Thermochimica Acta, 39 (1980) 151—158

USE OF ISOTHERMAL MICROCALORIMETRY DATA FOR THE DETERMINATION OF INTEGRAL MOLAR ENTROPIES OF ADSORPTION AT THE GAS—SOLID INTERFACE BY A QUASI-EQUILIBRIUM PROCEDURE

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(Received 2 January 1980)

ABSTRACT

The aim of this paper is to describe the present position in the experimental determination of entropies of adsorption. After pointing out the limitations of the "isosteric" approach and after stressing the fact that the most interesting entropy to know is the integral molar entropy of adsorption, the authors show how the use of isothermal adsorption microcalorimetry, with a special quasi-reversible procedure, allows this entropy to be determined satisfactorily from the thermodynamic point of view.

INTRODUCTION

It is known (see for instance refs. 1 and 2) that the method most commonly followed for the evaluation of the enthalpies of adsorption makes use of a set of "adsorption isotherms" (equilibrium pressure vs. amount adsorbed) determined at various temperatures. This method is based on a relationship similar to that of Clausius—Clapeyron concerning the change of state of a pure substance in which the equilibrium pressure only depends on the absolute temperature, T. The adsorption of a pure gas or vapour may indeed be considered as a special change of state, where the equilibrium pressure, p, depends both on the temperature and on a second parameter which may be the amount adsorbed, n^a, the surface concentration, Γ^a, or the surface pressure π^{a*}. Keeping the parameter n^a constant (and therefore, keeping constant the "volume adsorbed" $n^a v_0$, where v_0 is the molar volume of the gas, supposed to be ideal, at STP) allows isochores or "isosteres" to be plotted (in terms of $\ln p$ vs. $1/T$) whose slope is directly related to the

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* For the notation see the appendix.

derivative enthalpy of adsorption (which we denote, as in ref. 3, by Δ ads $\dot{h}$)

$$\left(\frac{\partial \ln p}{\partial(1/T)}\right)_{n^{a},A^{s}} = \frac{\Delta \text{ ads } \dot{h}}{R}$$

where A^{s} is the surface area of the adsorbent and R the gas constant.

In practice, the integrated form of the above relationship, applied between two neighbouring temperatures, is normally used to calculate Δ ads $\dot{h}$ at a given amount adsorbed n^{a}. Hill [4] has shown that the derivative enthalpy of adsorption (more commonly called the "isosteric heat of adsorption") is related to the derivative entropy of the adsorbed phase $(\partial S^{a}/dn^{a})_{T,A^{s}}$, which we denote by $\dot{s}^{a}$, by

$$\Delta \text{ ads } \dot{h} = T(\dot{s}^{a} - s^{g})$$

where s^{g} is the molar entropy of the adsorbate in the gaseous state and at the equilibrium temperature and pressure. Although experimentally convenient (since it avoids the use of a calorimeter), the "isosteric" approach suffers from severe limitations when the uncertainty of the equilibrium pressure is of the same order of magnitude as the pressure variation between the two isotherms chosen to apply the method. As we showed in previous works [5,6], this situation can easily occur, especially at low temperatures, for coverages up to 0.5, i.e. for low equilibrium pressures, giving rise not only to errors in the measurement itself but also to false equilibria: in molecular sieves, at 77 K, thermally activated diffusion is poor and the achievement of a true equilibrium may take days [7]. These uncertainties are, of course, carried into the calculation of the molar entropy obtained by integration from zero coverage.

Because the first stages of the adsorption process are the most interesting insofar as the adsorbate—adsorbent interactions are concerned, it seemed worthwhile to take advantage of the possibilities of the calorimetric approach. Theoretically, the entropy change associated with the adsorption process can then only be measured in the case of a reversible heat exchange. Our aim is to show how it now becomes possible, due to recent improvements in isothermal * adsorption microcalorimetry, to obtain directly and continuously the integral entropy of adsorption, i.e. the one which is of prime interest to check the theoretical models of adsorption, as Hill said [4]. We shall make use of the formula previously established in ref. 9 where the calculation of the integral entropy of adsorption from data obtained in open systems is carried out.

