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A METHOD TO MEASURE THE NET HEAT OF ADSORPTION AND THE ADSORPTION ISOTHERM SIMULTANEOUSLY

J.J.G.M. VAN BOKHOVEN

Prins Maurits Laboratorium TNO, P.O. Box 45, 2280 AA Rijswijk ZH (The Netherlands)

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ABSTRACT

A new method is described to measure net differential heats of adsorption; it is applied to the adsorption of water vapour on active carbon and synthetic zeolite samples. The method seems equally appropriate for many other systems. By compensating the heat of adsorption instrumentally with the heat of condensation during an adsorption process, it is possible to measure directly the net differential heat of adsorption.

Amounts adsorbed are also measured calorimetrically, while the pressure is registered simultaneously. The method may be operated in either a stepwise or a continuous dosing mode. A procedure is given to derive from the experimental data (adsorption isotherm and differential heat of adsorption) the differential entropy and energy of adsorption.

LIST OF SYMBOLS

Intrumental	g_A, g_E	($W V^{-1}$)	Thermopile sensitivity at adsorption and evaporation side, respectively
Experimental	Q_A, Q_E	(J)	Heat effect caused by adsorption or evaporation
	EMF_E	(V)	Thermo E.M.F. at the evaporation side (+)
	EMF_A	(V)	Thermo E.M.F. at the adsorption side (—)
	EMF_Δ	(V)	$EMF_E + EMF_A$
	n_A	(mmole)	Total amount adsorbed
	Δn_A	(mmole)	Amount adsorbed during one dose (+)
	Δn_E	(mmole)	Amount evaporated during one dose (+)
	$\dot{n}_A$	(mmole sec^{-1})	Rate of adsorption (+)
	$\dot{n}_E$	(mmole sec^{-1})	Rate of desorption (+)
	A_Δ	(Vs)	EMF_Δ integrated over time interval 0—*t*
	q_d	(J $mmole^{-1}$)	Differential heat of adsorption (generally +)

	q_{th}	(J mmole^{-1})	Isothermal heat of adsorption (generally +)
Thermo-dynamic	T	(K)	Absolute temperature
	R	(J mole^{-1} K^{-1})	Gas constant
	Σ	(m^2 g^{-1})	Specific surface area
	e_G	(J mmole^{-1})	Molar internal energy of gaseous phase
	e_A	(J mmole^{-1})	Molar internal energy of adsorbed phase
	e_L	(J mmole^{-1})	Molar internal energy of liquid phase
	s_G	(J mmole^{-1} K^{-1})	Molar entropy of gaseous phase
	s_A	(J mmole^{-1} K^{-1})	Molar entropy of adsorbed phase
	s_L	(J mmole^{-1} K^{-1})	Molar entropy of liquid phase
	$\Delta_c E$	(J mmole^{-1})	Energy of condensation
	$\Delta_c H$	(J mmole^{-1})	Enthalpy of condensation
	$\overline{\Delta_A E}$	(J mmole^{-1})	Differential energy of adsorption $= \left\{\frac{\partial n_A(e_A - e_G)}{\partial n_A}\right\}_{T,\Sigma}$
	$\overline{\Delta_A e}$	(J mmole^{-1})	Net differential energy of adsorption $= \left\{\frac{\partial n_A(e_A - e_L)}{\partial n_A}\right\}_{T,\Sigma}$
	$\overline{\Delta_A S}$	(J mmole^{-1} K^{-1})	Differential entropy of adsorption $= \left\{\frac{\partial n_A(s_A - s_G)}{\partial n_A}\right\}_{T,\Sigma}$
	$\overline{\Delta_A s}$	(J mmole^{-1} K^{-1})	Net differential entropy of adsorption $= \left\{\frac{\partial n_A(s_A - s_L)}{\partial n_A}\right\}_{T,\Sigma}$

INTRODUCTION

Adsorbents which are used to purify contaminated atmospheric air must primarily possess adsorptive properties towards the gaseous components to be removed. The atmospheric humidity dictates a second requirement that is related to the water vapour affinity of the adsorbent: the more hydrophilic the material is, the stronger water adsorption may hinder the adsorption of the gases one wishes to remove. This explains why the hydrophobic adsorbent active carbon is often an appropriate material in air purification. Application of active carbon in gas masks for protection against chemical warfare agents requires the carbon to be impregnated with inorganic salts to obtain sufficient protective capacity against a few specific agents [1]. However, these impregnates introduce a certain degree of hydrophilicity in the adsorbent. In our laboratory this increase of the carbon's water sensitivity is the subject of investigations that are presently taking place. In particular, we are studying whether, and if so how, the water sensitivity may be limited by adapting the impregnation procedure.

In order to have a complete description of the thermodynamic equilibrium conditions of the water vapour adsorption we designed a calorimetric equipment and an experimental method to measure both the adsorption isotherm and the differential heat of adsorption curve in a single experiment. The temperature range of interest is ~0—45°C. The adsorption heats of water on carbonaceous materials often do not differ much from the heat of evaporation in either a positive or negative sense [2], so only very accurate methods may provide information on the sign and value of the adsorption heat. The availability of a home-constructed heat flow calorimeter equipped with four identical cells enabled us to devise a method in which the difference between the heats of adsorption and condensation is measured directly.

Compared to a method where the heat of adsorption is measured and diminished with the heat of condensation, the direct measurement of the net heat of adsorption may be an order of magnitude more accurate, at least for water—carbon systems. Apparently the method bears a resemblance to the measurement of heat of immersion. In this new method, however, both the adsorption isotherm and the differential heat of adsorption curve are entirely measured during a single experiment. Moreover, the amounts of adsorbed species are derived from heat measurement.

This paper describes the instrumental and experimental aspects of the method; it is less concise than a short former description [3]. It also pays attention to the calculation procedures that allow the derivation of the energy of adsorption and differential entropy of adsorption from the experimental data.

EXPERIMENTAL

Principle of the condensation compensation method for direct measurement of net heat of adsorption

Figure 1 illustrates the principle of the method. Two identical thermopiles, acting as heat flow meters, are connected in series in electrically equal direction. The cold junctions of both piles are in thermal contact with the heat sink of the calorimeter, which is at constant temperature. One cell contains the evaporation vessel (E) which is filled with liquid adsorbate. Vapour may flow to the adsorption vessel (A) via a valve (V).

