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DIRECT DETERMINATION OF ADSORPTION HEATS *

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ABSTRACT

Energy changes occurring during adsorption in gas–solid and solution–solid systems are considered in connection with measurement of the adsorption enthalpies. Some experimental apparatuses allowing determination both of heat evolved and adsorbed amounts are described, with special regard to those using heat-flow microcalorimeters. Calibration techniques and experimental data reliability are also discussed.

INTRODUCTION

The surface of a condensed phase (solid or liquid) exerts an attractive force on chemical species coming into contact with it owing to incomplete saturation of the coordination sphere of atoms, ions or molecules at the surface. Adsorption is thus an accumulation of the adsorptive on the surface of the adsorbent, giving rise to the adsorbate (or adsorbed phase).

adsorptive + adsorbent → adsorbate on adsorbent

Adsorption influences all phenomena depending on the properties of surface, e.g., it constitutes the primary step in corrosion as well as the prerequisite for every catalytic reaction involving solid catalysts.

As a spontaneous process, adsorption involves a decrease in free enthalpy ($\Delta G < 0$). Since the adsorbate is more ordered than the adsorptive, there is a decrease in entropy, too. From the relationship

$$\Delta G = \Delta H - T\Delta S$$

it follows that adsorption is generally exothermic ($\Delta H < 0$). The heat evolved is called heat of adsorption [1,2]. This will be more precisely defined in the thermodynamic section.

The strength of the binding forces between the adsorbed molecules or atoms and the adsorbing surface has been frequently used as a criterion to distinguish "chemisorption" from "physisorption". Thus, if the heat of

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adsorption exceeds ~ 20 kJ mol^{-1} the process is regarded as chemisorption, whereas physisorption occurs if it is less [3]. A more detailed distinction of the two processes is as follows.

In physisorption, the adsorbate is kept at the adsorbent surface by Van der Waals forces, so that the heat of adsorption (i.e., the binding energy) will be of the same order as the condensation heat (around 20 kJ mol^{-1}). This interaction will become effective at very low temperatures, when the weak attractions prevail. Furthermore, in these conditions an increase in the adsorptive pressure or concentration may easily produce multilayer adsorption.

Chemisorption can be considered as a form of chemical reaction between the adsorptive and the surface. The molecular structure of the adsorbed species is usually modified, sometimes so drastically that its homolytic dissociation occurs (dissociative chemisorption). Energy changes in chemisorption are of the same order of magnitude as the bonds in free molecules (40–600 kJ mol^{-1}), e.g., for the adsorption of CO on transition metals, energies comprised between 170 and 350 kJ mol^{-1} are obtained. Due to the high-energy short-range interaction characterizing chemisorption, this process takes place only before the monolayer completion, but may occasionally prosecute if an adsorptive–adsorbent reaction occurs.

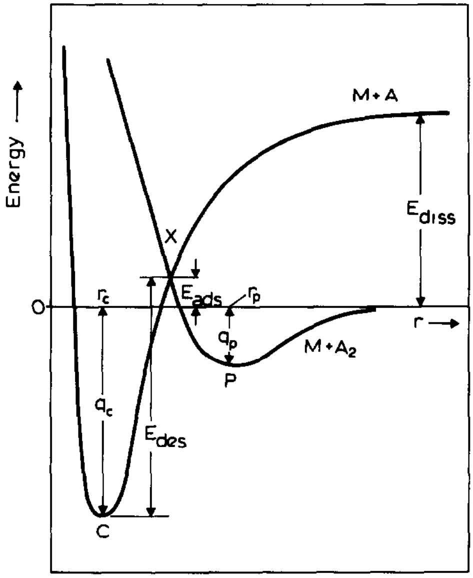
Reversible adsorption is typical of physisorption: in few cases chemisorption may exhibit some reversibility, so that this feature cannot be assumed as a criterion for distinction.

ENERGETICS OF ADSORPTION

Description of adsorption processes by potential energy diagrams

A very useful description of the adsorption process and its energetic changes is represented by the potential energy curves plotted against the distance of the adsorptive molecule from the surface [4,5]. The energy zero has been chosen for the situation in which the molecule is infinitely distant from the surface.