THE VARIOUS ENTROPIES OF ADSORPTION

Since the term "entropy of adsorption" is able to cover a great number of different functions, it is always necessary to specify whether the function

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* Because they involve a necessary temperature change (and therefore a partial desorption and a change in the heat content of the adsorbate—adsorbent system) adiabatic and isoperibol calorimetry (using the definitions previously given in ref. 8) are not so well suited, in our opinion, for that type of determination.

considered is a derivative or an integral, and also whether it refers to an equilibrium state (defined by p and T) or to a standard state (defined by p^0 and T). Moreover, various entropies of adsorption may be defined after the standard state chosen for the adsorbate (this state may be gaseous, but also liquid or solid).

One may first define the entropy, $\bar{s}^a$, of an adsorbed mole. This is a mean integral quantity, taken over the whole amount adsorbed and characteristic of a given state of equilibrium of the system (state defined by p and T). This quantity may be compared with the entropy of the same substance in the gas state (supposed ideal) and under the same p and T conditions. This allows us to define the integral molar entropy of adsorption as

$$\Delta\,\text{ads}\,\bar{s} = \bar{s}^a - s^g$$

Nevertheless, this definition is useless if one is interested in following the variation of the entropy, S^a, of the adsorbed phase as a function of coverage. Indeed, because of the pressure dependence of s^g, the derivative $(\partial S^a/\partial n^a) = \dot{s}^a$ cannot be directly obtained from the derivation of Δ ads $\bar{s}$. This is why there is a need to define a standard integral molar entropy of adsorption as

$$\Delta\,\text{ads}\,\bar{s}^{\,0} = \bar{s}^a - s^{g,0}$$

where the entropy of one adsorbed mole is now compared with the entropy $s^{g,0}$ of the same substance in the gas state (supposed ideal) and at the same temperature but under the standard pressure. The derivative of the standard integral molar entropy of adsorption, expressed by

$$\frac{\partial}{\partial n^a}(\Delta\,\text{ads}\,\bar{s}^{\,0}) = \dot{s}^a - s^{g,0} = \Delta\,\text{ads}\,\dot{s}^0$$

is called the standard derivative entropy of adsorption. This derivative function may be obtained from the derivative entropy of adsorption (usually called "differential" entropy of adsorption, although it is a derivative, not a differential), viz.

$$\Delta\,\text{ads}\,\dot{s} = \dot{s}^a - s^g$$

through the relationship

$$\Delta\,\text{ads}\,\dot{s}^0 = \dot{s}^a - s^g - R\ln\frac{p}{p^0}$$

or, as in ref. 10

$$\Delta\,\text{ads}\,\dot{s}^0 = \frac{\Delta\,\text{ads}\,\dot{h}}{T} - R\ln\frac{p}{p^0}$$

The sole interest of the derivative entropy of adsorption itself is to be easily assessed, experimentally, from the derivative enthalpy of adsorption. But attention must be paid to the fact that this quantity is not a derivative proper, nor an integral molar quantity, since

$$\frac{\partial}{\partial n^a}[n^a(\bar{s}^a - s^g)] = \dot{s}^a - s^g - n^a\frac{\partial s^g}{\partial n^a}$$

and hence

$$\Delta \text{ ads } \dot{s} = \frac{\partial}{\partial n^a}[n^a \Delta \text{ ads } \bar{s}] + n^a \frac{\partial s^g}{\partial p}\frac{\partial p}{\partial n^a} \tag{1}$$

Δ ads $\dot{s}$ proves to be the derivative of Δ ads $\bar{s}$ in the only case when the adsorption takes place under constant pressure (and temperature). This situation may be found when a two-dimensional phase change is taking place, leading to a vertical step of the adsorption isotherm (the case of highly homogeneous adsorbents) and also, much more frequently, at the beginning of the adsorption (the steeply rising part of the isotherm where $(\partial p/\partial n^a) \simeq 0$). If, moreover, in that region, Δ ads $\dot{s}$ does not depend on coverage, which is approximately the case with homogeneous adsorbents, then the derivative entropy of adsorption, Δ ads $\dot{s}$, is identical with the integral molar entropy of adsorption Δ ads $\bar{s}$.

