimetric determinations, the accurate measurement of the adsorbent temperature is uncertain [8].

In the low-pressure region, the presence on the adsorbent surface of a small number of sites which retain the adsorptive irreversibly may also be the source of errors. Activated diffusion of the adsorbate may give rise to an apparent adsorption equilibrium, especially when adsorption is achieved at a low temperature. In the high relative pressure range, the nature of the adsorbed species may change, for a given surface coverage, when the temperature varies. Figure 2, which reports the isosteric and calorimetric heats of adsorption of oxygen on a 13 X zeolite at 77 K, may serve to illustrate the influence of the above-mentioned phenomena on the accuracy of determination of isosteric heats [11]. Isosteric heats are too low for small coverages and too high for high coverages. Diffusional limitations probably explain the low initial isosteric heats, and small variations, with temperature, in the filling of the zeolite cavities (at a constant coverage) probably explain the high isosteric heats for high coverages [11]. The uncertainty of adsorption isotherms in the low-pressure range and its influence on calculated isosteric heats has also been discussed by Julis et al. [12].

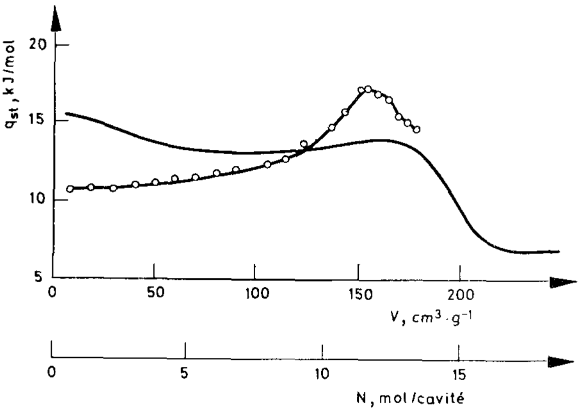

Fig. 2. Isosteric heats of adsorption of oxygen on a 13 X zeolite at 77 K, determined from equilibrium data (open points) and by calorimetry (solid line) [11]

Miscellaneous adsorption methods

The change of any property of the system, associated with changes of surface coverage by the adsorbate, may be used to plot adsorption isotherms. One of the first examples of such investigations was published by Esterman in 1925 [13]. He showed that, when a stream of metallic vapor impinges on a cold surface, a deposit is formed provided the temperature of the surface is below a certain critical temperature. From measurement of this critical temperature as a function of the density of the vapor, the heat of adsorption of cadmium vapor on glass surfaces, for instance, was calculated.

In recent years, numerous isotherms have been obtained, and numerous sets of isosteric heats calculated, from the data given by the modern techniques for studying adsorption on oriented planes at a single-crystal surface. This method is probably the best one, at the moment, to determine adsorption heats on quasi-ideal surfaces and thus to provide accurate data for theoretical calculations.

A few examples will be presented:

Germer and McRae, by measuring the temperatures at which a given LEED pattern disappears for different gas pressures, determined the isosteric heats of adsorption of hydrogen and deuterium on a (110) plane of nickel [14].

Kottke et al. [15] have determined the isosteric heat of adsorption of carbon monoxide on polycrystalline gold by measuring the intensity of the ~ 2120 cm^{-1} IR absorption band, corresponding to adsorbed carbon monoxide at different coverages and temperatures.

Changes of work function associated with adsorption have also been utilized to calculate isosteric heats. Field-emission microscope data have been used for this purpose by Drechsler et al. [16] to study hydrogen on tungsten; by Kraemer et al. [17] to study hydrogen on ruthenium; and by Bermond et al. [18] to study lead on tungsten. The vibrating condensor method has been used by Christmann et al.

[19], in addition to LEED and Auger electron spectroscopy, to study the adsorption of CO on silver-palladium alloys and to calculate the isosteric heats of adsorption. Auger electron spectroscopy can also be used to measure the surface coverage by adsorbed species and thus to determine adsorption isotherms: the isosteric heat of adsorption of oxygen on the (111) plane of tungsten at elevated temperatures (1800–2750 K), for instance, has been measured by Baenninger et al. [20] by means of this technique.

The use of physical techniques to determine adsorption equilibrium data is, of course, not limited to ultra-high vacuum studies. Adsorption of hydrogen on alumina-supported platinum catalysts has thus been studied by Primet et al. [21] by means of IR spectroscopy. Clarkson et al. [22] have used the width of an ESR line, as a pressure indicator, to study the adsorption of oxygen on Vycor glass. Charging curves, as a function of the adsorptive pressure, measured in electrolytic cells, were used by Varushchenko et al. [23] to determine the adsorption isotherms of hydrogen on boride-platinum group metal catalysts, and by Podvyazkin et al. [24] in the case of the hydrogen-platinum black system in sulfuric acid solution.

The rpeceding examples show that the method has a broad applicability. However, in order to obtain reliable results, it should be demonstrated in each particular case that:

i) all data refer to a reversible equilibrium of the adsorbate;
ii) the same quantitative relation exists between surface coverage, at any temperature and pressure, and the value of the physical property which is used to characterize the surface coverage;
iii) the same surface species are formed upon adsorption in the whole pressure and temperature ranges investigated.

When one or more of these requirements are not fulfilled, serious errors may result in the calculation of the isosteric heats. In order to show that these requirements are met, it is often necessary to use other, complementary physical techniques. For example, the relation between work function values and surface coverage may be verified by performing a desorption of the adsorbate and by measuring the number of desorbed species by means of a mass-spectrometer. It must also be proved that the use of a physical technique does not perturb the adsorbate and its bonding with the adsorbent surface: the electric field which exists at the adsorbent tip in a field-emission microscope may polarize the adsorbed species and thus create an additional bond energy. Experiments using different field intensities are required to study this phenomenon and eventually correctits effects [16]

Desorption methods

Equilibrium data are sometimes more easily or more accurately obtained from desorption than from adsorption experiments .Because of the impossibility of cooling a nickel film down to ~ 78 K in a reasonably short time at the low working pressure and to keep this temperature constant during a whole adsorption-isotherm run, Schram [25] used, for instance, the principle of reversibility of physical adsorption and measured the equilibrium values of the volume of adsorbed argon at slowly rising temperature. When the eventuality exists during adsorption of a simultaneous formation of both reversibly and irreversibly adsorbed species, desorption experiments can be performed to determine equilibrium data. For instance, Micale et al. [26] studied the desorption of water from the surface of rutile at temperatures varying from 298 to 373 K by means of a quartz reed microbalance and calculated isosteric heats of desorption from their data.