When a molecule (or atom) approaches the surface, the change in energy is represented as in Fig. 1. The physisorption process (curve P) shows an exothermic effect, corresponding to the depth of the minimum (q_p). The process is a non-activated one, the distance of the molecule from the surface is r_p, and the energy of adsorption corresponds to the activation energy for desorption. Curve C represents chemisorption: its heat production is usually higher (q_c), and the distance from the surface (r_c) is smaller than for physisorption. For dissociative chemisorption, the chemisorbed phase can equally well be produced in either of two ways. The adsorptive molecules can first be dissociated (E_{diss}) and then allowed to react as atoms with the



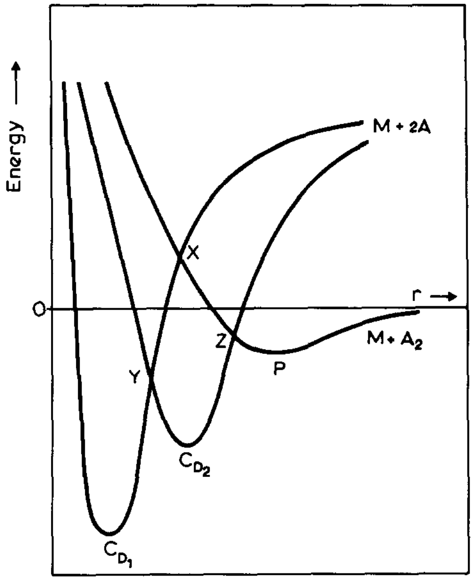


Fig. 1. Potential energy changes for the physisorption (P) and dissociative chemisorption (C) of an adsorptive A_2 on an adsorbent M as a function of the distance (r) from the surface. q_p, heat of physisorption; q_c, heat of chemisorption; E_{diss}, dissociation energy of A_2; E_{ads}, activation energy for chemisorption; E_{des}, activation energy for desorption of chemisorbed species; r_p, r_c, equilibrium separation for physisorbed and chemisorbed species, respectively.

Fig. 2. Dissociative chemisorption on two distinct sites with different energy wells (a priori heterogeneity). D_2, non-activated intermediate chemisorbed species.

adsorbent. Alternatively, the molecules may be allowed to react directly with the surface to dissociate and give the chemisorbed phase via the physisorbed state acting as a precursor, which is the actual path due to evident energetic reasons.

The two potential energy curves cross at X. The position of X with respect to the zero energy is decisive in determining the rate of transfer of the adsorptive molecules into the chemisorbed state (i.e., the chemisorption rate) [6]. The height of X represents the magnitude of the activation energy for chemisorption (E_{ads}). By contrast it is possible to desorb chemisorbed molecules only if the energy supplied exceeds the heat of chemisorption by an amount corresponding to the X height (E_{des}). We have so far assumed that the surface is ideal and entirely homogeneous and we did not consider any interaction between adsorbed molecules (or atoms). Actually, any surface is heterogeneous, i.e., its adsorption sites have different potential well depths. Such a priori heterogeneity may arise from the different geometry of the adsorption sites. In this case, one or more additional potential curves would be needed (Fig. 2), and corresponding to point X there would be points Y, Z, etc., whose position will determine the transition from one state of

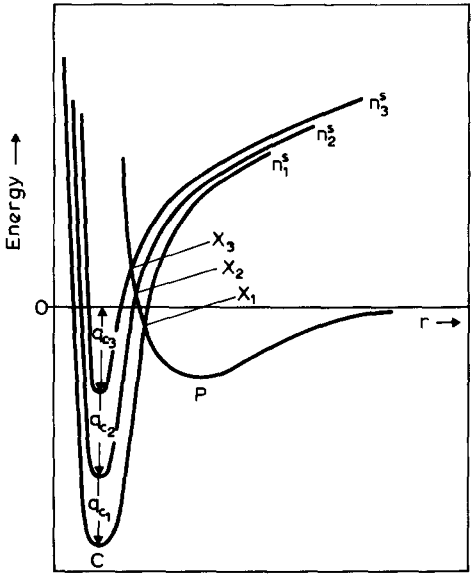


Fig. 3. Influence of the coverage on the potential curves (induced heterogeneity). As the coverage progresses ($n_1^s < n_2^s < n_3^s$), the heat of adsorption decreases and the activation energy increases.

adsorption to another. On the other hand, lateral interactions between adsorbed molecules (or atoms) may also result in variations of the adsorption energy vs. coverage. This effect, indeed, slightly alters the equilibrium distance, r_c, from the surface and alters the depth of the potential energy well, q_c, to a much greater extent (induced heterogeneity). The heat of adsorption appears to be smaller when the coverage fraction rises (Fig. 3). The position of the cross-over point is also affected and the activation energy for chemisorption increases with coverage. A special type of induced heterogeneity arising from a modification of the site reactivity to be ascribed to changes in electronic properties of the adsorbent along the coverage was observed on metals [7].