Before an experiment air is removed from the entire system. In a situation of thermal equilibrium a small amount of vapour is dosed to the adsorbent by opening valve V for a short period. Two processes now occur largely simultaneously: vapour adsorbs on the adsorbent, causing a heat flow $\dot{Q}_A$ and water evaporates from the liquid in vessel V, giving rise to a heat flow $\dot{Q}_E$. These two oppositely directed heat flows evoke in the two equally

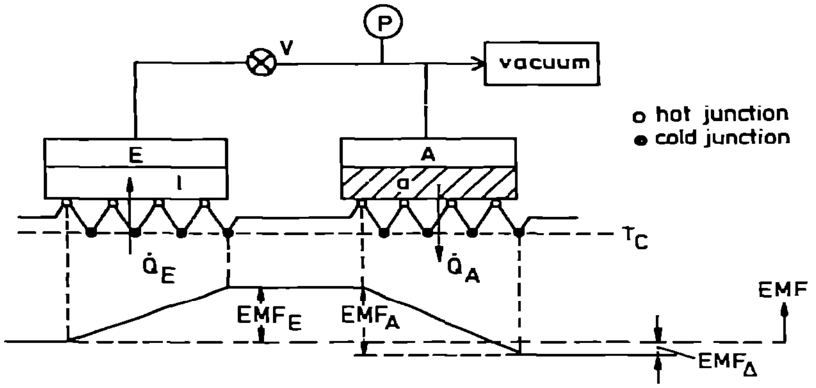


Fig. 1. Principle of the condensation compensation method. T_C, constant temperature of the calorimeter heat sink; E, evaporation vessel; A, adsorption vessel; l, liquid phase adsorbate; a, adsorbed phase adsorbate; $\dot{Q}_E$, heat flow due to evaporation heat effect; $\dot{Q}_A$, heat flow due to adsorption heat effect; V, needle valve; P, pressure gauge; EMF, thermo E.M.F. in the thermocouple wire.

directed thermopiles opposite E.M.F.'s: EMF_E and EMF_A. The net value that results is defined as EMF_Δ. In the compensation method both EMF_E and EMF_Δ are measured. Integration of EMF_E over the entire time of the signal is an exact measure for the amount of evaporated water. Similar integration of EMF_Δ is a direct measure for the difference between energy of adsorption and energy of evaporation. Its precise meaning will be made clear in a following section; there it will also be shown that proper corrections may be made for the difference in sensitivity of both cells and for the difference in the amounts evaporated and adsorbed. In a well designed apparatus these corrections are very small and are accurately known.

When equilibrium is re-established after a vapour dose, pressure may be read from gauge P. The amount adsorbed already being known, one thus finds a point of the adsorption isotherm. Repeating the dosing procedure, one gradually learns the differential heat of adsorption curve and the adsorption isotherm.

In heat flow calorimetry it is general practice to apply a reference cell to compensate for the spurious heat flows through the thermopiles due to uncontrolled temperature variations. Although perfect symmetry is unattainable, zero line fluctuations may be reduced by a factor 50 [4]. As in the present case two cells are required for the measurement of the desired signal (EMF_Δ), two reference cells are needed to compensate for spurious heat flows: one filled with water and the other with the adsorbent (see Fig. 2). Apparently the four cells have to be coupled electrically two by two in opposite sense. Figure 2 also shows that it is possible to make simultaneously separate zero line reference for the evaporation signal.

Apparatus and procedure

The calorimeter used for the present purpose is of the heat flow type and operates as the instrument described previously [4]. A few minor modifica-

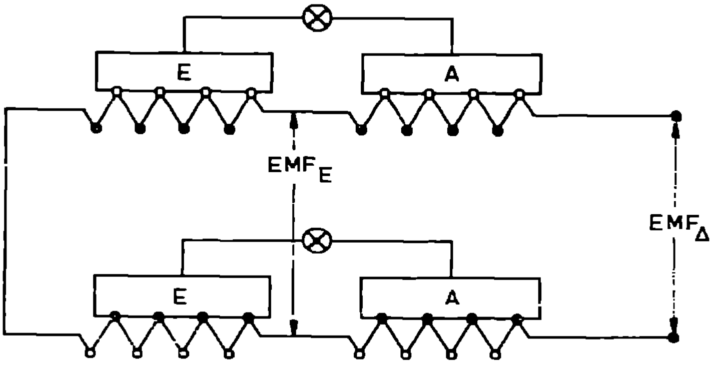
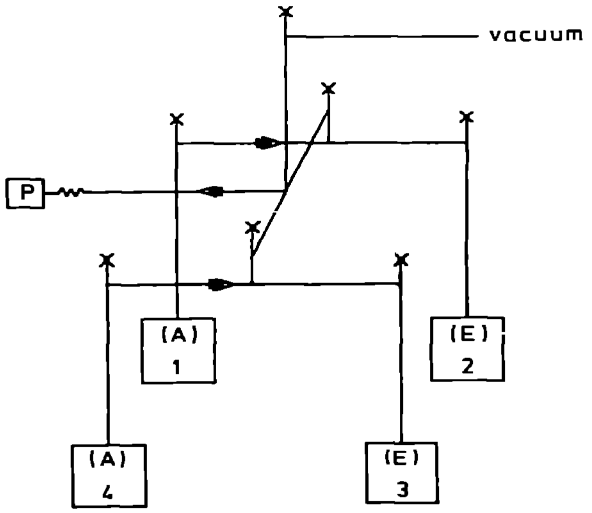


Fig. 2. Electric compensation method to rule out the effect of uncontrolled temperature fluctuations both in the evaporation (EMF$_E$) and the difference signal (EMF$_\Delta$); E and A are as in Fig. 1.

tions related to the thermostatting of the central part have been brought about. The only change relevant to the present subject is the number of measuring cells which has been extended from two to four. As follows from the principle of the compensation method, all four cells are needed in an experiment.

The four vessels are connected by glass tubes for vapour transport and evacuation, as shown in Fig. 3. During an experiment the pressure gauge is connected to the pair of vessels in use; meanwhile there is a static vacuum in the other pair of vessels. All valves in Fig. 3 are of the type shown in Fig.



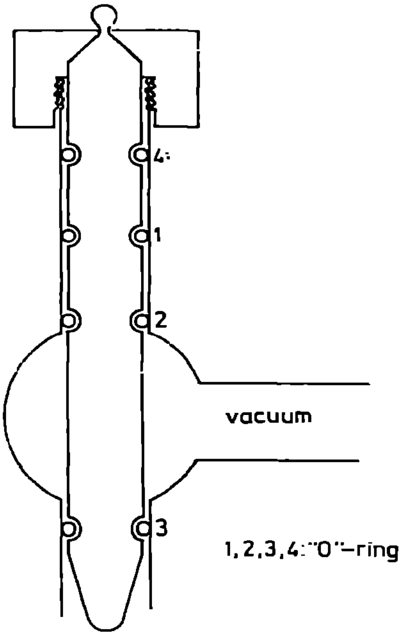


Fig. 3. Scheme of the dosing system; the system contains 3 "O" ring couplings.

