REFINEMENT OF A CALORIMETRIC METHOD OF MEASURING HEATS OF ADSORPTION AND A COMPARISON WITH AN ALTERNATIVE METHOD

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ABSTRACT

A previously described method of obtaining thermodynamic information on gas–solid adsorption is further elaborated and completed. The calculation of the net differential entropy of adsorption is made more precise by omitting undue approximations. The amounts of adsorbate are better defined and a computational correction is introduced. Most important is the completion of the procedure to derive thermodynamic state functions of the adsorbate phase from one single experiment. The procedure is linked to the work of Hill in the early 1950's. Finally a basic comparison is made with a different calorimetric method for heats of adsorption.

INTRODUCTION

The description of thermodynamic state functions of an adsorbate phase on a solid adsorbent requires knowledge of the energy and entropy of adsorption. Information on these quantities may be gained from direct calorimetric measurements during the adsorption process. As heat is not a thermodynamic state function, the path of the process must be well defined for the results to be suitable for exact thermodynamic interpretation. This general requirement for a precise understanding of heat measurements can be met more closely nowadays on account of the availability of better instrumentation in conjunction with improved experimental procedures and by the development of computational methods. Recently the work by Rouquérol et al. [1] has contributed to the progress in this field. They devised a method to derive the differential enthalpy of adsorption defined as $[\partial n_A(h_A - h_G)/\partial n_A]_{A,T}$ directly from calorimetric measurement (see list of symbols). An essential factor in their method is that the heat developed by the adsorption process is measured while this proceeds quasi-reversibly. In practice they dose the adsorptive in a continuous flow.

A different method to derive thermodynamic quantities from calorimetric

data has been described by the present author [2]. The experimental part differs from the method of Rouquérol in that the net differential heat of adsorption (defined as $[\partial n_A(e_A - e_L)/\partial n_A]_{A_s,T}$) is measured directly. This method is called here the condensation compensation method (CCM). Another feature is the fact that amounts adsorbed are also measured calorimetrically. The CCM has been successfully applied to a number of adsorbent–adsorbate pairs in the temperature range 0–45°C: benzene and water have been measured in combination with carbon black, activated carbon, synthetic zeolites and porous polymers. Some results are shown in [2]; others will be published elsewhere [3].

The aim of the present paper is to complete the previously presented thermodynamic derivations [2] and to correct them for a few computational errors. The basic features of the CCM will be compared with the method of Rouquérol et al.

INSTRUMENTAL

Condensation compensation method (CCM)

The previously presented computations for the interpretation of the experimental data obtained from the CCM are refined in this section. This refinement has to be read in conjunction with the original derivations in ref. 2. The principle of the CCM is illustrated in Fig. 1. Evaporation vessel E (containing liquid adsorptive, 1), adsorption vessel A (containing an adsorbent, a) and the connecting tube with restriction V_r form a closed thermodynamic system. Heat exchange takes place only through the two identical measuring thermopiles one side of which is in contact with E and A, respectively, and the other with a heat sink of constant temperature T_C. After evacuation of air from the system and thermal equilibration, adsorptive is admitted to the adsorbent by opening restriction V_r for a short time. This gives rise to two heat flows; because of evaporation in E there is a heat flow $\dot{Q}_E$ and because of adsorption in A there is a heat flow $\dot{Q}_A$. After integration over the time needed for establishing a new equilibrium, the EMF_E that is generated is a measure of the amount of adsorptive that has been evaporated and also, after correction for the dead volume, of the amount adsorbed. The electrically parallel connection in series of the two thermopiles allows the direct measurement of the difference between heat of adsorption and heat of evaporation; this difference is obtained by integrating EMF_Δ over time. A similar pair of thermopiles is coupled to the pair shown in Fig. 1 in electrically opposite sense in order to compensate for spurious heat flows. The advantage of measuring EMF_E and EMF_Δ instead of EMF_E and EMF_A is that the accuracy is enhanced; the extent of improvement depends strongly on the value of the difference between EMF_E

and EMF_A. Pressure gauge P allows the continuous recording of the pressure, so that the adsorption isotherm results simultaneously from the same experiment.

Dosing may be performed continuously instead of stepwise. The greatest advantage is found in a better resolution both in the adsorption isotherm and in the adsorption heat curve. However, conditions for the performance have to be defined precisely in order to interpret the experimental data correctly.