Thermodynamic definition of "heats" of adsorption

The adsorption equilibrium is the fundamental condition for thermodynamic definition of the adsorption heats. Only in this case can we establish precise relationships between measured heats and the change in thermodynamic functions of the interacting system during the adsorption process. Besides, as the heat is not a state function it will depend on the experimental conditions as well as the methods of measurement. In what follows, the main definitions of the adsorption heats in gas–solid [8,9] and solution–solid equilibria [10] are reported.

The "integral heat" (Q^{int}) is obtained in accordance with the first law when n^s moles are adsorbed at constant temperature. In a closed gas–solid system no volume work is done, so that

$$Q^{\mathrm{int}} = n^{\mathrm{s}}(u^{\mathrm{s}} - u^{\mathrm{g}}) \tag{1}$$

u^{s} and u^{g} being the molar internal energy of the adsorbed and gaseous phases, respectively. The molar integral heat of adsorption represents the change in internal energy during the adsorption process $(\Delta_{\mathrm{ads}}u)$

$$q^{\mathrm{int}} = \frac{Q^{\mathrm{int}}}{n^{\mathrm{s}}} = u^{\mathrm{s}} - u^{\mathrm{g}} = \Delta_{\mathrm{ads}}u \tag{2}$$

The "differential heat" of adsorption is related to the integral heat according to

$$q^{\mathrm{d}} = \left[\frac{\partial Q^{\mathrm{int}}}{\partial n^{\mathrm{s}}}\right]_{T,A} = \Delta_{\mathrm{ads}}\dot{u} \tag{3}$$

A gas–solid open system, in which, e.g., adsorption is brought about by continuous or stepwise admission of the adsorptive, will exchange not only heat, but work and matter too. The work will consist of a reversible and isothermal transfer of matter both to the gaseous phase $(V^{\mathrm{g}}\mathrm{d}p)$ and the adsorbed phase $(RT\mathrm{d}n^{\mathrm{s}})$. By integrating 0 and n^{s}

$$Q^{\mathrm{exp}} = n^{\mathrm{s}}(u^{\mathrm{s}} - u^{\mathrm{g}}) - RTn^{\mathrm{s}} - V^{\mathrm{g}}p \tag{4}$$

The measured heat (Q^{exp}) in a calorimeter at constant temperature is then an isothermal heat, differing from the integral heat by the amount of work done $(RTn^{\mathrm{s}} + V^{\mathrm{g}}p)$. The differential heat can be obtained from the experimental heats measured in isothermal conditions.

$$q^{\mathrm{d}} = \left[\frac{\partial Q^{\mathrm{exp}}}{\partial n^{\mathrm{s}}}\right]_{T,A} + RT + V^{\mathrm{g}}\left[\frac{\partial p}{\partial n^{\mathrm{s}}}\right]_{T,A} \tag{5}$$

The last term represents the compression work (or the expansion work, for desorption), which becomes zero when the two calorimetric cells, one with sample, are connected differentially.

In general, the condensed phase has a very small pressure dependence, so that $H^{\mathrm{s}} \approx U^{\mathrm{s}}$. Since $h^{\mathrm{g}} = u^{\mathrm{g}} + RT$

$$\Delta_{\mathrm{ads}}h = \Delta_{\mathrm{ads}}u - RT \tag{6}$$

and, in differential form

$$\Delta_{\mathrm{ads}}\dot{h} = \Delta_{\mathrm{ads}}\dot{u} - RT \tag{7}$$

By comparison with eqns. (2) and (4), and with eqns. (3) and (5), we can deduce that the experimental heats measured in the above conditions are in fact enthalpies (integral or differential) of adsorption [9]

$$\Delta_{\mathrm{ads}}h = \Delta_{\mathrm{ads}}u - RT = \frac{Q^{\mathrm{exp}}}{n^{\mathrm{s}}} + \frac{V^{\mathrm{g}}p}{n^{\mathrm{s}}} \tag{8}$$

$$\Delta_{\mathrm{ads}}\dot{h} = \Delta_{\mathrm{ads}}\dot{u} - RT = \left[\frac{\partial Q^{\mathrm{exp}}}{\partial n^{\mathrm{s}}}\right]_{\mathrm{T,A}} + V^{\mathrm{g}}\left[\frac{\partial p}{\partial n^{\mathrm{s}}}\right]_{\mathrm{T,A}} \tag{9}$$