It may be also interesting to compare the entropy of the adsorbed state with a condensed state (liquid or solid) of the adsorbate. This leads us to what Lamb and Coolidge [11] call "net entropies of adsorption", where the reference state does not depend on the pressure:

(a) If the standard state is the liquid state of the adsorbate (in equilibrium with its saturating vapour pressure p_0^l at temperature T), we obtain

$$\dot{s}^a - s^l = \frac{\partial}{\partial n^a}[n^a(\bar{s}^a - s^l)] = \Delta \text{ ads } \dot{s} + \frac{\Delta \text{ vap } h}{T} - R \ln \frac{p}{p_0^l}$$

which may be also written

$$\dot{s}^a - s^l = \frac{\dot{h}^a - h^l}{T} - R \ln \frac{p}{p_0^l}$$

$\dot{h}^a$ being the derivative enthalpy (and also the derivative energy) of the adsorbate and h^l the molar enthalpy (or energy) of the liquid adsorbate.

(b) If the standard state is the solid state of the adsorbate (in equilibrium with its saturating vapour pressure p_0^s at temperature T), we obtain

$$\dot{s}^a - s^s = \frac{\partial}{\partial n^a}[n^a(\bar{s}^a - s^s)] = \frac{\dot{h}^a - h^s}{T} - R \ln \frac{p}{p_0^s}$$

h^s being the molar enthalpy (or energy) of the solid adsorbate.

DERIVATION OF ENTROPIES OF ADSORPTION FROM MICROCALORIMETRIC EXPERIMENTS CARRIED OUT QUASI-REVERSIBLY USING OPEN SYSTEMS

The derivation of entropies of adsorption may be carried out from actual calorimetric experiments provided the necessary care is taken in ensuring the reversibility of the heat exchanges. The use of isothermal microcalorimetry with a procedure of discontinuous introduction of the adsorbate may be used [12]. But a more convenient and safe way is likely to be the use of the procedure of slow and constant introduction of adsorbate.

The experimental assemblies and procedures have been described previously [5,13]. It is necessary only to point out that the gaseous adsorbate is introduced continuously and at a very slow and constant rate in the range of 1 cm^3 STP h^{-1}. Throughout the adsorption experiment (which usually lasts between 5 and 15 h before the monolayer is completed) the adsorbent temperature is constant within a few 10^{-2} K. The heat flow generated by the adsorption (and detected by a set of twin Tian-Calvet thermopiles) is continuously recorded. The main interest of this procedure is as a quasi-equilibrium procedure. It permits the determination, at any time, of a set of parameters (amount adsorbed, heat evolved and adsorption pressure) which are equal, within experimental error, to those determined after stopping the gas flow and waiting for a "true" equilibrium. Moreover, we may consider, and this is of the utmost importance for our purpose here, that the heat measured is exchanged in a quasi-reversible process. Let us then note, following a former description [14] that the adsorption system (i.e. all the adsorbent and adsorbate contained in the calorimetric cell) is an open one exchanging both heat, work and matter with the outside. In these conditions, the entropy change of the system, when it follows a quasi-reversible path during the introduction of dn mole of adsorbate (taken at temperature T and pressure p), may be written

$$\mathrm{d}S = \frac{(\delta Q\ \mathrm{ex})\ \mathrm{rev}}{T} + s_T^{\mathrm{g}}\,\mathrm{d}n \tag{2}$$

where $(\delta\ Q\ \mathrm{ex})$ rev is the amount of heat experimentally measured (in the above quasi-reversible conditions) and s_T^{g} is the molar entropy of the adsorbate (supposed to be an ideal gas at temperature T) such that

$$s_T^{\mathrm{g}} = \frac{S_T^{\mathrm{g}}}{n^{\mathrm{g}}} = s_T^{\mathrm{g},0} - R \ln \frac{p}{p^0}$$