Measurement of amounts adsorbed

In contrast to the statement in ref. 2 that the amounts of evaporated liquid adsorptive Δn_L and $\dot{n}_L$ (and consequently Δn_A and $\dot{n}_A$) have to be calculated from the evaporation heat effect using the energy of evaporation, it is obvious that in practice, where evaporation is always accompanied by the performance of some work, neither energy nor enthalpy is the pure measure for the calculation of the amount of evaporated adsorptive. The problem was practically solved by carrying out calibration experiments for the relation between heat effect and amount evaporated under the same conditions as an adsorption experiment. The values obtained did not deviate significantly from the enthalpy of evaporation from the liquid adsorptive plus solute.

This corrective remark does not affect the quantitative considerations for the net heat of adsorption that are based on (internal) energy. Whether the evaporation is isothermal or not, the heat needed for the expansion work at the evaporation side is taken up and measured in the evaporation cell. As in
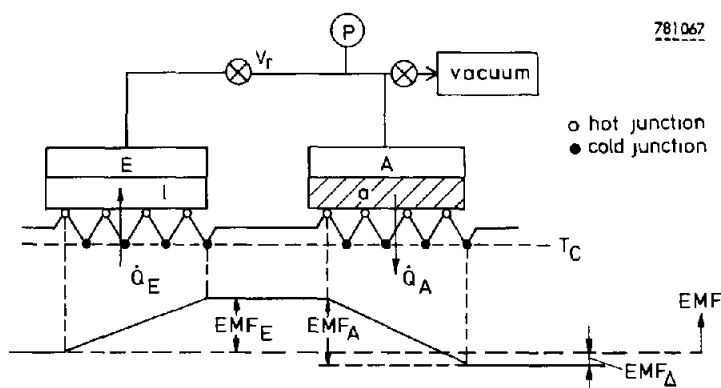

Fig. 1. Schematic view of the calorimetric set-up to measure adsorption isotherm and net differential heat of adsorption simultaneously: (E) evaporation cell with liquid adsorptive (l); (A) adsorption cell with adsorbent (a); (V_r) valve with adjustable restriction; (P) pressure gauge; (T_C) constant temperature zone; ($\dot{Q}_E$) heat flow caused by evaporation; ($\dot{Q}_A$) heat flow caused by adsorption; (EMF_E, EMF_A) EMF's over the thermopiles that measure respective heat flows (EMF_Δ, EMF_E are actually measured).

the thermal model of the instrument it is assumed that no heat is lost otherwise than through the cells, exactly the same amount of work is performed onto the adsorption cell giving rise to an equivalent loss of heat. Because of the parallel connection of the cells the two effects (RT at most) cancel out.

The same argument may be formulated in more general terms. The entire system can be thought to be divided into two subsystems, the boundary being the restriction in the line between the cells. Since no volume change of the entire system occurs, no external work is performed. This has two consequences. The first is that the only possible work is performed by one subsystem on the other. This work requires heat in one subsystem and generates the same amount in the other. Hence, regardless of the exact amount of work, the net effect in the entire system is zero. This implies that there is no requirement for an isothermal performance of the entire process, as far as the measurement of the net heat of adsorption is concerned.

The second consequence is that the sum of the two effects has to be interpreted as a change in internal energy of the system.

THERMODYNAMIC INTERPRETATION OF DATA

Refinement of previous calculations

For the sake of clarity the same equation numbers will be used as in the original paper [2]. An asterisk added to an equation number means that the original equally numbered equation has to be replaced by the one with the asterisk. In order to have the complete set of equations the most important relations are repeated here. The annotation is the same with two exceptions: instead of using Δn_E and $\dot{n}_E$ (amount evaporated and rate of evaporation, respectively), the related quantities will be expressed in the amount of liquid adsorptive (n_L) and the changes of it (Δn_L and $\Delta \dot{n}_L$). The definition of n_L implies that $\Delta n_L + \Delta n_G + \Delta n_A = 0$ and $\dot{n}_L + \dot{n}_G + \dot{n}_A = 0$. For the specific surface area the symbol A_s is used instead of Σ.