In the uptake from solution on a solid surface (i.e., solution–solid adsorption) one can infer

$$q^{\mathrm{exp}} = (\Delta_{\mathrm{ads}}h_1 - \Delta_{\mathrm{ads}}h_2 + \Delta_{\sigma}h_2 - \Delta_{\sigma}h_1) + \Delta_{\mathrm{dil}}h \tag{10}$$

where $\Delta_{\mathrm{ads}}h_1$ and $\Delta_{\mathrm{ads}}h_2$ can be equated to the net molar integral enthalpies of adsorption for components 1 and 2 (e.g., solute and solvent, respectively); $\Delta_{\sigma}h_1$ and $\Delta_{\sigma}h_2$ are the terms corresponding to the change of the adsorbate–solution interface during the adsorption process; $\Delta_{\mathrm{dil}}h$ is the dilution enthalpy [10].

If the adsorption is performed with dilute solutions, $\Delta_{\sigma}h_1$ and $\Delta_{\sigma}h_2$ should be considered as negligible, and $-\Delta_{\mathrm{ads}}h_2$ (enthalpy of desorption of the solvent) as well as $\Delta_{\mathrm{dil}}h$ (enthalpy of dilution of the solution when the adsorption takes place) as constant values. To obtain $\Delta_{\mathrm{ads}}h_1$ it is, thus, necessary to know the enthalpy of adsorption of the solvent, and the enthalpy of dilution, which for very dilute solutions can be taken as zero. The equation can be thus simplified

$$\Delta_{\mathrm{ads}}h_1(\mathrm{solute}) = q^{\mathrm{exp}} + \Delta_{\mathrm{ads}}h_2 - \Delta_{\mathrm{dil}}h \tag{11}$$

EXPERIMENTAL DETERMINATION OF HEATS OF ADSORPTION

Indirect methods: equilibrium data, adsorption isotherms at two or more temperatures; kinetic data, activation energy for desorption, from the rate of desorption as a function of temperature.

Direct methods: calorimetric measurements, by isothermal, adiabatic and isoperibolic calorimeters (continuous or discontinuous methods of adding adsorptive).

Indirect methods

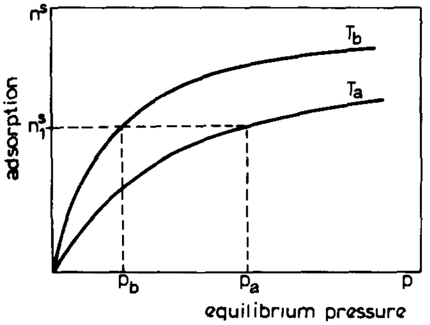
Equilibrium data

The adsorption isotherms measured at two (or more) temperatures can be used to obtain heat of adsorption at constant coverage ("isosteric heat", q^{st}) from the Clausius–Clapeyron equation

$$q^{\mathrm{st}} = RT^2\left[\frac{\partial \ln p}{\partial T}\right]_{n^{\mathrm{s}},A} = \Delta_{\mathrm{ads}}\dot{h} \tag{12}$$

The isosteric heats are obtained from the horizontal separation of the two (or more) curves at a given coverage together with their temperature difference (Fig. 4). If q_1^{st} is the isosteric heat of adsorption for the coverage n_1^{s}, by integrating the above equation we obtain

$$\ln\frac{p_{\mathrm{a}}}{p_{\mathrm{b}}} = \frac{q_1^{\mathrm{st}}}{R}\left[\frac{1}{T_{\mathrm{b}}} - \frac{1}{T_{\mathrm{a}}}\right] \tag{13}$$



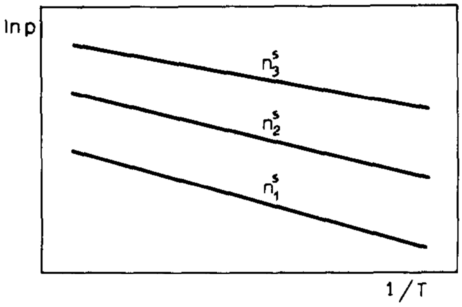


Fig. 4. Adsorption isotherms at two temperatures ($T_a > T_b$), for determination of the isosteric heat of adsorption (q^{st}) according to eqn. (13).