When the adsorptive is also a component of the adsorbent (as in the case, for example, of oxygen adsorption on metal oxides), a correct definition of surface coverage is difficult, since there exists a continuous transition from adsorbed species to lattice species. A method which has been frequently used to determine the bond energy of oxygen on metal oxides [27, 28] consists in enclosing a sample of oxide, after a suitable and reproducible pretreatment in oxygen, which defines the initial coverage, in a closed volume and in following thereafter the changes of the equilibrium pressure of oxygen with temperature. Once a first isochore has been obtained, a known fraction of the gas may be removed and a second isochore may be established corresponding to a second series of surface coverages.

This method may be used as an example to illustrate some of the difficulties which one must overcome in order to calculate reliable heats of adsorption from equilibrium data [29]. If N is the total number of adsorbate molecules that the adsorbent sample may retain, $N\theta_0$ (θ_0: initial coverage) will be the quantity of adsorbate initially present on the adsorbent when it is placed in the closed and evacuated volume V. When equilibrium is reached at temperature T, the coverage becomes θ ($< \theta_0$) and the gas pressure is then given by:

$$P = N(\theta_0 - \theta)\frac{kT}{V}. \tag{8}$$

If P_0 is the pressure that would be obtained after the complete desorption of the adsorbate,

$$P_0 = N\theta_0\frac{kT}{V} \tag{9}$$

$$\text{then} \quad \theta = \theta_0\left(1 - \frac{P}{P_0}\right). \tag{10}$$

The desorption equilibrium can be determined graphically (Fig. 3) since it is given by the intersection of the adsorption isotherm, e.g. for temperature T_1 with the straight line corresponding to Eq. (10) for temperature T_1. The Figure also represents the equilibrium state of the system for temperature T_2 ($> T_1$). For a correct application of the Clausius-Clapeyron equation ((Eq. (5)) all p-T

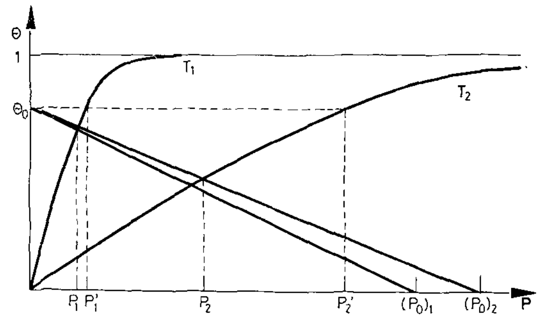

Fig. 3. Determination of heats of adsorption by the isochore method [29] (see the text)

data must correspond to a *constant* coverage, θ, of the adsorbent. It is evident from Fig. 3 that pressure P_1 and P_2, which are experimentally measured when equilibrium is reached at temperatures T_1 and T_2, do not correspond to coverage θ_0. Pressures P_1' and P_2' should be used in the calculation of the isosteric heat for coverage θ_0. Measured pressures are too low and the error increases as the temperature is increased. The heats calculated from the experimental P-T data are therefore too low and the error is larger when the coverage is larger. In order to decrease the experimental error, the equilibrium data should be collected at low temperatures. However, at low temperatures, desorption rates are low and, even after many hours, it is difficult to decide whether equilibrium has been reached or not. If the adsorption isotherms were known, it would be easy to correct the data, but in many cases they cannot be accurately determined. It appears, therefore, that, as a result of this experimental artefact and of the decreasing error as the coverage decreases, the calculated heats will increase as the surface coverage decreases. A distribution of adsorbate-adsorbent bond energies will thus be assumed which does not actually exist at the adsorbent surface. In order to limit the error due to this artefact, the ratio $\frac{N}{V}$ must be as large as possible: it is therefore recommended to use a large mass of adsorbent placed in a small, closed volume.

Gas-chromatographic methods

Dynamic methods which make use of gas-chromatographic detectors have also been developed to determine equilibrium data. James and Philips [30] have used a *frontal gas chromatographic technique* for the determination of adsorption isotherms. The adsorbent is packed into a column and a stream of carrier gas is passed through it. At a measured instant, the carrier gas is mixed with a known concentration of a vapor or another gas (the adsorptive) and the mixture is passed through the column. Before the column of adsorbent is in equilibrium with the adsorptive, it strips all adsorptive out of the carrier gas and the detector at the end of the column shows no response. When the adsorbent surface contains an equilibrium amount of adsorbate, the adsorptive breaks through and a step shows on the recorder. The time taken from the start to the breakthrough, the flow rate and the partial pressure of the adsorptive enable one to calculate the amount of gas adsorbed. Reversibility of the adsorption process may be readily assessed by following the evolution of the recorder response when pure carrier gas is again passed through the column. By repeating this procedure at different partial pressures of the adsorptive and/or different temperatures of the column, different points on the isotherm and/or different isotherms are obtained. It should not be forgotten that this or other gas chromatographic techniques do not actually yield information about the adsorption of the pure adsorptive, but rather about the adsorption of the adsorptive from a *mixture of adsorptive and carrier gas*. However, in many cases, the carrier gas is not adsorbed to an appreciable extent under the conditions of the experiment and this distinction may be ignored.

The frontal gas-chromatographic technique is theoretically sound and reliable (for recent applications, see e.g. [31]). It is also time-consuming since it requires a separate experiment for every point on every isotherm. *Elution* techniques are more rapidly rewarding and, for this reason, are generally preferred.

With these techniques, a slug of adsorptive is introduced in the carrier gas which passes continuously through the column filled with the adsorbent. When the front of the slug reaches the adsorbent, adsorption takes place. All adsorbate is desorbed, however, as the end of the slug crosses the adsorbent column and is detected at the end of the column.