Discontinuous dosing mode

The expression for the net differential energy of adsorption, which is fundamental in the CCM is maintained apart from the replacement of Δn_E by $(-\Delta n_L)$.

$$\overline{\Delta_A e} = \frac{g_A}{\Delta n_A} A_s + \Delta_c E \left(\frac{-\Delta n_L}{\Delta n_A} \frac{g_A}{g_E} - 1 \right) \tag{2}$$

Equation (4) is transferred to eqn. (5) by equating Δn_A and $(-\Delta n_L)$, which differ from each other by the small amount of each dose that remains in the gas phase (Δn_G). Although this approximation is practically admissible, it is

undue at this point. First of all eqn. (4) is given in the correct form

$$Q^{\text{rev}} = \Delta n_{\text{L}}\left(\Delta_{\text{c}}H + RT \ln\frac{p_1}{p_0}\right) - \Delta n_{\text{A}}(q_{\text{d}} + RT) - V_{\text{G}}(p_2 - p_1) \tag{4*}$$

The exact form of eqn. (5) becomes

$$Q^{\text{rev}} = \Delta n_{\text{A}}\overline{\Delta_{\text{A}}e} + \Delta n_{\text{L}}RT \ln\frac{p_1}{p_0} - \Delta n_{\text{G}}\Delta_{\text{c}}H - V_{\text{G}}(p_2 - p_1) \tag{5*}$$

The elaboration of eqns. (7), (8) and (9) leading to eqn. (10) contains a mistake that causes the erroneous presence of a term with s_{L}, that disappeared again farther on in the derivation. If this mistake is corrected and if again Δn_{A} and Δn_{E} (now $-\Delta n_{\text{L}}$) are not untimely equated, one arrives at the following expression for the change in entropy of the entire system produced by one single dose

$$\Delta S = \Delta n_{\text{A}}\overline{\Delta_{\text{A}}s} - \Delta n_{\text{G}}\frac{\Delta_{\text{c}}H}{T} + R\left(n_{\text{G},2} \ln\frac{p_2}{p_0} - n_{\text{G},1} \ln\frac{p_1}{p_0}\right) \tag{10*}$$

Equation (10*) is a mere description of the system's entropy change in terms of entropy contents of all involved phases before and after the dosing. This treatment implies that the adsorbent is considered unperturbed; this assumption is maintained throughout this paper.

By means of

$$\Delta S = \frac{Q^{\text{rev}}}{T}$$

eqns. (5*) and (10*) may be combined to give an exact expression that replaces eqn. (11)

$$\overline{\Delta_{\text{A}}s} = \frac{\overline{\Delta_{\text{A}}e}}{T} + \Delta n_{\text{L}} \ln\frac{p_1}{p_0} - \frac{V_{\text{G}}}{T}(p_2 - p_1) + R\left(n_{\text{G},2} \ln\frac{p_2}{p_0} - n_{\text{G},1} \ln\frac{p_1}{p_0}\right) \tag{11*}$$

Continuous dosing mode

The expression for the net differential energy of adsorption remains, apart from a slightly different annotation, the same

$$\overline{\Delta_{\text{A}}e}(t) = \Delta_{\text{c}}E\left[\frac{-\dot{n}_{\text{L}}(t)g_{\text{A}}}{\dot{n}_{\text{A}}(t)g_{\text{E}}} - 1\right] + \frac{g_{\text{A}}}{\dot{n}_{\text{A}}(t)}\text{EMF}_{\Delta}(t) \tag{12}$$

To obtain more accurate expressions for the net differential entropy of adsorption we proceed essentially in the same way as earlier, however, basing ourselves now on the corrected equations for the discontinuous mode, viz. (5*) and (10*).

The reversible heat Q^{rev} of the discontinuous dosing mode can be expressed as a flow of reversible heat by taking the derivatives with respect to

time of both sides of eqn. (5*)

$$\frac{dQ^{rev}}{dt} = \dot{n}_A \overline{\Delta_A e} + \dot{n}_L RT \ln \frac{p}{p_0} - \dot{n}_G \Delta_c H - V_G \frac{dp}{dt}$$

or, using $\dot{n}_L + \dot{n}_G + \dot{n}_A = 0$

$$\dot{Q}^{rev} = \dot{n}_A \overline{\Delta_A e} - \dot{n}_A RT \ln \frac{p}{p_0} - \dot{n}_G \left(RT \ln \frac{p}{p_0} + \Delta_c H \right) - V_G \frac{dp}{dt} \tag{13*}$$

Equation (13*) is the dynamical equivalent of eqn. (5*) and replaces eqn. (13).