Fig. 5. Adsorption isosters at increasing coverage ($n_1^s < n_2^s < n_3^s$) according to eqn. (14).

The accuracy of the determination of q^{st} can be improved by using more than two isotherms. In this case, the q^{st} value is obtained from the slope of the isoster of adsorption

$$\ln p = \text{const} - q^{st}/RT \qquad (14)$$

The dependence of the isosteric heat of adsorption on coverage may thus be measured, since eqn. (14) can be applied to a number of different uptakes of adsorbate [11], as shown in Fig. 5.

Furthermore, it may be noted that the isosteric heat of adsorption should itself be a function of temperature, because of the difference ΔC_p in the partial molar heat capacities of the adsorptive and the adsorbate at constant pressure and composition. Kirchhoff's law gives

$$q^{st} = q_0^{st} + \int_0^T \Delta C_p \, dT \qquad (15)$$

where q_0^{st} is the heat of adsorption at absolute zero.

The temperature range of the isotherms used for the calculation of the isosteric heats should therefore be quite narrow.

Kinetic data

If a sufficient amount of energy is given to an adsorbate–adsorbent system, progressive detachment of the adsorbed species can be induced. According to the energetics of adsorption (Fig. 1), the activation energy for desorption is the sum of the heat of adsorption (q_{ads}) and its activation energy (E_{ads})

$$E_{des} = q_{ads} + E_{ads} \qquad (16)$$

By heating, it is thus possible to obtain desorption spectra and from the temperature at which pressure maxima occur one may derive E_{des}. This, in turn, is a measure of the binding strength [12].

The energy necessary for desorption can be given not only by heating (thermal desorption), but also by other methods: radiations of suitable energy (photodesorption), high intensity electrical fields (field desorption), electron beam irradiation (electron-stimulated desorption).

Direct methods

The calorimetric determination of heats of adsorption

Measurement of heat of adsorption by a suitably adapted calorimeter is undoubtedly the most reliable method, for two main reasons:

(i) the expected physical quantity is directly measured;

(ii) no hypotheses on the actual equilibrium of the system are needed.

However, the preference often given to indirect methods is not so surprising if we consider:

(i) the relatively small number of commercial calorimeters that can be adapted to adsorption measurements;

(ii) the difficulty of reproducing, inside the calorimeter, the experimental conditions required for a precise determination;

(iii) the need to measure the adsorbed amounts, i.e., the necessity for adsorption isotherms, from which the heat is indirectly obtainable.

Experimental calorimetric determination of the heat of adsorption is seemingly quite simple. One must bring the adsorptive into contact with the adsorbent and measure the heat emitted, maintaining the calorimetric vessel at a predetermined temperature. Furthermore, as the heats are expressed in energetic units per mole of adsorbate and usually plotted as a function of adsorbed amounts, this quantity is also necessary, though not for drawing so-called calorimetric isotherms (integral heats vs. equilibrium pressure or concentration) [13].

As the heats of adsorption range between a few kJ mol^{-1} and 500 kJ mol^{-1} the determination of integral adsorption heats does not need very highly sensitive apparatus, but studies with low sensitivity calorimeters are always on rather large coverage fractions of the adsorbent surface.

In fact, real surfaces show a pronounced variation, usually a decrease, of adsorption heat along uptake. Knowledge of the changes of adsorption integral heat along the coverage thus becomes of the greatest importance. From those data it is also possible to draw differential adsorption heats and their variation with coverage. For this purpose, one must carefully follow the successive steps of coverage by measuring the thermal effect corresponding to very small increases of adsorbate. The importance of using very highly sensible calorimeters is thus evident.

The factors affecting variations in differential heats of adsorption can be schematically summarized as follows.

(a) Factors depending on the physical and chemical characteristics of the adsorbent (a priori heterogeneity): chemical purity, microporosity, structural heterogeneity due to surface defects and/or differences in the adsorption sites (Fig. 2).

(b) Factors depending on the adsorbate situation ("induced" heterogeneity): lateral interactions (Fig. 3), phase transitions and multilayer build up, variety of adsorbed species, as well as changes in site reactivity induced by adsorbate [7].

(c) Physical factors (essentially temperature) capable of altering (a) and (b) [18].