The shape of the gas-chromatographic peak thus obtained is a function of the operation of the column and is also related to the way in which the adsorptive is introduced and adsorbs on the adsorbent. The usual effect of the column is to broaden out any given input distribution of the adsorptive so as to make the peak shape broader and shallower. For heuristic purposes, however, an ideal column may be defined in which broadening factors are absent. The shape of the peak will be affected only by the adsorptive interaction with the stationary phase: it will thus be related to the adsorption isotherm.

From the analysis of the peak shape, it is therefore possible to determine the adsorption isotherm. Methods have been proposed by Wilson [32], Weis and De Vault [33] and especially Glueckauf [34] (see also [35]). From the equation describing the dynamic mass balance in a section of the column, it can be shown that:

$$n_a = \frac{1}{m} \int_0^c V'_c \, dc \qquad (11)$$

where n_a is the quantity of adsorbate when the adsorptive concentration in the gas phase is c, m is the mass of adsorbent, and V'_c is the reduced retention volume of the adsorptive when its concentration is c.

Integration of Eq. (11) for different values of the concentration gives the adsorption isotherm ($n_a = f(c)$ equivalent to $n_c = f(p)$ since $p = cRT$). However, in order to determine V'_c as a function of c from the elution peak, the relationship between retention times and concentration must first be determined.

The ordinate of the peak is, at any time, proportional to c:

$$c = kh \quad \text{or} \quad dc = k\ dh \tag{12}$$

k is determined by calibration.

The reduced retention volume V'_c is defined as:

$$V'_c = Df\ (t_c - t_0) \tag{13}$$

where Df is the gas flow rate measured at the end of the column, t_c and t_0 are respectively the retention time of the adsorptive when its concentration is c and the retention time of a plug of non-adsorbable gas (the "gas hold-up time").

From Eqs (11), (12) and (13) it appears that

$$n_a = \frac{Dfk}{m} \int_0^h (t_c - t_0)\, dh. \tag{14}$$

The quantity, n_a, corresponding to concentration c of the adsorptive in the gas phase, is therefore given by the peak area limited i) by the base-line, ii) by a parallel to the ordinate axis at time $t = t_0$ and iii) by the diffuse profile of the elution peak from $t = t_\infty$ (when $c = 0$) to t_c (Fig. 4). The procedure may be repeated for any available values of c or t_c and the adsorption isotherm is thus obtained. Application of the Clausius-Clapeyron equation ((Eq. (5)) to at least two isotherms drawn for

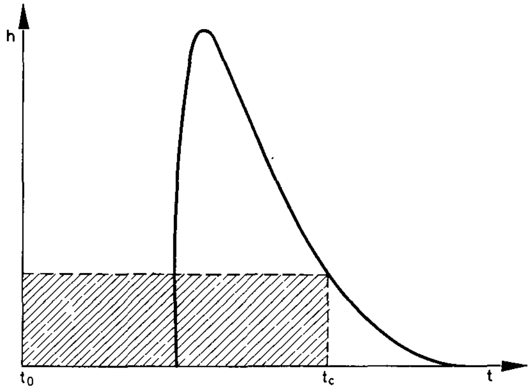

Fig. 4. Determination of adsorption isotherms from asymmetric chromatographic peaks (see the text)

different temperatures yields the isosteric heats. For a review on the applications of this chromatographic method, see [36]. This method is theoretically simple and sound. In practice, however, diffusional limitations in the stationary phase may limit its applicability (for a discussion on diffusional limitations in microporous adsorbents, see e.g. [37]. Approximate methods of correction have been proposed, e.g. [38]. Moreover, the accuracy of the partial integrations of the peak area may be decreased when the base-line of the gas chromatographic records is not excellent.

The most commonly used gas chromatographic method for the determination of isosteric heats is based upon the change of the retention volume (or time) of the adsorptive as a function of the temperature of the column. Since the works of Prior [39] and Greene and Pust [40] it has been known that, when the column is *ideal* and when the adsorption isotherm is *linear* (Henry's law):

$$q_{st} = RT \, \mathrm{Ln} \frac{V_s}{RT} \tag{15}$$

where V_s is the specific retention volume, calculated, at the temperature of the column, per unit surface area of the adsorbent.

The isosteric heat of adsorption is therefore given by the slope of the straight line which is obtained when V_s/T in logarithmic coordinates is plotted as a function of the reciprocal temperature. Since the surface area is usually independent of the column temperature, the retention volume (V_R) may also be used in the calculation. Figure 5 shows an application of this method in the case of the adsorption of xenon, at different temperatures, on a NaX zeolite [41]. The heat derived from the slope of the linear plot of Ln V_R/T as a function of $1/T$ is 4.4 kcal/mole. The V_R values were calculated from the retention times corresponding to the maximum ordinate of the chromatographic peaks. Equilibrium data, obtained from static measurements, give a very similar value (4.5 kcal/mole for $\theta = 0$) [36].

Henry's law is generally applicable only to that part of the adsorption isotherm which corresponds to small partial pressures of the adsorptive. However, the range of small partial pressure may be investigated, with modern gas-chromatographic equipment, for many adsorptives. The determination of isosteric heats from retention volumes is therefore frequently used. The second condition of its application, i.e. the ideality of the column, should be carefully verified however in all cases. Any broadening of the peaks, which may nevertheless remain symmetrical, may be considered an indication that mass transfer within the adsorbent or at the adsorbent surface is becoming difficult and that equilibrium is probably not achieved in the column. Theories have been presented to describe the gas-chromatographic peaks when the column is non-ideal and non-linear, e.g. [42], and they can be used to reduce, to some extent, the distortion that non-ideal behaviour of gas chromatographic columns introduces in the calculation of isosteric heats [43]. However, when equilibrium conditions are not attained in the column and when the adsorption process therefore goes on more slowly that the chromatographic process [44], the interaction between adsorbate molecules may differ from that