Fig. 4. Construction of the vacuum valves as used in the dosing system shown in Fig. 3.

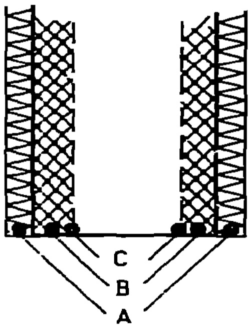


Fig. 5. Schematic cross-section of a measuring cell; A, thermopile; B, adsorbent; C, inert metal support.

4. The space between rings 1 and 2 may be evacuated by bringing the plunger to a sufficiently low position for a few seconds, so that connection is made with the dynamic vacuum. This offers the advantage that during an experiment the internal static vacuum is bordered by another vacuum space. Vacuum is obtained from a combined rotary-mercury diffusion pumping system provided with a liquid nitrogen trap. Leakage into the dead volume (68 cm^3) above the adsorbent is 6.9×10^{-2} Torr/24 h. The pressure gauge is a capacitance type instrument of Datametrics, type 1018, with a Barocel sensor applicable for pressure differences of 0—100 Torr. Both the pressure and the evaporation signal and the difference signal are registered on punch tape for easy data handling.

In a normal experiment the adsorbent is piled up against the cylindrical wall of the vessel as shown in Fig. 5. The material is held in place by a cylindrically shaped, very thin, perforated piece of inert metal. In order to have an equally large thermal contact between the liquid water and the vessel wall in the evaporation vessel, filter paper, wetted thoroughly with the liquid adsorbate, was shaped against the wall and supported in the same way as the adsorbent.

Calibration

The sensitivity of the thermopiles, expressed in W/V, is dependent on the contents of the vessels. If for the calibration a heat flow is established by the Joule effect in a resistor, one finds for the sensitivity a value of about 18.5 W V^{-1}; if one takes the heat consumed by evaporation of a certain amount of liquid (water or benzene) one finds a value of about 17.5 W V^{-1}. Also, the rearrangement of the heat source within the cell may influence the sensitivity to an extent that is non-negligible for accurate measurements. For this reason calibration was performed while the liquid (or adsorbent) was arranged exactly as in a proper experiment. Moreover, the heat was produced by evaporation or adsorption according to the function of the cell. Water was evaporated by connecting the vessel to vacuum; the rate of evaporation was chosen about equal to the rate during an experiment. The measured heat represents, therefore, the change in internal energy of the amount evaporated (see further). The amount evaporated is known from the loss of weight. At the adsorption side a similar procedure was applied; adsorption was carried out in a coverage interval where the adsorption energy ($\Delta_A E$) was constant.

The situation here was more complicated, because a very precise value for the energy of adsorption for any adsorbate—carbon system was lacking. This difficulty was circumvented by the following procedure. With the experimental and calculational methods described in the following sections, values for $\Delta_A E$ for the system water—active carbon were determined using estimations for g_A obtained from electrical calibrations. The order of magnitude of the deviation in g_A being known, the deviation in $\Delta_A E$ was calculated to be only about ±0.06 J mmole^{-1}; this means that the deviation in $\Delta_A E$ is only about 0.5%. Therefore, g_A may now be determined within 0.5% deviation. Further iterative calculation may deliver better values; it is, however, hardly relevant.

The values established for the different cells are: for adsorption cells 1 and 4, 16.64 ± 0.12 and 16.27 ± 0.10 W V^{-1}, respectively; for evaporation cells 2 and 3, 16.16 ± 0.16 and 17.11 ± 0.44 W V^{-1}, respectively. It was verified by means of electrically developed heat flows that the sensitivity did not change if water vapour pressure varied from 0.5 to 24 Torr. Below 0.5 Torr there was a gradual increase to ~20 W/V at $P \leqslant 10^{-5}$ Torr.

Stepwise dosing

In the way described above a series of doses is admitted to the adsorbent. The number of doses depends on the accuracy required, resolution and, of course, duration.

Continuous dosing

Water vapour may be dosed continuously at a low rate by appropriately adjusting valve V; to this end the valves on the tops of vessels 2 and 3 (see Fig. 3) were adapted. This dosing method has the same advantages as the dosing at constant rate described by Berezin et al. [5] and also used by Rouquérol [6]; for the water—carbon system it is particularly favourable because of the strong hysteresis in the adsorption isotherm.

Certain requirements have to be met, however, for the method to be applied successfully: (i) dosing rate has to be small enough in order to have a quasi-equilibrium situation which is pertinent both to the isotherm and differential heat curve; (ii) at this necessarily low rate, the heat flow signals of evaporation and of the net heat of adsorption must be still strong enough to be measured with sufficient accuracy.

THERMODYNAMIC CONSIDERATIONS

This section shows how information on the thermodynamic state of the adsorbed phase is derived from the experimental data. The thermodyamic

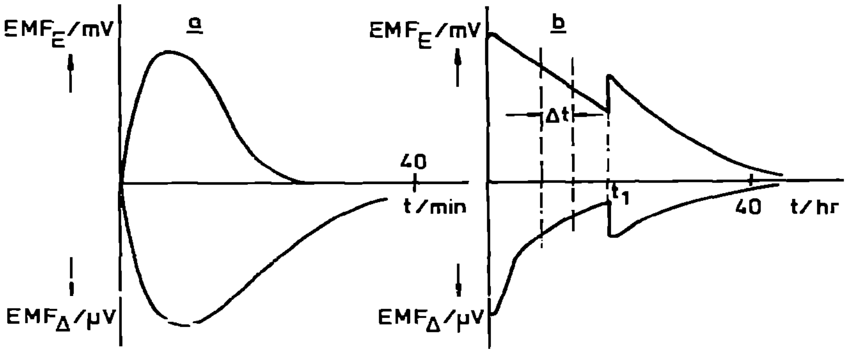


Fig. 6. Time dependence of the heat flow signals if water is adsorbed dose-wise (a) or continuously (b). At time t_1 in (b) the rate of adsorption is increased by adjusting a needle valve.

system to be considered consists of the material in the two vessels and in the connecting gas line; sometimes the system is divided into two subsystems. It will be assumed that there is only heat exchange with the surroundings via the heat flow meters (this assumption will be made plausible in one of the following sections).