ADSORPTION CALORIMETRY

Adsorption calorimeters

Quite a large number of calorimeters have been used for heat of adsorption measurements [14]. A few of them belong to the two classes of adiabatic and isothermal calorimeters [15], but most fall within the so-called non-isothermal–non-adiabatic category. For this large, and rather indeterminate, class of calorimeters the heat evolved is measured by determining its fraction crossing the wall of the calorimetric cell, following the Tian equation

$$\mathrm{d}Q/\mathrm{d}t = p\Delta T + c\,\mathrm{d}(\Delta T)/\mathrm{d}t \tag{17}$$

where ΔT is the temperature difference between cell and shield, p the heat transfer coefficient between these two parts, and c the heat capacity of the cell and of its content [16]. Calorimeters with small p values are very similar, at least at the beginning of the experiments, to adiabatic ones. By contrast, calorimeters showing large values of p can be assimilated to the isothermal ones and are well suited for adsorption experiments. Because they do not involve an appreciable temperature change (and therefore a partial desorption and a change in heat content of the adsorbate–adsorbent system), the measured heats of adsorption will correspond to the changes in thermodynamic functions (see the thermodynamic section).

A calorimeter suitably adaptable to heat of adsorption measurements is required to have the following characteristics.

(1) High sensitivity, to follow, with sufficient precision, the changes with coverage of integral and differential heats of adsorption, thus allowing the use of very small amounts of adsorbent.

(2) High thermal stability, to have a well-stabilized baseline, decisive in the study of slow, or very slow, adsorption processes. This characteristic also depends on the thermostatic conditions of the room.

(3) Large interval of utilization temperature. This is important for studying the interactions of different reactants on the surface. Besides, with very versatile calorimeters the indispensable thermal pretreatment and outgassing of the adsorbent can be brought about in situ.

(4) Good accessibility of the calorimeter proper (i.e., thermal sensors), allowing connections with the volumetric apparatus (or other experimental device for the measurement of the adsorbed amounts). Relatively large dimensions as well as suitable geometry of the calorimetric cells are also required for the same purposes.

Heat-flow calorimeters

In a heat-flow, or conduction, calorimeter there is a mechanically defined path for transferring heat from the calorimetric cell to the surroundings. The heat flux is measured by the temperature difference (ΔT) between the cell and the external shield, whose heat capacity should be very high to have good isothermal conditions. The heat conductor makes the heat transfer easier, and this type of calorimeter can therefore be considered quasi-isothermal, or isothermal tout court [15]. Because of the very low values of ΔT (10^{-2} K, or less), the thermal sensor that measures the heat flux must be very sensitive. A calorimetric element of a typical heat-flow calorimeter, the Tian–Calvet calorimeter, is represented in Fig. 6. Heat flows along the wires of a large number of differential thermocouples grouped in series (thermopile). To improve the stability of the baseline (absence of production of heat), two thermopiles are connected differentially and placed in the same metal block, carefully thermostated. Microfluctuations of temperature are, thus, well compensated and deviations of the baseline can be reduced to values much smaller than the highest sensitivity of these calorimeters (~ 1 μW mm^{-1}).

The thermal response of a heat-flow (or conduction) calorimeter is a representation, deformed by thermal lags, of the phenomenological evolution of the adsorption process under study. The aspect of the recorded signal is that of a peak which comes to the baseline after very different lengths of time (from a few minutes to some hours, or days in exceptional cases). It measures the thermal flux, dQ/dt, according to Tian's equation. When the integration limits are comprehensive of all thermal effects (i.e., from the beginning of the deviation until the return to the baseline) the heat emitted is proportional to the peak surface.

$$Q = p\int_{t_1}^{t_2} \Delta T \,\mathrm{d}t \qquad (18)$$

Since the second term of Tian's equation is zero, as $d(\Delta T) = 0$, the term containing the heat capacity of the cell and its content does not appear: the change in the cell content may thus modify the peak profile, but not its total surface. The p coefficient represents the heat actually recordable by the thermal sensors (heat-transfer coefficient). It is then a measure of the sensitivity of the calorimetric apparatus and must be determined by means of suitable calibration tests, possibly in operative conditions. For the most sensible calorimeters, it is usually of the order of 1–10 μW mm^{-1}.

The calibration of a calorimeter adapted to adsorption measurements

The calibration of a calorimeter may be done by means of a well-known thermal effect produced in suitable conditions inside the cell. Different sources of heat can be used:

(1) chemical processes (mixing, dilution, reactions, etc.);
(2) physical processes (evaporation, melting, radioactivity);
(3) electrical phenomena (Joule effect).