On the other hand, the entropy change of the system may be written in terms of the molar entropies of all involved phases. If this is done for two times t_2 and t_1, one obtains, on the basis of eqn. (10*)

$$S(t_2) - S(t_1) = n_A(t_2)[s_A(t_2) - s_L] - n_A(t_1)[s_A(t_1) - s_L]$$

$$- [n_G(t_2) - n_G(t_1)] \frac{\Delta_c H}{T}$$

$$- R \left[n_G(t_2) \ln \frac{p(t_2)}{p_0} - n_G(t_1) \ln \frac{p(t_1)}{p_0} \right] \tag{14*}$$

If one divides now by $(t_2 - t_1)$ and takes the limit for $t_2 \rightarrow t_1$ one obtains the entropy change per unit of time

$$\frac{dS}{dt} \equiv \lim_{t_2 \rightarrow t_1} \frac{S(t_2) - S(t_1)}{(t_2 - t_1)}$$

Straightforwardly it follows that

$$\frac{dS}{dt} = \dot{n}_A \overline{\Delta_A s} - \dot{n}_G \frac{\Delta_c H}{T} - R \frac{d}{dt} \left[n_G(t) \ln \frac{p(t)}{p_0} \right]$$

or

$$\frac{dS}{dt} = \dot{n}_A \overline{\Delta_A s} - \dot{n}_G \frac{\Delta_c H}{T} - R \dot{n}_G \ln \frac{p}{p_0} - R n_G \frac{1}{p} \frac{dp}{dt} \tag{15*}$$

Equation (15*) is the dynamical equivalent of eqn. (10*) and replaces eqn. (15).

Equations (13*) and (15*) will now be combined by the relation

$$\frac{dS}{dt} = \frac{\dot{Q}^{rev}}{T}$$

If this is done, considering that the last term in eqn. (15*) may be rewritten according to

$$R n_G \frac{1}{p} = \frac{V_G}{T}$$

one finally obtains

$$\overline{\Delta_A s} = \frac{\overline{\Delta_A e}}{T} - R \ln \frac{p}{p_0} \tag{16*}$$

Equation (16*) is a corrected form of eqn. (16). It is noted that the relation in no way is based on approximations in the derivation.

The equations that are of practical interest for the interpretation of experimental data are (2) and (11*) for the discontinuous and (12) and (16*) for the continuous dosing modes. All equations are exact within the limitations of the thermal model that has been assumed to describe an experiment that is performed according to the CCM.

The use of $\overline{\Delta_A s}$

The net differential entropy of adsorption provides the possibility of calculating the entropy difference between two absorbate phases

$$\int_{(1)}^{(2)} \overline{\Delta_A s}\, dn_A = \int_{(1)}^{(2)} \frac{\partial n_A (s_A - s_L)}{\partial n_A} \partial n_A = n_{A,2} s_A(2) - n_{A,1} s_A(1) \tag{17}$$

However, $\overline{\Delta_A s}$ does not relate the entropy content of the adsorbate phase directly to that of a different phase whether gaseous or liquid. This may be seen from eqns. (11*) and (16*) that are not defined for pressure p and p_1 equal to zero; not even the limit $\lim\limits_{p \to 0} \overline{\Delta_A s}$ exists. It is therefore impossible to apply eqn. (17) to the first dose of a discontinuous experiment or, in case of continuous dosing, to an interval comprising the bare adsorbent as one of the two states. This inconvenience originates from the fact that the reversible adsorption for the first dose cannot be performed by the fictitious reversible adsorption experiment described by Hill [4] and implied in the derivations of the previous [2] and present papers. Hill's experiment gives rise to a relation between the isothermal and differential heat of adsorption, q_{th} and q_d, respectively

$$q_d = q_{th} - RT - V_G \left(\frac{dn_A}{dp} \right)_{T,A,} \tag{18}$$

It would require for the first dose an infinitely large dead volume V_G for the pressure to be zero. Such an experiment is not feasible, so one must accept that calculation of reversible heat and the related change in entropy cannot be performed in this way. Besides it is clear that the fictitious experiment can only be performed in those pressure intervals where no hysteresis occurs.

In an interval where $\overline{\Delta_A s}$ is known, the entropy of all states of the adsorbate phase can be calculated with eqn. (17), if only one entropy value in the interval is known. Generally the CCM does not yield that information. However, in one particular case the single value wanted is available. In those adsorption systems where the adsorption process is reversible up to a

coverage where the difference between adsorbate and pure liquid phases has practically vanished, s_A equals s_L at the prevealing temperature. Then all s_A values may be calculated backwards. As a matter of fact the absence of hysteresis in the adsorption–desorption isotherm is a condition for this favourable situation to occur.