Figure 6 shows schematically the heat flow signals obtained from a single dose in the stepwise dosing technique (a) and from the entire experiment in the continuous dosing technique (b). Scales along the axes indicate the orders of magnitude of the observed parameters. From Fig. 6(a) it may be seen that, although the process of evaporation is faster than that of adsorption, the larger part of heat of adsorption is registered simultaneously with the heat of evaporation. In the continuous dosing method the compensation is even better, because of two combined reasons: (i) the rates of adsorption and evaporation at a given time are nearly equal; (ii) the changes in rate for the two processes are so slow, that except for times where the needle valve V is adjusted (e.g. at times 0 and t_1), the thermal inertia of the instrument mat be neglected.

Stepwise dosing

The total heat of evaporation is related to the function EMF$_E$ from Fig. 6(a) according to

$$Q_E = \int_0^\infty \mathrm{EMF}_E \times g_E \, dt \qquad \text{(unit : J)}$$

As no work is performed, Q_E represents the change in internal energy. A similar expression holds for the total heat of adsorption (Q_A). If the dose of adsorbate is small enough, the quotient $(-Q_A)/\Delta n_A$ is a good measure of the differential heat of adsorption (q_d) which is defined as [7]

$$q_d = e_G - e_A - n_A\left(\frac{\partial e_A}{\partial n_A}\right)_{\Sigma,T}$$

where e_G and e_A are the molar internal energies of the gaseous and adsorbed phase, respectively and Σ is the specific surface area of the adsorbent. (Note that q_d has the opposite sign of what is normal for heat transfer to or from a thermodynamic system.) The integrated net voltage

$$A_\Delta = \int_0^\infty \mathrm{EMF}_\Delta \, \mathrm{d}t$$

may be equated to

$$A_\Delta = \frac{Q_E}{g_E} + \frac{Q_A}{g_A}$$

(From the definition of the thermodynamic system it is clear that Q_A is negative and Q_E positive; A_Δ is generally negative.) When Q_E and Q_A are written as the changes of internal energies, it follows that

$$A_\Delta = \frac{(e_G - e_L)\,\Delta n_E}{g_E} + \frac{\{e_A - e_G + n_A(\partial e_A/\partial n_A)_{\Sigma,T}\}\,\Delta n_A}{g_A} \tag{1}$$

It is practical to proceed now using differential instead of integral quantities, because in the experiments the relation between different states of adsorption is measured. The differential energy of adsorption is defined as

$$\overline{\Delta_A E} \equiv \left\{\frac{\partial n_A(e_A - e_G)}{\partial n_A}\right\}_{T,\Sigma} = e_A - e_G + n_A\left(\frac{\partial e_A}{\partial n_A}\right)_{T,\Sigma}$$

As in the presently applied method, net differential heats of adsorption are involved, it is more appropriate to use the net differential energy of adsorption $(\overline{\Delta_A e})$, and then the mere condensation component in the energy of adsorption is precluded

$$\overline{\Delta_A e} = \left\{\frac{\partial n_A(e_A - e_L)}{\partial n_A}\right\}_{T,\Sigma}$$

or

$$\overline{\Delta_A e} = e_A - e_L + n_A\left(\frac{\partial e_A}{\partial n_A}\right)_{T,\Sigma}$$

If this equality is substituted into eqn. (1), it follows that

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

The second term of the right member corrects for the difference between the sensitivities of the thermopiles and for the difference in amounts adsorbed and evaporated. In ideal cases the term vanishes, apparently.

By simulating an isothermal reversible process having an identical initial and final state, Hill [7] related the differential heat of adsorption to the isothermal heat of adsorption

$$q_{th} = q_d + RT + V/(\partial n_A/\partial P)_T \tag{3}$$

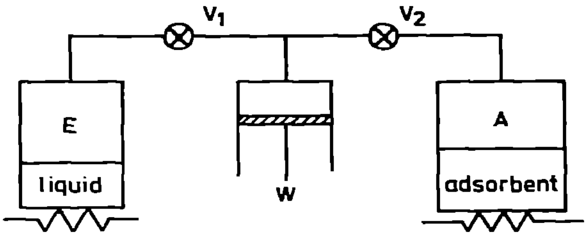


Fig. 7. Fictitious apparatus to transfer reversibly an amount of water from the liquid phase in E to the adsorbed phase in A; V_1 and V_2 are valves, W is an auxiliary volume that may be varied by means of a piston.

Via the relation $\Delta S = -q_{th}/T$ the entropy change in the entire system becomes known. From a similarly simulated somewhat more complex process an equation that is analogous to eqn. (3) may be derived for the entire thermodynamic system presently under consideration (see Fig. 7).

Transport of an amount of liquid to the adsorbent is thought to take place in three stages: (i) with valves V_1 open and V_2 closed an amount of Δn_E mmoles water is evaporated by changing the auxiliary volume W from zero to the required value; $-\Delta n_E \times \Delta_c H$ J are taken up by the system; (ii) with both valves closed, the volume W is expanded until the pressure is equal to the equilibrium pressure P_1 in the adsorbent vessel; $-\Delta n_E RT \ln(P_1/P_0)$ J are taken by the system; (iii) with valves V_1 closed and V_2 open, the auxiliary volume is brought back to zero, giving rise to an adsorption of Δn_A mmoles and to an equilibrium pressure of P_2. As the relation between the differential and reversible heat of adsorption is given by eqn. (3), the system loses an amount of heat during the adsorption stage, that follows from integration

$$Q_A^{rev} = \int_{(P_1)}^{(P_2)} - \{q_d + RT + V/(\partial n_A/\partial P)_{T,\Sigma}\} \, dn_A$$

Because $(\partial n_A/\partial p)_{T,\Sigma}$ is known (being the derivative of the adsorption isotherm), Q_A^{rev} may be easily computed. Summing up the contributions of the three subsequent stages one finds

$$Q^{rev} = -\Delta n_E\left(\Delta_c H + RT \ln\frac{P_1}{P_0}\right) - \Delta n_A\left(q_d + RT\frac{P_2}{P_2 - P_1}\ln\frac{P_2}{P_1}\right) \tag{4}$$

or, equating Δn_E and Δn_A

$$q^{rev} = -\Delta_c H - q_d + RT\left(\ln\frac{P_1}{P_0} - \frac{P_2}{P_2 - P_1}\ln\frac{P_2}{P_1}\right) \tag{5}$$