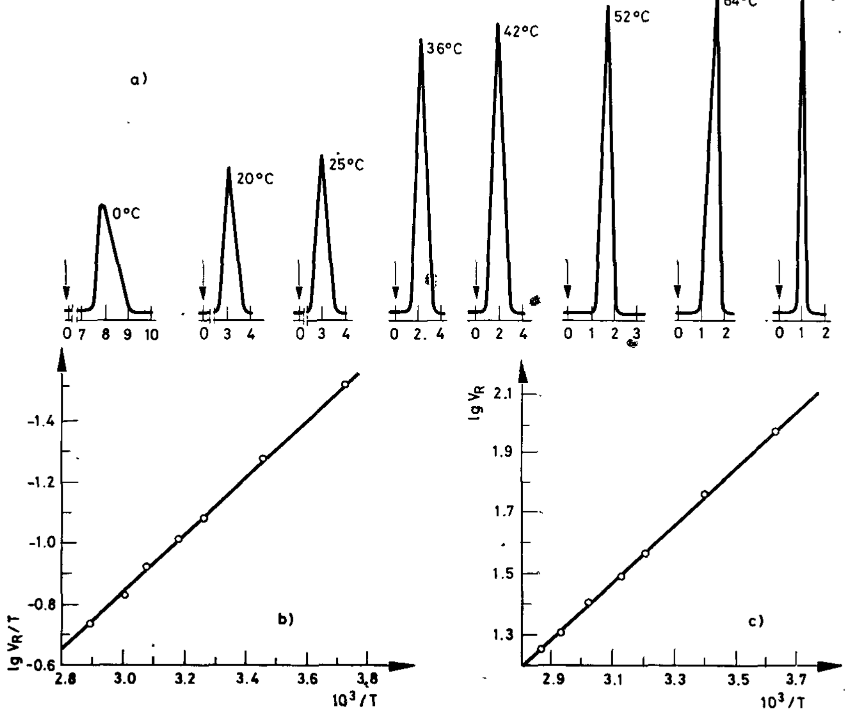

Fig. 5. A, Chromatograms of xenon on zeolite NaX at several temperatures; B and C, corresponding plots of log V_R and log V_R/T as functions of reciprocal temperature [36]

taking place under static conditions. As a consequence, the values of the calculated heats are too low as they reflect only the interaction between adsorbate and adsorbent [45]. This effect is particularly important in the case of the adsorption of large molecules (hydrocarbons with $C > 4$) and in the case of very reactive adsorbents. In these cases, it is advisable to decrease the amount of adsorbent packed in the chromatographic column [46].

The present success of the gas-chromatographic determination of isosteric heats of adsorption by means of elution techniques is not surprising since these techniques require only rather simple and versatile equipment and yet allow the determination of heats of adsorption in a vast temperature range (as an example of the versatility of these techniques, see [47]. In addition, the heats of adsorption of several substances being adsorbed simultaneously on the adsorbent may be determined. However, one should remain aware of the main limitations and requirements of the simple techniques which have been described in this Section:

a) The adsorptive is supposed to be an ideal gas. However, corrections for the non-ideality of the adsorptive have been proposed [48].

b) A reversible adsorption equilibrium must be established in all parts of the column and, hence, only reversible adsorptions can be studied by means of these techniques.

c) The column must be operating near ideal conditions. Furthermore, if adsorption heats are to be derived from measurements of the retention time, the adsorption isotherm must be linear.

d) A constant temperature must be maintained in all parts of the adsorbent.

e) The carrier gas must not be adsorbed, and

f) it must be free from adsorbable impurities.

g) A vacuum pretreatment of the adsorbent, packed in the column, is often difficult.

Determination of heats of adsorption from kinetic data

The application of all the techniques which have been described in the preceding Section is limited to *reversible* adsorption phenomena. However, it is an experimental fact that, in the case of many chemisorptions, the evacuation of the gaseous phase does not produce the desorption of the adsorbed gas. It is often necessary to raise the temperature in order to expel the adsorbate from the surface, desorption beginning at this temperature for which the desorption rate exceeds the rate of readsorption, under selected experimental conditions.

Now, according to the transition state theory, the rate of desorption at temperature T is related, *inter alia*, to the activation energy of desorption:

$$r_\mathrm{d} = \frac{kT}{h} n \exp \frac{\Delta S^*}{R} \exp \frac{-E_\mathrm{d}}{RT} \tag{16}$$

where r_d is the rate of desorption, k and h are Boltzmann's and Planck's constants, respectively, and n is the coverage. Making the usual Frenkel's assumption that $\Delta S^* = 0$ [49], Eq. (16) is approximated by:

$$E_\mathrm{d} = RT \operatorname{Ln} \left(\frac{kT}{h} \right) \tau_\mathrm{d} \tag{17}$$

where τ_d is the half-life value of the desorption process starting at full coverage. Numerical values for the activation energy of desorption can therefore be estimated from the measured desorption times and temperatures. In their studies of the desorption of nitrogen from platinum [50] and iridium [51] surfaces, or the desorption of hydrogen from platinum [52], in a field-emission microscope, Nieuwenhuys *et al.* estimated τ_d from the changes of the emission current upon desorption. More specifically, τ_d was supposed equal to the time required for the field-emission current to change by $\frac{1}{2}(\mathrm{i}_{\theta=1} - \mathrm{i}_{\theta=0})$, at constant temperature and pressure.

As the activation energy for adsorption in these systems is approximately zero, the calculated activation energies for desorption are nearly equal to the heats of adsorption. Isosteric heats, from isochores, and activation energies for desorption in the case of the N_2/Pt system [50] are indeed in reasonable agreement (values from 7 to 9 kcal/mole). This comparison indicates moreover that the application of Frenkel's assumption is justified in this case.

Characteristic changes of the field-emission pattern have been used by Goymour and King [53] to calculate activation energies for desorption. For this purpose, Eq. (16) may be rewritten as:

$$-\frac{dn}{dt} = \nu_1 n \exp\left(-\frac{E_d}{RT}\right) \qquad (18)$$

where ν_1 is the first-order rate constant for desorption. The change in coverage from n_1 to n_2 which takes place during time t at temperature T may be expressed by:

$$\mathrm{Ln}\, t = \mathrm{Ln}\left[\mathrm{Ln}\left(\frac{n_1}{n_2}\right)\right] - \mathrm{Ln}\, \nu_1 + \frac{E_d}{RT}. \qquad (19)$$

Sets of values of t vs. T for a characteristic pattern change (corresponding to $n_1 \rightarrow \rightarrow n_2$) can be determined and the activation energy for desorption is calculated from the slope of the straight line which is obtained when Ln t is plotted as a function of reciprocal temperature (Eq. (19)). Desorption of atomic oxygen from a tungsten tip was studied by this method [53]. An additional advantage of the method must be mentioned: when the change in θ is small (≤ 0.1), the value of the first term in Eq. (19) is small compared to Ln ν_1 and ν_1, the first-order rate constant, may be calculated from the Ln t vs. $\frac{1}{T}$ plot.