Molar entropy of the adsorbate phase

A single experiment according to the CCM provides sufficient information to calculate the entropy of the adsorbate phase in arbitrary cases. The equation to be used is that of Jura and Hill [5] which, expressed in the annotation of the present article, reads

$$n_A T(s_A - s_L) = [U(n_A) - U_0] + \phi A_s - n_A RT \ln\frac{p}{p_0} \tag{19}$$

where $U(n_A)$ and U_0 are the residual heat of immersion and heat of immersion, respectively, and ϕ stands for the two-dimensional pressure of the adsorbate. The residual heat of immersion is related to the differential net heat of adsorption by

$$U(n_A) = -\int_{n_A}^{\infty} \overline{\Delta_A e}\, dn_A' \tag{20}$$

(The minus sign stems from the convention to consider U as a positive quantity if the immersion process is exothermic.) ϕ is calculated by applying Gibb's relation (T constant)

$$d\phi = \frac{n_A}{A_s} RT d \ln p \tag{21}$$

or in integrated form

$$\phi(n_A) = \int_0^{n_A} n_A' \frac{RT}{p}\, dp \tag{22}$$

to the known adsorption isotherm. The calculation of the last term in eqn. (19) needs no further explanation.

Finally it may be noted that eqn. (16*) derived in the present paper is closely allied to eqn. (19) of Jura and Hill [5]. If the latter is differentiated with respect to n_A one obtains (T and A_s constant)

$$T\left(\frac{\partial n_A(s_A - s_L)}{\partial n_A}\right)_{T,A_s} = \overline{\Delta_A e} + A_s\left(\frac{\partial \phi}{\partial n_A}\right)_{T,A_s} - RT \ln\frac{p}{p_0}$$

$$- n_A RT \frac{1}{p}\left(\frac{\partial p}{\partial n_A}\right)_{T,A_s} \tag{23}$$

The second and fourth terms at the right-hand side of this expression are easily seen to cancel out because of Gibb's equation (21). The left-hand side

equals, by definition, $T\,\overline{\Delta_A s}$, so that the expression finally passes into eqn. (16*).

COMPARISON OF BASIC FEATURES OF TWO METHODS

According to the thermal model adopted in the CCM the (closed) system can exchange heat only through the measuring cells; so every heat exchange is known. Although this assumption is, of course, a simplification, it is justified by the thermal properties of the instrument. The model implies, since no change in the volume of the system occurs, that the total heat effect is a measure of the change in internal energy of the system.

The difference with the method of Rouquérol et al. [1] is best illustrated by considering eqn. (18), which is used in both cases. In the method of Rouquérol the reversible heat q_{th} is measured directly; the quasi-isothermal experiment that is performed for this purpose is, in fact, the fictitious experiment of Hill [4] that leads to eqn. (18), which is Hill's eqn. (28).

In the CCM, however, q_d is measured, or, more precisely, the difference between q_d and the (constant) $\Delta_c E$ is recorded. Subsequently, making use of the adsorption isotherm and taking into account instrumental properties, the reversible heat is derived from q_d by computation. The expressions for q_{th} in the CCM (see eqns. 5* and 13*) are less simple than eqn. (18), because the present instrument and the experimental procedure are more complex than Hill's fictitious experiment; as a matter of fact eqns. (5*) and (13*) contain eqn. (18).

The difference in approach between the method of Rouquérol and that of the present author leads to subtly distinct requirements for the realization of an adsorption experiment. If q_{th} is to be measured directly in the open system of Rouquérol et al. the adsorption process must proceed quasi-reversibly. If q_d is to be measured in the CCM, there is, from the point of view of heat measurement, no principal requirement for the adsorption process to be reversible, neither in the stepwise nor in the continuous dosing mode. However, there are some further practical requirements for the CCM. As mentioned before, the calorimetric measurement of the amount of adsorptive involved, requires a well-defined evaporation process; the only feasible way within the experimental set-up of the CCM seems to be an isothermal performance. This is true for both the stepwise and the continuous dosing mode. For the former there is no additional condition.