As already pointed out by Hill the entropy change found by means of eqn. (3) is of limited interest; $-q_{th}/T$ does not give information on the absolute entropy content of the adsorbed phase. This is understood from the fact that eqn. (5) cannot be applied to the first dose of vapour, as P_1 would then be zero; so entropy changes in the adsorbed phase that occur during the second or later doses are relative to the (unknown) value prevailing after the first dose. The relation can be simply established by summing up the entropy contributions of all three phases (liquid, gaseous, adsorbate) before and after a dose. The resulting equation is

$$s_A(P_{i+1}) = \left\{\frac{Q^{\text{rev}}}{T} - B + n_{A,i}s_A(P_i)\right\}\frac{1}{n_{A,i+1}} \tag{6}$$

where $s_A(P_i)$ is the average molar entropy of the adsorbed phase, when it is in equilibrium with gas of pressure P_i, $n_{A,i}$ is the total number of mmoles after dose no. i and B is a function of known quantities of the liquid and gaseous phases

$$B = \Delta n_E s_L + (n_{G,i+1} - n_{G,i})\frac{\Delta_E H}{T} + n_{G,i+1}R\ln\frac{P_0}{P_{i+1}} - n_{G,i}R\ln\frac{P_0}{P_i}$$

where s_L is the molar entropy of the liquid phase and $n_{G,i}$ and $n_{G,i+1}$ represent the numbers of gaseous mmoles in the dead volume before and after dosing, respectively. Equation (6) contains two unknown parameters $s_A(P_i)$ and $s_A(P_{i+1})$. The equations may be extended to a set of n equations with $n + 1$ parameters, which is, of course, of no use. Although, therefore, no values for the adsorption entropy can be calculated, it is possible to compute the net differential entropy of adsorption ($\overline{\Delta_A s}$) which is defined analogously to the net differential energy of adsorption

$$\overline{\Delta_A s} \equiv \left\{\frac{\partial n_A(s_A - s_L)}{\partial n_A}\right\}_{T,\Sigma}$$

or

$$\overline{\Delta_A s} = \left\{\frac{\partial n_A s_A}{\partial n_A}\right\}_{T,\Sigma} - s_L \tag{7}$$

The system entropy change by the transfer of an amount of water from the liquid to the adsorbed phase may be expressed as a function of the total amounts in the various phases before and after transfer

$$\Delta S = -\Delta n_E s_L - (n_{G,2} - n_{G,1})\left(\frac{\Delta_c H}{T} - s_L\right) + n_{G,2}R\ln\frac{P_0}{P_2} - n_{G,1}R\ln\frac{P_0}{P_1} + n_{A,2}s_A(P_2) - n_{A,1}s_A(P_1) \tag{8}$$

If the dose is small enough, the last two terms of the right member may be rewritten as

$$n_{A,2}s_A(P_2) - n_{A,1}s_A(P_1) = \left(\frac{\partial n_A s_A}{\partial n_A}\right)_{T,\Sigma}\Delta n_A \tag{9}$$

If the difference between Δn_A and Δn_E is neglected, eqns. (7), (8) and (9) may be combined to

$$\Delta S = (n_{G,2} - n_{G,1})\left(s_L - \frac{\Delta_c H}{T}\right) + R\ln P_0(n_{G,1}\ln P_1 - n_{G,2}\ln P_2) + \overline{\Delta_A s}\,\Delta n_A \tag{10}$$

The entropy difference is also equal to Q^{rev}/T, which is known from eqn. (4); this leads to an expression for the net differential entropy of adsorption

$$\overline{\Delta_{\text{A}}s} = -\frac{\Delta_{\text{c}}H + q_{\text{d}}}{T} - R\left(\ln\frac{P_1}{P_0} + \frac{P_2}{P_2 - P_1}\ln\frac{P_2}{P_1}\right) + (n_{\text{G},2} - n_{\text{G},1})\left(s_{\text{L}} - \frac{\Delta_{\text{c}}H}{T}\right)\frac{1}{\Delta n_{\text{A}}}$$

$$+ R\ln P_0(n_{\text{G},2}\ln P_2 - n_{\text{G},1}\ln P_1)\frac{1}{\Delta n_{\text{A}}} \tag{11}$$

Continuous dosing

Equation (2) may be adapted to the continuous dosing procedure as follows. For each time interval Δt in the curves of Fig. 6(b) a consistent set of values for A_{Δ}, Δn_{A}, Δn_{E} in eqn. (2) may be derived by integrating the appropriate quantities over time and by making pressure correction. If now both members of eqn. (2) are divided by Δt and if the limit is taken for $\Delta t \to 0$ one obtains

$$\lim_{\Delta t \to 0} \frac{n_{\text{A}}(t + \Delta t) - n_{\text{A}}(t)}{\Delta t}\overline{\Delta_{\text{A}}e}(t) =$$

$$\lim_{\Delta t \to 0}\left[\frac{A_{\Delta}(t + \Delta t)}{\Delta t}g_{\text{A}} + \Delta_{\text{c}}E\left\{\frac{n_{\text{E}}(t + \Delta t) - n_{\text{E}}(t)}{\Delta t}\frac{g_{\text{A}}}{g_{\text{E}}} - \frac{n_{\text{A}}(t + \Delta t) - n_{\text{A}}(t)}{\Delta t}\right\}\right]$$

or

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

It follows from definition that

$$q_{\text{d}}(t) = -(\Delta_{\text{c}}E + \overline{\Delta_{\text{A}}e}(t))$$

In a similar way eqn. (4) for the heat exchange of the fictitious reversible process may be adapted to the continuous dosing procedure

$$\dot{Q}^{\text{rev}} = \dot{n}_{\text{E}}\left(-\Delta_{\text{c}}H + RT\ln\frac{P}{P_0}\right) - \dot{n}_{\text{A}}(RT + q_{\text{d}}) \tag{13}$$

Finally, eqn. (10) must be "dynamized"; to this end it is written as

$$S(t_2) - S(t_1) = \{n_{\text{G}}(t_2) - n_{\text{G}}(t_1)\}\left(s_{\text{L}} - \frac{\Delta_{\text{c}}H}{T}\right) + R\{n_{\text{G}}(t_2) - n_{\text{G}}(t_1)\}\ln P_0 +$$

$$-R\{n_{\text{G}}(t_2)\ln P(t_2) - n_{\text{G}}(t_1)\ln P(t_1)\} + \Delta_{\text{A}}s\{n_{\text{A}}(t_2) - n_{\text{A}}(t_1)\} \tag{14}$$