It is necessary to perform calibration tests in conditions as close as possible to the experimental ones [13,17,18]. So far, however, no adsorbent–adsorptive standard systems have been defined. Thus, because of the very small dimension of an electrical resistance, the Joule effect is the heat source most frequently used in adsorption calorimetry, especially for gas–solid systems.

Precautions to avoid (or minimize) interfering thermal effects

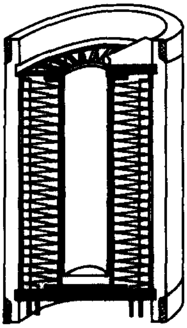
These effects may be divided into two categories: "variable" (changing during the experiment) and "constant" (typical of the calorimetric cell adopted). Constant effects can be minimized with a suitable experimental assembly designed to prevent thermal leaks. Variable effects are, for example, the compression/expansion heat in gas–solid adsorption, and the dilution of the solute and the desorption of the solvent in solution–solid adsorption. In gas–solid measurements, it is possible to avoid compression/expansion effects by means of two cells, one of which contains the adsorbent, placed in two calorimetric sensors connected differentially. The same principle may be used for the interfering effects that can be compensated by a differential assembly.

Calibration by the Joule effect

A cell very similar to the experimental one must be used, in which the electrical resistance should be situated in the place of the sample (Fig. 7). Furthermore, the Joule effect must be prevented in the connection wires outside the zone of the thermal sensor, and thermal leaks along the wires must be carefully minimized. The calibration tests can be performed in two different ways.

"Power" calibration. After a short time, depending on the calorimetric inertia, application of a constant power produces a constant deviation from the baseline. The conversion factor can thus be obtained for a given experimental assembly from the ratio between the power applied (Watts = J s^{-1}) and the recorded deviation (Volts = mm), i.e., J mm^{-1} s^{-1}. The applied power is obtained from the Joule equation $W = RI^2 = V^2/R$.

"Energy" calibration. A given power is applied for a short time and the peak obtained is graphically integrated. The conversion factor is obtained in J mm^{-1} s^{-1} from the relation $Q = RI^2t$ and by taking into account the



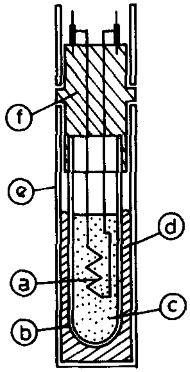


Fig. 6. Thermal sensor (thermopile) adopted in a heat-flow microcalorimeter (Tian–Calvet type).

Fig. 7. Calibration by Joule effect of a calorimetry assembly for gas–solid adsorption studies. (a) electrical resistance; (b) glass cell; (c) adsorbent simulation (oil); (d) mercury; (e) stainless-steel container in contact with the thermopile; (f) Teflon insulating plug.

recorder chart speed (peak area in mm s^{-1}). A particular case of calibration is obtained with very short pulses of electrical current giving rise to the so-called "ballistic" peaks, in which the height of the peaks may, under certain conditions, be proportional to the power applied during each pulse [16].

Determination of adsorbed amounts

Direct determination of adsorption heats requires parallel measurement of the adsorbed amounts corresponding to the measured emitted heat at each coverage step.

Gas–solid adsorption

A volumetric assembly must be connected to the cell(s) in the calorimetric

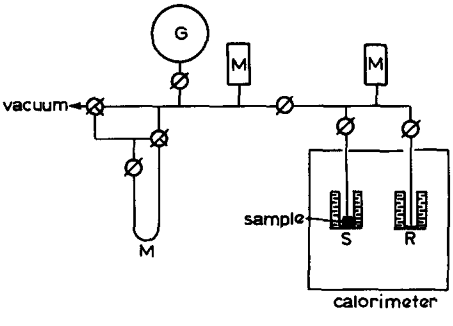


Fig. 8. A volumetric assembly associated with a heat-flow calorimeter (Tian–Calvet type) for adsorption measurement by successive doses of gas. G, adsorptive (gas or gaseous mixture); M, manometers; S, sample cell; R, reference cell.

apparatus (Fig. 8). Measurements can be made with successive doses of adsorptive (gas or gaseous mixture) and the adsorbed amounts are calculated from the difference between the admission and the equilibrium pressure after the adsorption process. The volumetric assembly is built in the same way as an adsorption isotherm apparatus [19]. It must be recalled that the main factors affecting the precision of the volumetirc measurement of adsorbed amounts in gas–solid adsorption are:

(1) precise determination of the admission and equilibrium pressures;

(2) accurate calibration of the volumes of the vacuum line;

(3) optimization of the ratio (1 : 1) between the admission and calorimetric cell volumes (see ref. 19, p. 39);

(4) minimization of the total known volume (admission + cells);

(5) thermostatization of the volumetric apparatus (or better of the whole room in which the apparatus is located).