For the continuous dosing mode there is one further requirement. The computations of $\overline{\Delta_A e}$ and $\overline{\Delta_A s}$ are based on the equations derived for the discontinuous dosing mode, which assume an equilibrium situation at discrete times. Therefore it follows logically that at each point of time considered in the continuous dosing mode, equilibrium has to be assumed as well; this is the only way for the system to be in a well-defined, known state.
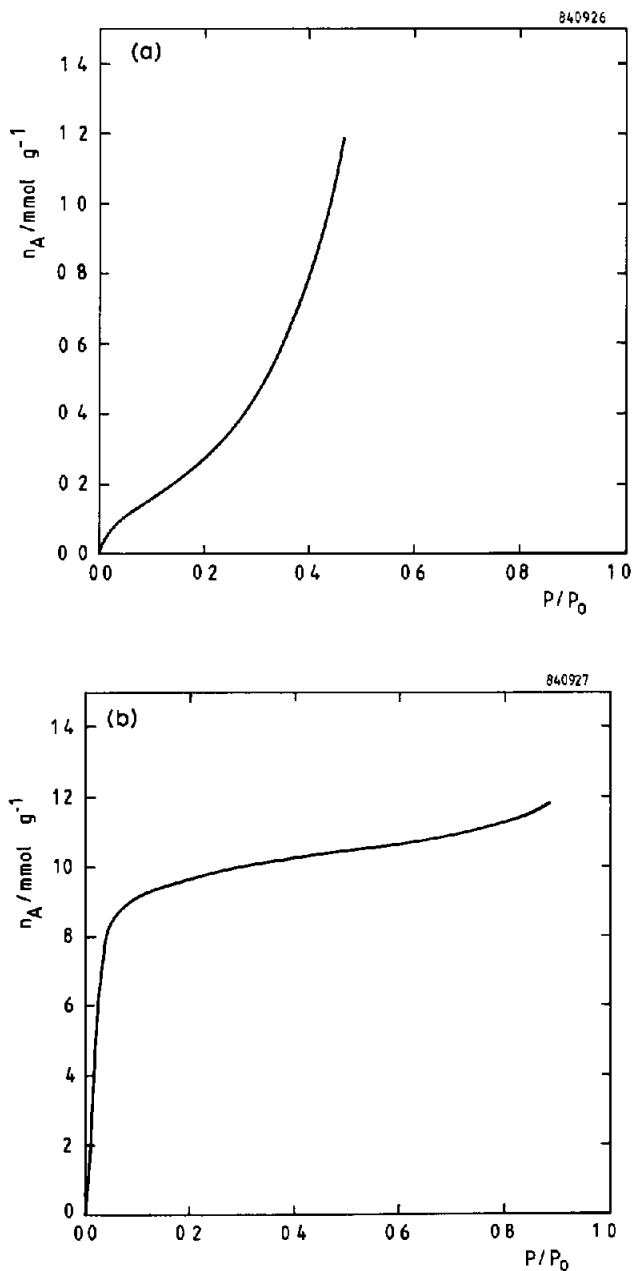
Fig. 2. (a) Initial part of the adsorption isotherm of water on a highly activated carbon at 25.00°C. (b) Adsorption isotherm of water on a synthetic zeolite at 25.10°C.

Therefore the system has to be in (quasi-)equilibrium all times during the adsorption process. Although this apparently implies that, as in the method of Rouquérol, the process has to proceed quasi-reversibly, the reasons are different.
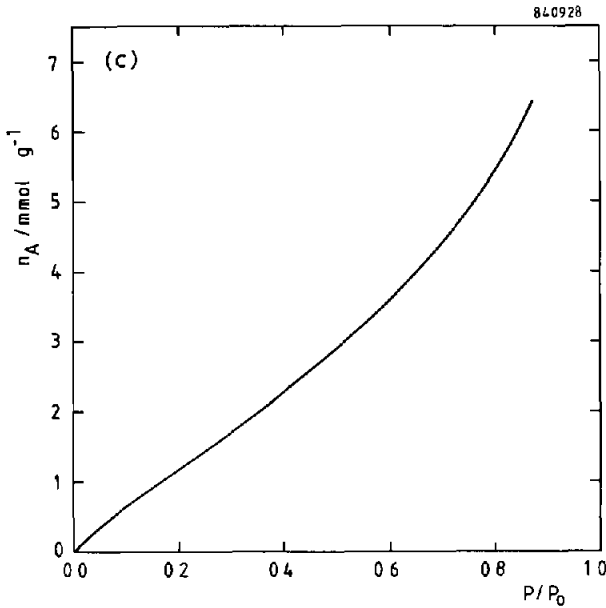
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Fig. 2. (c) Adsorption isotherm of benzene on a porous polymer at 25.25°C.

The quasi-reversible performance of an adsorption experiment according to the CCM allows the interpretation of the results according to the method of Rouquérol, as all three experimental parameters that are needed are known: reversible heat of adsorption, the amount of vapour added to the adsorption cell and the pressure above the adsorbent.