$s_T^{\mathrm{g},0}$ being the standard molar entropy of the adsorbate at temperature T and at standard pressure p° (and also supposed to be an ideal gas). Part of the amount dn of adsorbate received by the system is adsorbed (let dn^{a} be this amount); the remainder increases by dp the pressure in the gaseous phase (in the void volume, V_{B}, of the calorimetric cell). If, following the usual convention, we admit that the entropy variation of the adsorbent is zero (which is a reasonable asumption in the case of physical adsorption, i.e. of weak interactions) we may write

$$\mathrm{d}S = \mathrm{d}(S^{\mathrm{a}} + S^{\mathrm{g}}) = \frac{\partial S^{\mathrm{a}}}{\partial n^{\mathrm{a}}}\,\mathrm{d}n^{\mathrm{a}} + s^{\mathrm{g}}\,\mathrm{d}n^{\mathrm{g}} + n^{\mathrm{g}}\,\mathrm{d}s^{\mathrm{g}} \tag{3}$$

Combining eqns. (2) and (3), we then obtain

$$\dot{s}^{\mathrm{a}} - s^{\mathrm{g}} = \Delta\ \mathrm{ads}\ \dot{s} = \frac{1}{T}\left(\frac{\delta Q\ \mathrm{ex}}{\delta n^{\mathrm{a}}}\right)_{T,A^{\mathrm{S}}} + \frac{V_{\mathrm{B}}}{T}\left(\frac{\partial p}{\partial n^{\mathrm{a}}}\right)_{T,A^{\mathrm{S}}} \tag{4}$$

or, introducing experimental data such as the heat flux, ϕ, the total volume, V^{g}, of the gaseous phase (including the void volume, V_{B}, of the calorimetric cell and the volume of the external tubings leading to the pressure gauge) and the constant flow, f, of gas entering the above volume, we obtain

$$\Delta\ \mathrm{ads}\ \dot{s} = \frac{1}{T\left(f - \dfrac{V_{\mathrm{g}}}{RT}\dfrac{\mathrm{d}p}{\mathrm{d}t}\right)}\left(\phi + V_{\mathrm{B}}\frac{\mathrm{d}p}{\mathrm{d}t}\right) \tag{5}$$

In these conditions, we may follow, practically from the beginning of the coverage (which is not the case, as we saw, for the isosteric method), the derivative entropy of adsorption and hence the standard derivative entropy of adsorption. The interest of a continuous measurement of the standard derivative entropy of adsorption stems from the fact that any variation of its magnitude provides information on (i) a variation of the adsorbate—adsorbent interactions as a function of coverage (it allows the heterogeneities of the adsorbing surface to be detected) (ii) a collective modification of the state of interaction of the molecules already adsorbed (it allows the detection especially of two-dimensional phase changes), or (iii) a combination of both. Nevertheless, as we have already noticed, one must be aware that the information contained in a curve of Δ ads $\dot{s}$ vs. n^a is nothing more than the information contained in a curve of Δ ads $\dot{h}$ vs n^a, since both curves only differ from one another by a (constant) factor $1/T$. This is the reason why the calculation of the integral molar entropy of adsorption Δ ads $\bar{s}$ is much more valuable since it really provides new information, especially useful for the selection of theoretical models. It may be calculated from eqns. (1) and (4) as previously derived in ref. 9

$$\Delta \text{ ads } \bar{s} = \bar{s}^a - s^g = \frac{Q \text{ ex}}{Tn^a} + \frac{V_{11}}{T}\frac{p}{n^a} + \frac{R}{n^a}\int_0^p n^a \, \mathrm{d} \ln p \qquad (6)$$