Both methods which have been described for determining the activation energy of desorption are based upon the analysis, according to the transition state theory, of the desorption rate at a given and constant temperature. Now, it is frequently observed that, upon continuous heating of the adsorbent at progressively higher temperatures, desorption does not occur continuously but that the desorption rate reaches maximum values for certain temperatures and decreases considerably thereafter. *Desorption spectra* are thus obtained which, upon analysis, may yield information about the nature of the adsorbed species and about their energy of desorption.

Two experimental methods have been proposed for the determination of desorption spectra, the theory of which being very similar. In the *Flash desorption technique* (for an early review, see Ehrlich [54]), a sample of adsorbent, which is frequently a metal filament, is very rapidly heated according to a given temperature schedule, whereas in the *temperature-programmed desorption* technique proposed by Anemomiya and Cvetanovic [55, 56], the adsorbent, a powder, generally, is more slowly heated in a stream of inert carrier gas. In the former method, desorption is followed by pressure measurement by means of ionization gauges or, better, mass-spectrometers; in the latter method, gas-chromatographic detectors may be used. The quantitative treatment of desorption kinetics has been presented by Redhead [57], Carter [58] Anemomiya and Cvetanovic [59] and programmed desorption techniques have been reviewed recently [60].

When the rate of readsorption is small compared to the rate of desorption, the desorption process, as the temperature of the adsorbent is raised linearly,

$$T_s = T_0 + \beta t \tag{20}$$

may be described by the two following equations [61]:

$$-\frac{dn}{dT_s} = \nu_i n^i \exp\left(\frac{-E_d}{RT_s}\right) \tag{21}$$

$$\frac{dn}{dT_s} = \frac{V}{ART_g}\left[\frac{P - P_{eq}}{\tau} + \beta\frac{dP}{dT_s}\right] \tag{22}$$

where i is the order of desorption; τ the pumping time constant; V the volume of the system; P the pressure; and A the surface area of the sample. Equation (21) is equivalent to Eqs (16) and (18). Equation [22] expresses the mass balance in the system.

Two extreme cases must be considered. When $\frac{dP}{dT_s} \gg \frac{P - P_{eq}}{\tau}$, then $P \simeq n$, an *integral* spectrum is obtained and pressure rises in the system as desorption occurs. Ehrlich [62] has discussed in detail the analysis of such spectra. The analysis is independent of the pumping rate constant, but with such spectra one has to look for inflection points in a rather structureless curve. In principle, this method may be used to estimate activation energies of desorption. However, readsorption may, in some cases, complicate the quantitative analysis of the data.

When $\frac{dP}{dT_s} \ll \frac{P - P_{eq}}{\tau}$, then $P \simeq \frac{dn}{dt_s}$ and a *differential* spectrum is obtained where each adsorbate state produces a peak. In this case, Redhead [57] showed that the activation energy of desorption can be simply related to the maximum temperature of the desorption peak:

In the case of lst-order kinetics:

$$\frac{E_d}{RT_m} = \mathrm{Ln}\frac{\nu_1 T_m}{\beta} - 3.64\,. \tag{23}$$

In the case of 2nd-order kinetics:

$$\frac{E_d}{RT_m^2} = n\frac{\nu_2}{\beta}\exp\left(\frac{-E_d}{RT_m}\right). \tag{24}$$

Equation (23) is an approximation, but the fit is ~ 2%. In the case of a lst-order desorption, the temperature T_m corresponding to the maximum desorption rate is independent of the initial coverage of the surface by the adsorbate. In the case of a 2nd-order desorption, the temperature for the maximum of the peak in the desorption spectrum changes with the initial coverage of the surface by the adsorbate. These equations may be used to calculate E_d when a "likely" value for the first- or second-order rate constants are assumed [57].

Activation energies for desorption can be calculated from desorption spectra without making any hypothesis as to the order, i, of the desorption kinetics or the value of the rate constant, provided that data corresponding to different heating rates, β, have been collected [63]. It can be shown that:

$$\mathrm{Ln}\left(\frac{T_m^2\, n_m^{i-1}}{\beta}\right) = \frac{E_d}{RT_m} + \mathrm{Ln}\,\frac{E_d}{i\, \nu_i\, R}. \tag{25}$$

The activation energy of desorption can thus be calculated from a plot of log $\left(\frac{T_m^2}{\beta}\right)$ vs. $\frac{1}{T_m}$. Application of this method, however, requires a large range of β values (2 orders of magnitude) [57] and considerable experimental precision since the initial surface coverage must be the same in all runs.

Activation energies can also be deduced from the peaks widths [61] or from the peaks heights [60]. Heating schedules, other than linear, have also been used and the corresponding mathematical analyses may be found in e.g. [60]. In all cases, it has been supposed that desorption occurs from a uniform surface which contains a homogeneous population of sites, so that ν and E_d are not functions of n. Desorption spectra, in the case of a pre-existing or induced heterogeneity, have been analyzed theoretically by Carter et al. [58, 66] and others [60]. Practical applications of the theory, however, are difficult.