Now both members are divided by Δt and the limits are taken for $\Delta t \to 0$. The left member then is equal to $\text{d}S/\text{d}t = \dot{Q}^{\text{rev}}/T$. Equation (14) transforms into

$$\frac{\dot{Q}_{\text{rev}}}{T} = \dot{n}_{\text{G}}\left(s_{\text{L}} - \frac{\Delta_{\text{c}}H}{T}\right) + R\,\dot{n}_{\text{G}}\ln\frac{P_0}{P} - R\frac{n_{\text{G}}}{P}\dot{P} + \Delta_{\text{A}}s\dot{n}_{\text{A}} \tag{15}$$

Combination of eqns. (13) and (15) leads to

$$\dot{n}_A \Delta_A \overline{s} = \frac{\dot{n}_E\left(-\Delta_c H + RT \ln \frac{P}{P_0}\right) - n_A(RT + q_d)}{T} - \dot{n}_G\left(s_L - \frac{\Delta_c H}{T}\right) +$$

$$-R\left(\dot{n}_G \ln \frac{P_0}{P} - \frac{n_G}{P}\dot{P}\right)$$

The difference between $\dot{n}_A$ and $\dot{n}_E$ as well as the terms in n_G appear practically to be negligible. Finally the dynamical equivalent of eqn. (11) becomes

$$\overline{\Delta_A s} = \frac{\Delta_A e}{T} + R \ln \frac{P}{P_0} \qquad (16)$$

The kinetic energy of the vapour flow

Throughout the preceding sections it was assumed that the only kind of energy involved was the internal energy of the various phases; in principle there might be an influence from transformation of internal energy into the kinetic energy of the flowing vapour and vice versa. In fact, as will be shown now, this influence is negligible.

To this end we consider the filling of an evacuated container by gas through a pipe line that is connected to a vapour source. The mean free path of the molecules is assumed to be short with regard to the dimensions of container and pipe line. If now the gas is allowed to flow to the container, the kinetic energy of the flowing gas may be expressed as a function of cross-section of the tube B(m^2), pressure P (Torr) and mass rate b (mmole sec^{-1})

$$E_{kin} = 2.61 \times 10^{-9} \left(\frac{\dot{b}}{P \times B}\right)^2$$

At slow flow rates the heat exchange with the wall is fast enough to maintain constant temperature; it is assumed that this is the case. The kinetic energy that the molecules have beside their internal energy is dependent upon the dimensions of the tube, the pressure and the flow rate. If the appropriate quantities for an adsorption vessel are filled into eqn. (18) viz. $b \simeq 10^{-4}$ mmole sec^{-1}, $S \simeq 10^{-4}$ m^2 and $P = 0.5$ Torr, then $E_{kin} \simeq 10^{-8}$ J mmole^{-1}. In order to have an experimental check we carried out a few expansions. With no adsorbent and liquid in vessels 3 and 4, we admitted air into vessel 3 up to a pressure of about 10 Torr. We then had the air expanded into vessel 4. The time in which pressure equilibrium was reached amounted to a few seconds giving rise to a mass flow that does not exceed 10^{-1} to 10^{-2} mmole sec^{-1}. (The experiment could not be performed at a mass flow as low as during a water adsorption experiment, because heat flow would then not be measurable.)

In a situation of steady state flow the values of 10^{-1} to 10^{-2} mmole sec^{-1} would give rise to a kinetic energy of the order of 1 to 10^{-2} J mmole^{-1}. In fact the average of the measured kinetic energy of air is between 1 and 5 J mmole^{-1}. Although the concurrence is not perfect, the conclusion seems justified, that at the actual flow rate of water vapour, which is 10^3 to 10^2 smaller, the kinetic energy of the adsorptive cannot possibly be detected.

RESULTS

As an illustration of the condensation compensation method two examples of experimental results are shown: Figs. 8—10 are pertinent to a highly activated active carbon, Figs. 11—13 to a synthetic zeolite (type 4A). The experiments were carried out at 298.2 K in the continuous dosing mode.

The two adsorption isotherms in Fig. 8 appear to be good duplicates, although they were measured in different pairs of cells. No desorption branches could be measured, because so far the condensation compensation method is confined to the adsorption process. However, the apparatus may be used for conventional volumetric determination of the desorption branch of the isotherm. If one would wish, the differential heat of desorption could be measured simultaneously. Figure 9 shows the curves for the net differential energy of adsorption that were obtained from the same experiments as the isotherms in Fig. 8. In view of the fact that actually different cells were used, the results compare very well. The mutual deviation is 1 J mmole^{-1} at most. For higher degrees of coverage the net differential energy of adsorp-

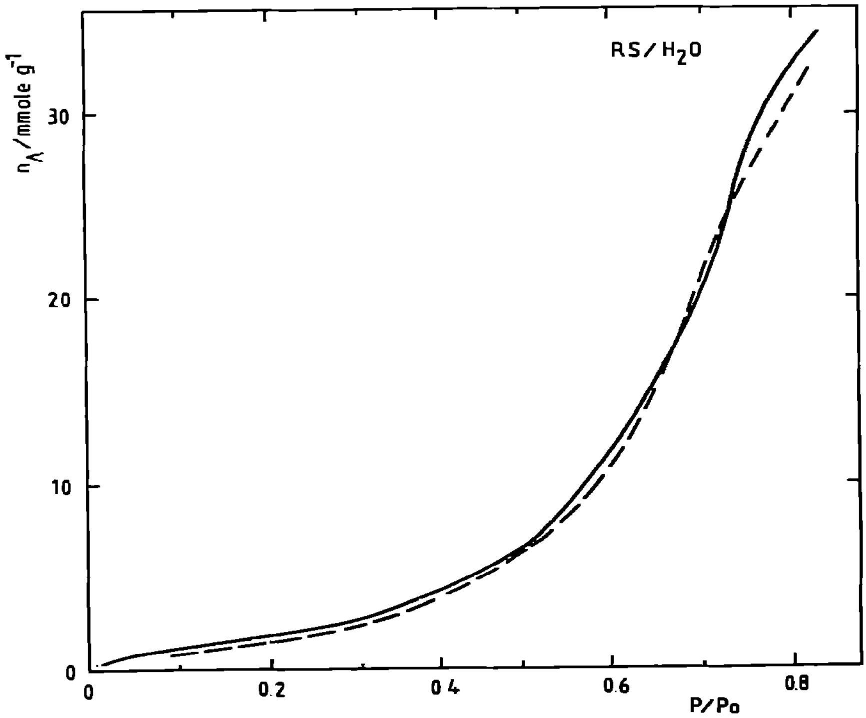


Fig. 8. Water vapour adsorption isotherms on active carbon that was impregnated with a few oxides; the two measurements were carried out in different pairs of cells at 298.2 K.