where Q ex is measured (in the experimental conditions given above, i.e. in quasi-equilibrium conditions) by the area under the curve of heat flux, ϕ, vs. time (from $t = 0$, when the adsorbent is under vacuum, to the time when an amount n^a is adsorbed). A problem remains with the calculation of the last term of eqn. (6), which requires knowledge of the relationship linking n^a to $\ln p$, from $n^a = 0$ *. Since the first experimental point of the adsorption isotherm corresponds to a finite value of n^a, an extrapolation down to the origin is therefore necessary. In the case when this first point may be considered to be in the "Henry law region", the extrapolation is linear (n^a = kp). Between the origin and the first experimental point we may then write

$$\int_0^p n^a \, \mathrm{d} \ln p = \int_0^p \frac{n^a}{p} \, \mathrm{d}p = kp = n^a$$

The lower the first equilibrium pressure measured (which depends on the sensitivity of the pressure gauge used), the more appropriate the above approximation.

It happens that we are now just reaching an experimental accuracy (both in the determination of the lower part of the isotherm and in the determina-

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* The last term of eqn. 6 is often related with the "two-dimensional pressure" or "surface pressure", π, through the Gibbs relationship

$$\pi = \frac{RT}{A^s}\int_0^p n^a \, \mathrm{d} \ln p$$

Nevertheless, we shall not make use of a concept which is not easy to handle in the case of localized adsorption.

tion of the heat exchanged reversibly) which allows meaningful values of the integral molar entropy of adsorption (i.e. values with an accuracy higher than the differences between the entropies calculated for various models of adsorption) to be obtained.

For the determination of the lower part of the isotherm, we obtain the highest accuracy by adsorption volumetry, using pressure transducers to record the pressure [15,16] (gravimetry yields the same high resolution but a lower accuracy [17]). The procedure of slow and constant introduction of the adsorbate now makes it generally feasible [by use of eqn. (6)] to determine the integral molar entropy of adsorption, especially in the region of coverage lower than 0.5, where experience shows that the safety of the isosteric method (especially for experiments carried out at $T < 100$ K) may often be questioned.

A later paper [19] will show the application of the methodology just described to the case of the argon—graphite system at low temperature, which is most interesting because it is extensively studied from the theoretical point of view.

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APPENDIX

The notation used here follows, in the main, the recommendations of the International Union of Pure and Applied Chemistry [18], viz.

V	volume
A	area
p	pressure
T	absolute temperature
n	amount of substance
Q	heat
U	internal energy
H	enthalpy = $U + pV$
S	entropy
R	molar gas constant
π	surface pressure

Capital letters are used systematically to represent extensive functions (except for the amount of matter, n) while lower case letters represent intensive functions (except for the absolute temperature T and the molar gas constant R).

It follows that for each extensive function X there is a corresponding intensive function x which may be defined by X/n [*].

We also suggest the use of $\dot{x}$ to represent the partial derivative $(\partial X/\partial n)$ of function X with respect to the amount of matter n [**].

A letter used as a superscript, on the right-hand side, indicates the state of the substance, viz g for the gaseous state, s for the solid state, and a for the adsorbed state [†].

Any variation in a state function, resulting from a change of state, is represented by the operator Δ followed by an appropriate subscript on right-hand side: here we use ads for an adsorption.

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[*] When we wish to stress that the intensive function is a mean quantity, we represent it by $\overline{x}$.

[**] The quantity $\dot{x}$ is related to $\overline{x}$ by the relationship $\dot{x} = \overline{x} + n\partial\overline{x}/\partial n$.

[†] In the particular, but frequent, case of the adsorption of only one gas by a solid adsorbent, the "surface excess amount of adsorbed substance", n_{i}^{σ}, and the "amount of adsorbed substance", n_{s}^{i}, defined by Everett [10] become equivalent and we represent them, in a simplified notation, by $n^{a} = n_{i}^{s} \simeq n_{i}^{\sigma}$.