Finally, it is also possible to determine E_d and ν_i from desorption experiments with an undetermined heating schedule. This method was first proposed by Ageev [64] and used e.g. by Lapujoulade [63]. The Arrhenius equation (Eq. (21)) may be rewritten as:

$$\mathrm{Ln}\left(-\frac{1}{n^i}\,\frac{\mathrm{d}n}{\mathrm{d}t}\right) = \mathrm{Ln}\,\nu_i - \frac{E_d}{RT}. \tag{26}$$

The quantities n and $\frac{\mathrm{d}n}{\mathrm{d}t}$ can be determined continuously during a desorption run [65] and Eq. (26) may be used to evaluate both E_d and ν_i from the linear plot which is obtained when a suitable value for the desorption order, i, has been selected. This method has been used, for instance, to study the desorption of hydrogen from polycrystalline nickel and has demonstrated that, in this system, desorption is a 2nd-order phenomenon [65]. Furthermore, by repeating the desorption runs for varying surface coverages, it has been possible to show that the activation energy of desorption is a function of the logarithm of the initial coverage [65]. This method, however, requires the precise determination of 3 parameters (n, $\frac{\mathrm{d}n}{\mathrm{d}t}$ and T) in the course of the desorption run, and for this reason it is less frequently utilized than the methods based upon a precise heating schedule and the determination of the peak maximum.

In the preceding discussion, it has been assumed that the rate of readsorption is negligibly small during the desorption run. When readsorption occurs and when a reversible equilibrium takes place during the programmed temperature increase, it is possible, in principle, to deduce the *heat of adsorption* from the experimental data [56, 60]. For applications of this method in the case of a closed system, see e.g. [67].

Desorption techniques are widely used, at the present time, to evaluate activation energies (or energies) of desorption in the case of adsorbate-adsorbent systems which cannot be conveniently investigated by other equilibrium or calorimetric techniques (studies of irreversible adsorption on single-crystal planes, for instance). However experimentalists should remain aware of the limitations and difficulties of these techniques:

a) the temperature of the adsorbent must be accurately measured.

b) Diffusion phenomena may perturb TPD experiments when microporous adsorbents are used [56].

c) E_d or ν are in some methods *(vide supra)* supposed to be independent of n.

d) In the case of simple instruments in which desorption is followed by pressure gauges, the experimentalist should make sure that i) no chemical reaction has occurred between the adsorbent and the adsorbate (hydrogen desorbing as water molecules from the surface of an oxide, for instance) or ii) desorption peaks are not produced by desorbing surface impurities (carbon monoxide is frequently present, as an impurity, in UHV systems, for instance).

e) Apparent variations of E_d vs. n may be caused by artefacts such as changes of the pre-exponential factor in the Arrhenius equation or the existence of binding states on the edges, steps or other surface imperfections that an apparently perfect single-crystal plane still contains.

In spite of these difficulties, desorption techniques applied to single-crystal planes have stimulated research in the field of adsorption on defined surfaces and have, in particular, contributed to the study of temperature-induced conversion between adsorbed states [68, 70], of order-disorder transitions during heating [69, 71], of induced heterogeneity [70, 72, 73], of bulk solution or incorporation of the adsorbate into the adsorbent lattice [70, 74] and of interactions between adsorbed species [68, 70, 71].

Calorimetric determination of heats of adsorption

The most straightforward method to determine heats of adsorption is to measure them in a calorimeter. Direct calorimetric measurements are indeed free from hypotheses on the attainment of equilibrium or on the desorption rate law that must be made when heats of adsorption are determined from, respectively, equilibrium or kinetic data. The surprising fact that indirect rather than direct methods are frequently preferred is probably explained by the small number of commercial instruments adapted to adsorption studies and also by the difficulties that one must overcome, in some cases, in order to reproduce, in the calorimeter, the conditions required by the system under investigation.

However, a very large number of adsorption calorimeters have been described and used. They have been reviewed recently [75]. Therefore, in this Section, the advantages and limitations of the main types of adsorption calorimeters will simply be recalled.

Adiabatic adsorption calorimeters have been frequently, but not exclusively, employed at low temperatures to study physical adsorption, see e.g. [76]. Their accuracy and sensitivity are satisfactory but their use requires a skilled experimentalist. They allow the measurement of heats of adsorption and also of the heat capacities of adsorbed layers. They can be used to study slow adsorption processes and the temperature of the adiabatic shield may be varied above the thermostat temperature. However, in order to minimize heat losses, the sample in the calorimeter cell must be connected to the external volumetric line via a capillary tube. The initial outgassing or pretreatment of the large samples which are frequently used in physical adsorption experiments is not easily achieved and the reproducibility of this operation is uncertain. Finally, it is clear that the measurements are performed under non-isothermal conditions.

Isothermal calorimeters have also been utilized to study adsorption. Imperfect isothermal calorimeters of the Bunsen type (liquid–gas or solid–liquid phase changes) were very commonly used in the 20's, see e.g. [77]. Their sensitivity is acceptable. However, their operation is difficult and time-consuming. Furthermore, they operate necessarily at a limited number of fixed temperatures. The modern, isothermal calorimeters which operate on the principle of a continuous compensation of the heat produced or absorbed in the calorimeter cell are more versatile and more efficient than phase-change calorimeters. The constant-heat exchange calorimeter described by Kiselev et al. [78] is a good example of modern isothermal calorimeters adapted to adsorption studies. These calorimeters may be used to study fast or slow processes at the surface of good or poor heat-conducting solids. In principle, there is no need to calibrate the calorimeter, this being continuously done during any experiment: these calorimeters can therefore be operated either at a constant or at a variable temperature. Furthermore, since thermal paths within the calorimeter vessel are short, the response of these instruments is rapid. However, they require high-quality electronics for the temperature controls and for the regulation of the power supply.

Quasi-isothermal calorimeters of the heat-flow type have also been frequently used in adsorption and heterogeneous catalysis studies [79]. Since a thermal conductor continuously evacuates the heat evolved in the calorimeter cell towards an external heat sink, the temperature increase caused by an exothermic phenomenon is generally very moderate. The stability of the record base-line is excellent and allows one to study fast or very slow processes. Moreover, many different versions of these calorimeters have been constructed for use at different temperatures and a given calorimeter may frequently be utilized over a broad temperature range. The main disadvantage of heat-flow calorimeters is that their response is usually slow. This is caused by the large heat capacity of the calorimeter proper and of the heat detectors.