In order to compare the two different treatments of one set of experimental data obtained with the CCM, three adsorption experiments are considered: water/activated carbon, water/zeolite and benzene/porous polymer. The results were treated according to the method of Rouquérol et al. and on the basis of the normal interpretation of the CCM. The former method leads to (annotation of the present article)

$$\overline{\Delta_a H} = \frac{\dot{Q}_A + V_B \dfrac{\mathrm{d}p}{\mathrm{d}t}}{\dot{n}_A} \tag{24}$$

In this interpretation the choice from the possible definitions of the enthalpy of the adsorbed substance [6] has been

$$h_A = e_A + PV_A$$

If the volume work by the adsorbed phase ($V_a = 0$) is neglected the differential enthalpy of adsorption $\overline{\Delta_a H}$ may be written as

$$\overline{\Delta_A H} = \left\{ \frac{\partial n_A (h_A - h_G)}{\partial n_A} \right\}_{A_\vee, T} = \left\{ \frac{\partial n_A (e_A - h_G)}{\partial n_A} \right\}_{A_\vee, T}$$
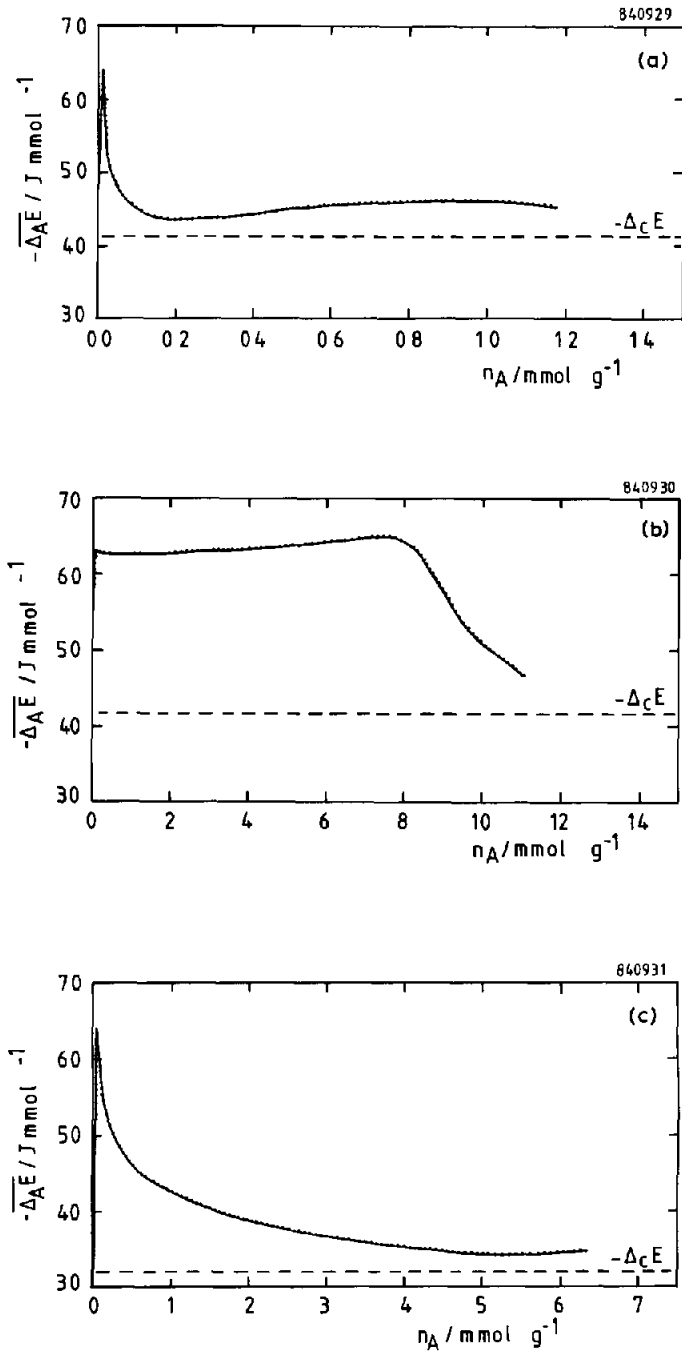
Fig. 3. Differential energy of adsorption obtained from the same experiments that led to the adsorption isotherms of Fig. 2. (———) Obtained from the interpretation of the experiment based on the thermal model adopted in the CCM. (●) Obtained from the interpretation of the experiment based on the thermal model of the method of Rouquérol. (a) Water/activated carbon, (b) water/synthetic zeolite, (c) benzene/porous polymer.