Flow methods have also been employed in the calorimetric study of adsorption as well as reaction processes. A single continuous experiment (6–8 h) has been set up with a small and constant flow of adsorptive in the calorimetric cell containing the adsorbent [20]. If the adsorption process is sufficiently fast, as for physisorption, the system can be considered constantly in equilibrium, so that the adsorption isotherms can be determined from the flow rate and the pressure in the cell. Furthermore, combination of the adsorption and calorimetric data will give directly differential heats of adsorption as a function of coverage. For the chemisorption study, the

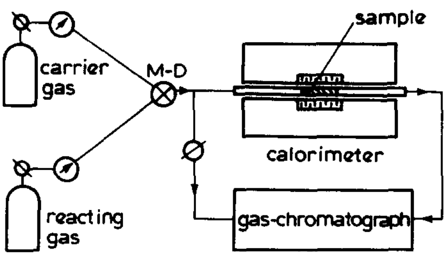


Fig. 9. Scheme of an assembly for chemisorption measurement by continuous or discontinuous gas-flow methods (also suitable for catalyzed reactions). M–D: mixer–doser.

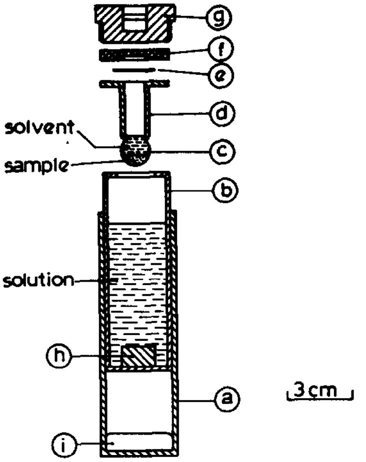


Fig. 10. Calorimetric cell for solution–solid adsorption measurements. (a) Stainless-steel container in contact with the thermopile; (b) glass cell; (c) glass bulb; (d) glass phial; (e) thin glass slide; (f) rubber sheet; (g) Teflon screw-plug; (h) metallic mass; (i) mercury.

association of a heat-flow calorimeter with a gas-chromatograph has been used [21], as schematically represented in Fig. 9. In this case, a stepwise (or discontinuous) gas-flow method can also be adopted.

Solution–solid adsorption

A calorimetric cell suitable for adsorption measurements from solutions is represented in Fig. 10. It was designed to be used in a rotating heat-flow calorimeter [22]. A glass cell, filled with solution, is introduced into the stainless-steel container in contact with the thermopile. The phial containing the outgassed adsorbent, covered in vacuo by the solvent to prevent pollution from the atmosphere, is sealed at the opening by a thin glass slide. Then the two parts of the cell (a and b) are glued together to create a perfect seal during the experiment. By rotating the calorimeter, the bulb is broken by the metallic mass: sample and solution come into contact and some further rocking ensures a good contact between the two phases. Ordinary analytical metods to determine the solution concentration before and after adsorption can be used. In this case, accuracy is solely dependent on the sensitivity of the method and the precision of calibration.

LIST OF SYMBOLS

The notation used throughout this paper follows, with slight modifications, the recommendations of the International Union of Pure and Applied Chemistry [1].

V	volume
p	pressure
A	area
T	absolute temperature
n	amount of substance
W	work
Q	heat
U	internal energy
H	enthalpy
S	entropy
G	free enthalpy

Superscripts

s	adsorbed state
g	gaseous state

Capital letters: extensive functions (except for n)
Small letters: intensive functions (except for T)

$x = X/n$: integral molar functions

$\dot{x} = \partial X/\partial n$: differential molar functions $(= x + n\frac{\partial x}{\partial n})$

State function variations resulting from adsorption are represented by the operator Δ followed by the subscript ads, e.g., $\Delta_{\text{ads}}H$ = enthalpy of adsorption.

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