Most of the calorimeters that have been used in adsorption cannot be classified in the preceding categories. They belong to the vast class of *isoperibol* calorimeters in which the inner cell is imperfectly insulated from its surroundings, usually maintained at a constant temperature. The calorimeter behaves as an adiabatic calorimeter at the initial time of the experiment, and thereafter heat flows from or to the inner cell along unspecified paths so that the analysis of the complete calorimetric curve is, in many cases, impossible. The use of these calorimeters must therefore be restricted to the study of fast phenomena which are completed under quasi-adiabatic conditions.

Isoperibol calorimeters can be adapted to very different experimental conditions. Some of these calorimeters, in which ultra-high vacuum can be attained, are extremely useful for the study of adsorption on "clean" metal films [80] or filaments [81]. By a careful study of heat-transfer in these calorimeters, moreover, it is possible to improve their performance [82].

Many isoperibol calorimeters have also been used for more ordinary adsorption studies. Thermal effects are then followed by measuring the temperature increase upon adsorption in a mass of adsorbent placed in an imperfectly insulated vessel within a thermostat. The thermometer frequently consists of a single thermocouple junction, but batteries of thermocouples or resistance thermometers have also been utilized for this purpose. The main justification for the use of such rudimentary instruments is that scientists working in laboratories which do not specialize in adsorption thermodynamics are apparently not prepared to build or buy elaborate instruments which are available, especially when calorimetric data are needed only occasionally in order to confirm or complete results obtained by more conventional techniques in adsorption or heterogeneous catalysis. This situation, however, is unfortunate, since, by means of these simple isoperibol calorimeters, it is hardly possible to achieve the accuracy which would be needed for a meaningful comparison of thermal data with data given by e.g. spectroscopic techniques. This, in turn, probably explains why indirect methods for the determination of heats of adsorption are frequently preferred to direct ones.

Indirect methods seem to be particularly suited for the study of physical adsorption, since a reversible equilibrium is, in principle, readily achieved. However, (see Section II) diffusional limitations may lead to apparent equilibria, especially in the low-pressure range and for microporous adsorbents. Excellent accuracy of the data is required moreover when heat capacities of adsorbed layers are to be deduced from equilibrium data, since their calculation involves a second differentiation of the adsorption isotherm, see e.g. [83]. Direct calorimetric measurements of adsorption heats and heat capacities of adsorbed layers are therefore more reliable. Heat capacities can be determined with adiabatic calorimeters. However, large samples must be used and the heat capacity of the adsorbed layer is then a small fraction of the total heat capacity of the calorimetric cell. Moreover, the Joule heating which is needed produces the desorption of part of the adsorbate. Corrections for this effect and for the simultaneous adsorptive compression are tedious. More promising appears to be the use of constant-heat exchange calorimeters, since changes of heat capacity with surface coverage are then simply deduced from the changes of the thermal power required to maintain a constant temperature in the cell, when adsorption equilibrium is attained. New developments of this technique are awaited, but the results already published are promising [84].

One of the distinct advantages of calorimetric measurements for the determination of heats of reversible adsorption is that they may reveal unexpected phenomena. This is particularly the case when continuous adsorption procedures, under quasi-equilibrium conditions, are utilized. Such procedures have been developed in connection with constant-heat exchange [85] and heat-flow calorimeters [86]. The calorimetric curve then recorded yields directly the changes of the differential heat of adsorption with surface coverage after the raw data have been corrected for the adsorptive compression (Eq. [2]) and, eventually, for the thermal lag in the calorimeter. The exothermic phenomenon which appears near the completion of the first monolayer when nitrogen is adsorbed on graphite at 77 K (Fig. 6) and which has been attributed to a transition in the adsorbed phase between a hypercritical liquid to a solid, may serve to illustrate the advantages of this direct calori-

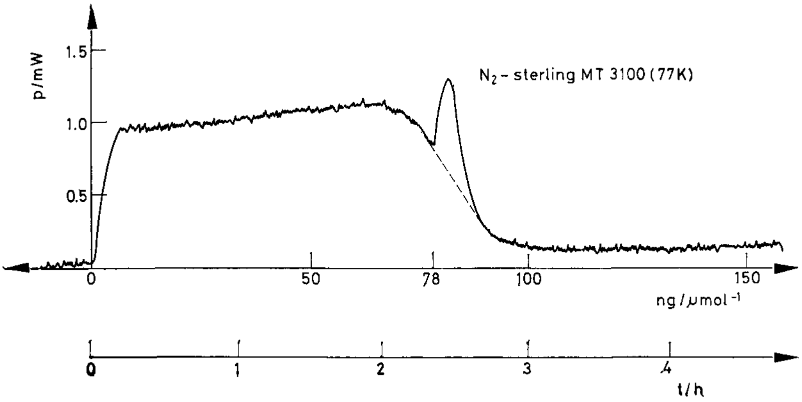

Fig. 6. Calorimetric curve produced by the adsorption of a steady flow of nitrogen on Sterling MT 3100 graphitized carbon black at 77 K [87]

metric procedure, since this phenomenon had not been previously detected by more conventional techniques [87].

Thermodynamics of the adsorption of hydrocarbons on solid adsorbents are frequently studied by gas-chromatographic techniques (see Section II). It is true that gas-chromatographs are commonly found in laboratories active in adsorption or heterogeneous catalysis. However, when the limitations and requirements of the chromatographic techniques *(vide supra)* are considered, it appears that they could advantageously be replaced by the techniques recently developed [88], associating a heat-flow (or a constant-heat exchange) calorimeter with a pulse or a dynamic reactor, analysis of the non-reacted adsorptive still being achieved chromatographically.

The main domain of application of calorimetric techniques is, of course, irreversible adsorption. Application of desorption techniques to the determination of energies should be reserved for systems which cannot be tackled conveniently by direct calorimetry. This is unfortunately the case, at the present time, for studies of irreversible adsorption on single-crystal oriented surface planes. It must be mentioned at this point that systems which are irreversible under ordinary conditions of pressure, may become equilibrated when adsorption is performed at extremely low partial pressures: thermodynamic quantities can then be advantageously determined from equilibrium data (CO on metals is an example of such systems) [15, 19]. In the case of systems studied under conditions where they are irreversible, desorption techniques should be considered as a useful complement to direct calorimetry their resolution in terms of number and nature of adsorbed species being, in some cases, superior to that of calorimetry.