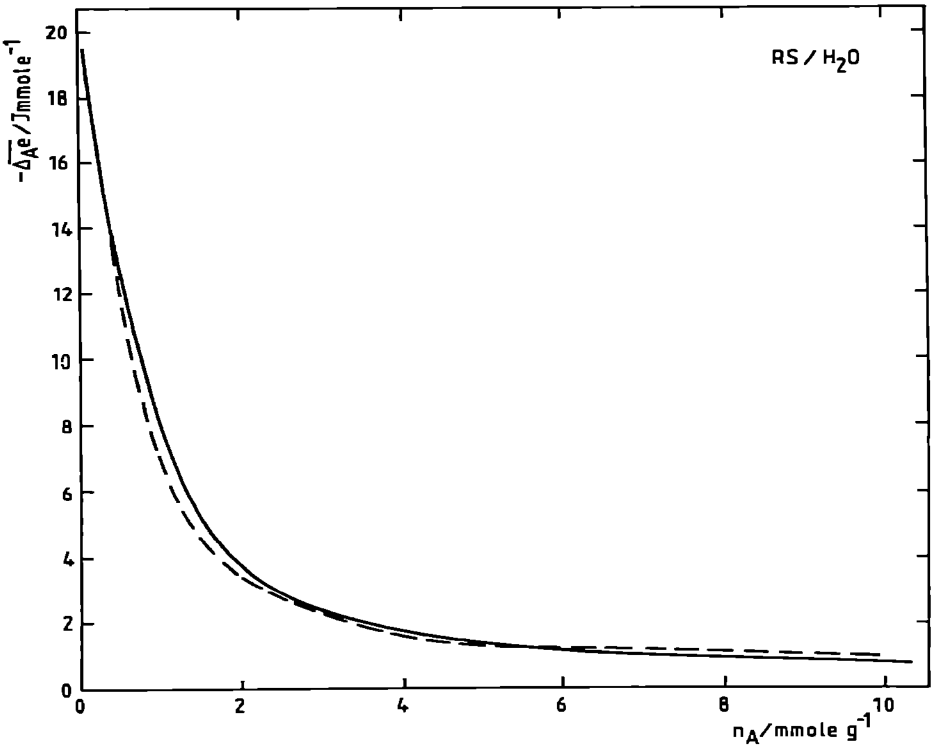


Fig. 9. The two differential heat of adsorption curves corresponding to the isotherms in Fig. 8.

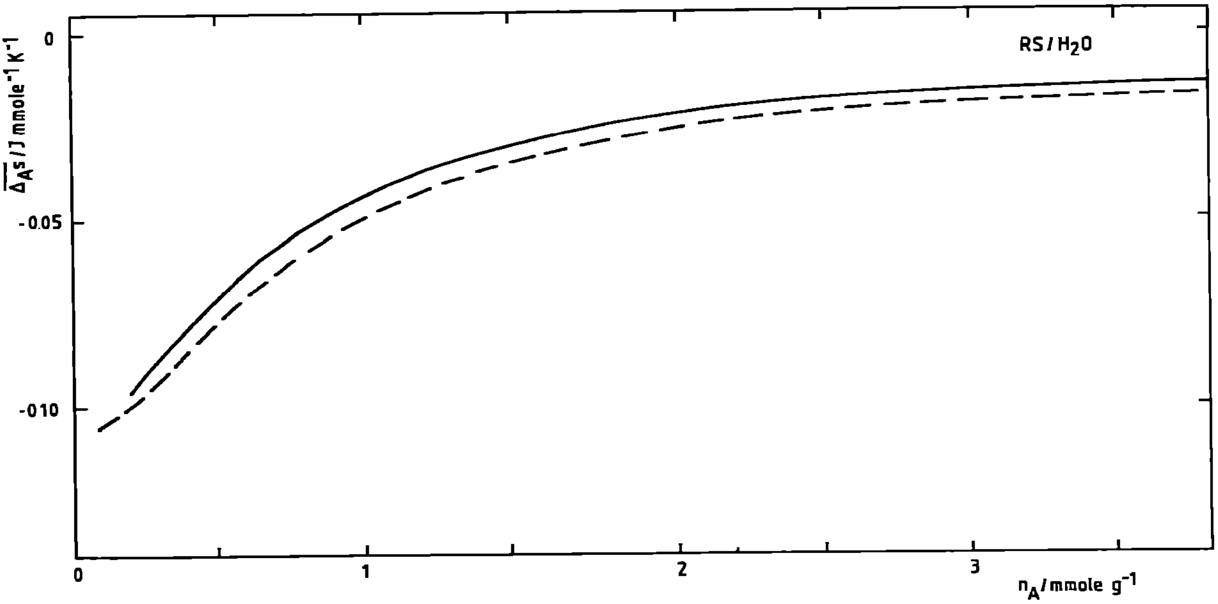


Fig. 10. Net differential entropy of adsorption calculated from eqn. (16) from the data shown in Figs. 8 and 9.

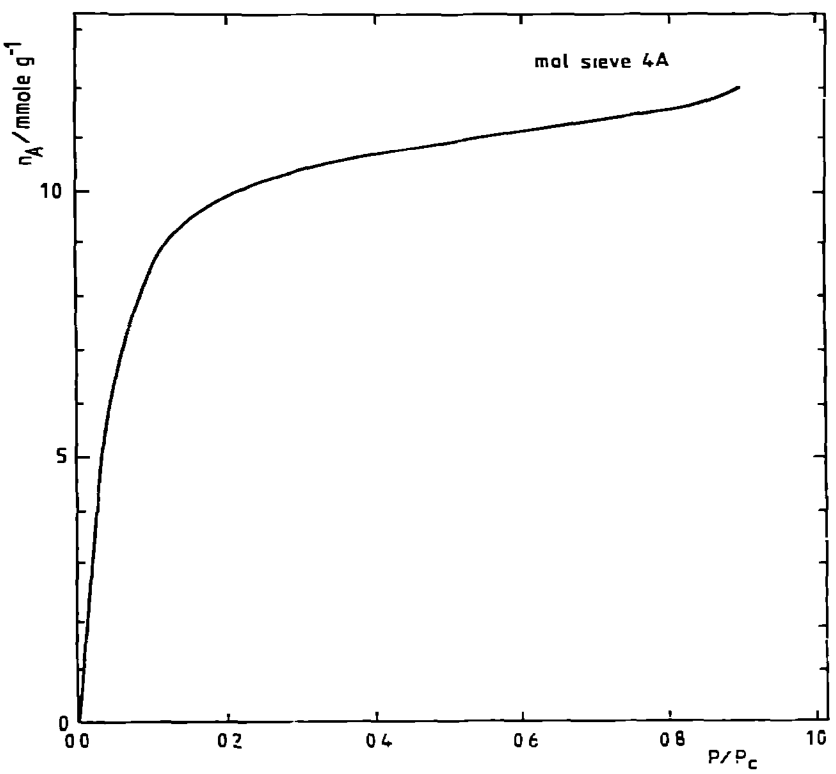


Fig. 11. Water vapour adsorption isotherm on a synthetic zeolite type 4A measured at 298.2 K.