This leads straightforwardly to

$$\overline{\Delta_A E} = \overline{\Delta_A H} + RT \tag{25}$$

For the sake of completeness the adsorption isotherms of the three systems mentioned are shown in Fig. 2. Figure 3 shows the values for $\overline{\Delta_A E}$ obtained according to the present method (using $\overline{\Delta_A E} = \overline{\Delta_C E} + \overline{\Delta_A e}$) and according to the method of Rouquérol (using eqns. 24 and 25). No significant deviations are seen. This means that the two different thermal models of an adsorption experiment are practically equivalent for the present experimental set-up.

CONCLUSIONS

(1) The previously reported experimental method (CCM) to measure the net heat of adsorption, and also the computational procedure to derive from it the quantities $\overline{\Delta_A e}$ and $\overline{\Delta_A s}$, have been stated more precisely. Exact expressions have been derived for both $\overline{\Delta_A e}$ and $\overline{\Delta_A s}$.

(2) If the CCM is applied in the stepwise dosing mode the adsorption need not proceed isothermally but the evaporation process has to.

(3) If the CCM is applied in the continuous dosing mode, the entire system must be continuously in quasi-equilibrium; therefore, both evaporation and adsorption have to proceed quasi-reversibly.

(4) A comparison of the CCM in the continuous dosing mode with the method of Rouquérol et al. reveals that the reasons for the required reversible performance of the two adsorption experiments are different. However, the experimental similarity allows the results obtained with the CCM to be interpreted according to the other method. Final results for the differential energy of adsorption do not differ, indicating that the present experimental set-up corresponds to both thermal models.

(5) The application of Hill's equation (18) does not permit the differential entropy of adsorption to be calculated for the first dose of adsorptive on a bare adsorbent; continuous quasi-reversible dosing cannot circumvent this problem.

(6) A single adsorption experiment according to the CCM provides sufficient information to calculate both the energy and entropy content of the adsorbate phase if the pure liquid phase in equilibrium with its saturated vapour is taken as a reference.

LIST OF SYMBOLS

Symbol	Unit	Quantity
Instrumental		
g_A, g_E	W V^{-1}	thermopile sensitivity at adsorption and evaporation side
V_g	cm^3	dead volume above adsorbent
V_h	cm^3	part of the dead volume V_g within the adsorbent cell
Experimental		
Q_A, Q_E	J	heat effect caused by adsorption and evaporation
EMF$_\Delta$	V	EMF over the two thermopiles
A_Δ	V s	time-integrated EMF$_\Delta$
Q^{rev}	J	heat effect of reversible process
n_A, n_L, n_G	mmol	amounts of adsorbate and of liquid and gaseous adsorptive
q_d	J mmol^{-1}	differential heat of adsorption
q_{th}	J mmol^{-1}	isothermal heat of adsorption
U_0	J g^{-1}	heat of immersion
$U(n_A)$	J g^{-1}	residual heat of immersion
ϕ	N m^{-1}	two-dimensional pressure
A_s	m^2 g^{-1}	specific surface area
V_A	m^3 mmol^{-1}	volume of adsorbate phase
p	Pa	equilibrium pressure
P	Pa	hydrostatic pressure
Thermodynamic		
T	K	absolute temperature
R	J mol^{-1} K^{-1}	gas constant
e_L, e_G, e_A	J mmol^{-1}	molar internal energies of related phases

LIST OF SYMBOLS (continued)

Symbol	Unit	Quantity
s_L, s_G, s_A	J mmol^{-1} K^{-1}	molar entropies of related phases
h_L, h_G, h_A	J mmol^{-1}	molar enthalpies of related phases
$\Delta_c E$, $\Delta_c H$	J mmol^{-1}	energy, enthalpy of condensation
$\overline{\Delta_A E}$	J mmol^{-1}	differential energy of adsorption $(= [\partial n_A(e_A - e_g)/\partial n_A]_{T,A})$
$\overline{\Delta_A H}$	J mmol^{-1}	differential enthalpy of adsorption
$\overline{\Delta_A e}$	J mmol^{-1}	net differential energy of adsorption $(= [\partial n_A(e_A - e_L)/\partial n_A]_{T,A})$
$\overline{\Delta_A s}$	J mmol^{-1} K^{-1}	net differential entropy of adsorption $(= [\partial n_A(s_A - s_L)/\partial n_A]_{T,A})$

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