The applications of direct calorimetric techniques in the study of irreversible (and reversible) adsorption are numerous (for a review, see [79]) but, in order to make the best use of these techniques, the calorimeter must be carefully selected. Stability of the base-line, sensitivity, convenience of operation, and temperature and pressure ranges are parameters for the selection, which remains difficult, however, since some of these parameters are mutually exclusive.

With the help of a suitable calorimeter, it is possible to determine not only differential heats of adsorption and their variation with coverage (for refinements in the calculations of differential and integral heats of adsorption, see [89]), but also the differential heats produced by the interaction, on the surface, of the different reactants of a given reaction to yield the reaction product. Thermochemical cycles may then be used to select probable reaction paths [90]. By means of dynamic techniques, adsorptions or surface reactions taking place during the catalytic reaction itself, which produce either an activation or a deactivation of the catalyst, can also be studied [88]. In all cases, calorimetric techniques offer the possibility of studying the adsorption or the catalytic reaction under investigation at the required temperature: this advantage, however, seems to be neglected in numerous studies with simple calorimeters.

Finally, when the thermal stability of the calorimeter is excellent, as is the case with constant-heat exchange calorimeters or with heat-flow calorimeters, the thermal power generated by the phenomenon under study may be recorded as a function of time. Calorimetric data thus provide information not only on the quantities of heat evolved, but also on the kinetics of their production. Applications of *thermokinetics* are numerous in the fields of adsorption and heterogeneous catalysis (for a review, see [75]): simple instruments may be used for routine catalyst screening; differential thermal analyzers and differential scanning calorimeters may serve to determine the activation energies and rate laws of catalytic reactions, etc. In order to measure the rate of heat production accurately, however, it is necessary to remove from the calorimetric data the distortion due to thermal lags. Deconvolution procedures, based on Fourier transform analysis [91], time-domain matrices and state-function theory [92] have been tested and used for this purpose. In all cases, the calorimeter must behave as a linear system with localized constants and methods are available to test the calorimeter's linearity [93]. Because of the sensitivity of modern calorimeters, deconvolution procedures can be used to determine the *spectrum of activity* that any catalytic surface presents with respect to an adsorptive or with respect to a reaction mixture (for an example of application, see [94]). Furthermore, the comparison of thermal and kinetic data is particularly justified in this case, since both sets of data are obtained from the same experiments.

The different applications of calorimetry, briefly summarized in this Section, indicate that, in many cases, calorimetry can compete favorably with indirect methods for the determination of heats of adsorption. In addition, calorimetry can give valuable indications on adsorption or reaction rates, on reaction mechanism, on the distribution of active sites and on the activation and deactivation of catalysts. For these reasons, calorimeters should be considered as important tools in all laboratories engaged in adsorption and heterogeneous catalysis studies.

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RÉSUMÉ — Diverses méthodes peuvent être utilisées pour déterminer les chaleurs d'adsorption, soit directement avec des calorimètres soit indirectement par application de l'équation de Clausius-Clapeyron aux isothermes d'adsorption réversible.

La détermination des isothermes d'adsorption est discutée dans la première partie de cet article. Les méthodes mettant en œuvre la chromatographie en phase gazeuse et une méthode basée sur la mesure de la pression d'équilibre dans le cas des systèmes oxygène-oxydes métalliques sont plus particulièrement décrites.

Lorsque l'adsorption n'est pas un phénomène réversible, il n'est pas possible d'utiliser l'équation de Clausius-Clapeyron. Les méthodes cinétiques qui permettent alors de déterminer les énergies d'activation de désorption sont présentées dans la seconde partie de cet article.

La troisième partie de cet article est consacrée à une présentation des méthodes calorimétriques qui peuvent être employées pour les études d'adsorption et de catalyse hétérogène. Des améliorations techniques récentes telles que celles qui permettent l'emploi de méthodes continues ou semi-continues ou la déconvolution des courbes calorimétriques sont décrites.

ZUSAMMENFASSUNG — Verschiedene Methoden können zur Bestimmung von Adsorptionswärmen eingesetzt werden, entweder Direktbestimmungen mit Hilfe von Kalorimetern oder indirekte Verfahren bei Anwendung der Clausius-Clapeyron-Gleichung auf Gleichgewicht.

Die Bestimmung von Gleichgewichtsdaten bei Adsorptionserscheinungen wird im ersten Teil dieser Übersicht diskutiert. Gaschromatographische Methoden und besonders eine auf der Messung des Gleichgewichtsdruckes von Sauerstoff über Metalloxiden beruhende Methode werden beschrieben.

Wenn die Adsorption unter Nicht-Gleichgewichtsbedingungen vor sich geht, scheidet der Einsatz der Clausius-Clapeyron-Gleichung aus. Eine kurze Beschreibung der Anwendung kinetischer Methoden zur Bestimmung von Aktivierungsenergien der Desorption wird im zweiten Teil der Übersicht gegeben.

Der dritte Teil der Übersicht ist den für das Studium der Adsorption und der heterogenen Katalyse geeigneten Methoden gewidmet. Neuere technologische Errungenschaften, z. B. der Einsatz kontinuierlicher oder semi-kontinuierlicher Verfahren, oder die Deutung kalorimetrischer Kurven werden beschrieben.

Резюме — Для определения теплот адсорбции могут быть использованы различные методы или непосредственно с помощью калориметров, или же косвенно, применяя уравнение Клауса—Клапейрона к равновесным данным. Определение равновесных данных в случае явления адсорбции обсуждено в первой части данного обозрения. В частности описаны газ-хроматографические методы и методы, основанные на измерении давления равновесия кислорода над окислами металлов. Использование уравнения Клауса—Клапейрона исключается, если адсорбция осуществляется при неравновесных условиях. Во второй части обозрения представлено краткое описание применения кинетических методов для определения энергий активации. Третья часть обозрения посвящена исследованию калориметрических методов, применяемых для исследования адсорбции и гетерогенного катализа. Описаны недавние технологические усовершенствования, как например, использование непрерывных и полунепрерывных методов или развертывание калориметрических кривых.