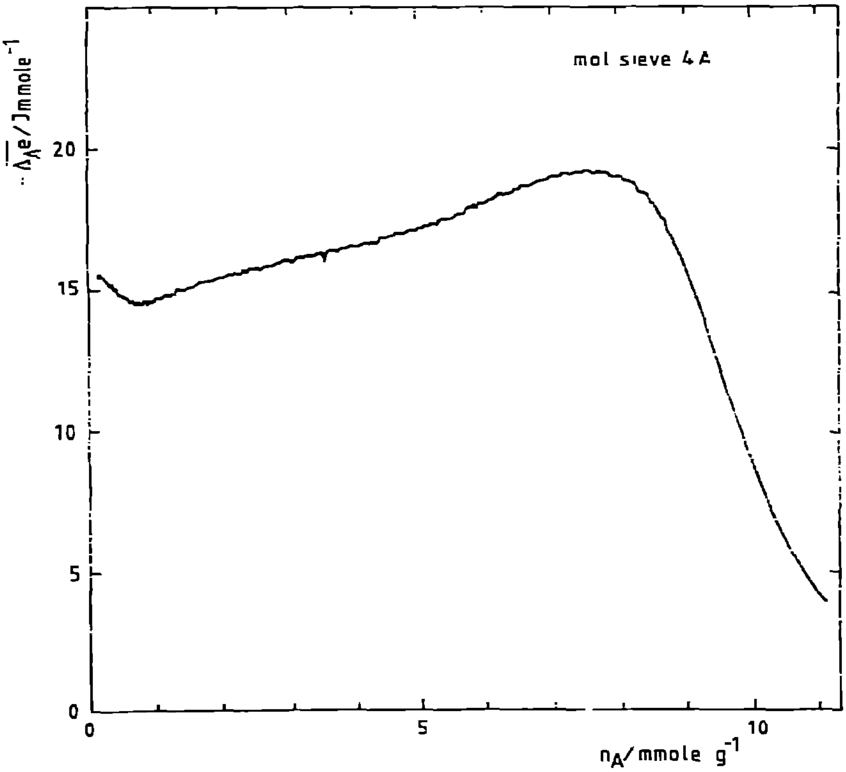


Fig. 12. Net differential energy of adsorption simultaneously measured with the isotherm in Fig. 11.

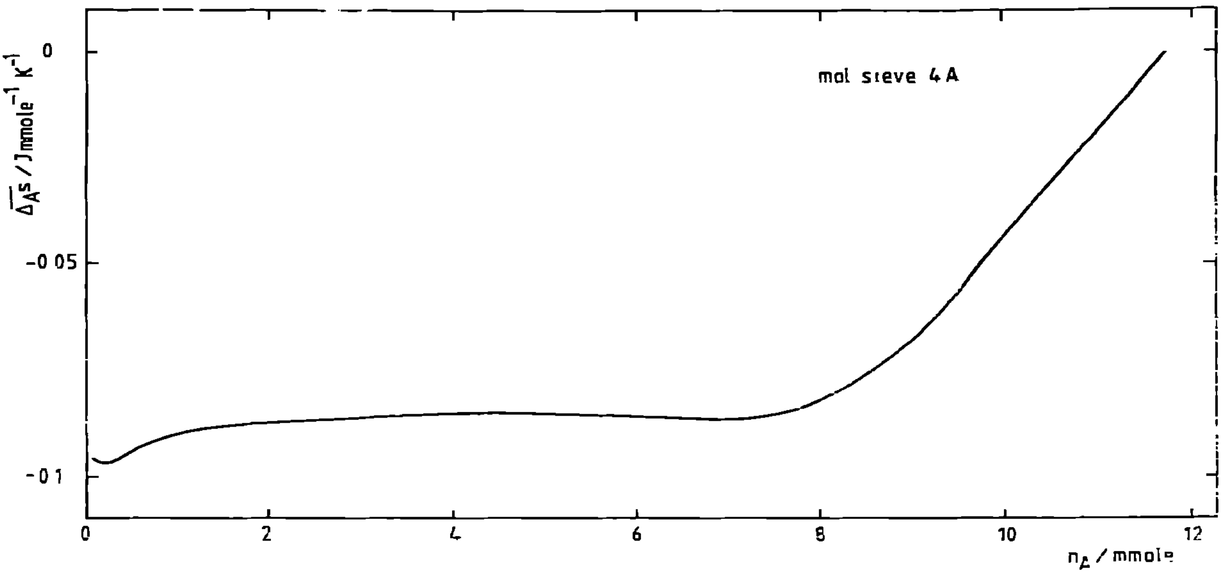


Fig. 13. Net differential entropy of adsorption calculated from eqn. (16) from the data of Figs. 11 and 12.

tion gradually decreases to a value of —0.2 J mmole^{-1} at 33 mmole H_2O g^{-1} carbon.

Figure 10 shows the net differential entropy of adsorption defined by eqn. (7) and calculated with eqn. (16). Figures 11—13 show the same quantities for a synthetic zeolite: the strongly different character in hydrophilicity of this sample with regard to active carbon is evident.

CONCLUSION

The net differential heat of adsorption may be measured directly by means of the condensation compensation method. As far as the author is aware the method is new. Simultaneous measurement of the adsorption isotherm has been incorporated into the procedure. The method may be applied either in the stepwise or continuous flow mode; the latter gives the best results.

From the combined experimental data one may derive the differential net energy of adsorption (eqn. (2 or 12)), the energy of adsorbed phase, and the net differential entropy of adsorption (eqn. (11 or 16)).

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