Calorimetry in the study of physical adsorption

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Abstract – Recent advances in both theory and experiment have stimulated
much research on films physically adsorbed on solid surfaces. From the
theoretical side, new deductions have been made about the growth of
adsorbed films and about melting and other structural transitions in
them. In addition, successful refinements have been made to the poten-
tials which describe admolecule-substrate and admolecule-admolecule
interactions. Measurements of thermodynamic properties of adsorbed
films – vapour pressures, heats of adsorption, heat capacities – yield
valuable information about phase diagrams and phase transitions as well
as interaction energies. Examples are given which are drawn mainly
from studies of adsorption on the surface of graphite.

INTRODUCTION

The study of the thermodynamics of physically adsorbing systems has a long and venerable
history. Countless papers have been written on the subject, and conferences held and books
published. In part, this is because of the universality of the phenomenon of physical
adsorption on surfaces and, in part, because of a need for understanding as a basis for
use in numerous industrial processes such as, for example, in the separation of gas
mixtures. Wartime needs for efficient adsorbents for gas masks led to much research on
the adsorptive properties of porous carbons or charcoals.

It is not the intention of this contribution to give an exhaustive historical survey of
calorimeters or of the application of calorimetry in the study of physical adsorption.
While some developments from the more distant past will be mentioned, much more attention
will be given to the role that calorimetry and thermodynamics can play in helping to
investigate relatively new fundamental deductions about systems with fewer than three
dimensions.

Many years ago, it was established theoretically (ref. 1) that crystalline order of the
familiar kind in three dimensions cannot exist in two dimensions at any finite temperature.
There can, however, be long range order of a bond orientational type in two dimensions. A
seminal theoretical paper by Kosterlitz and Thouless (ref. 2) proposed that first order
freezing (or melting) in bulk systems would become a continuous process in two dimensional
systems. At about the same time and as a consequence of some elegant adsorption experi-
ments by Thomy and Duval (ref. 3), many researchers began to realize that the basal plane
of graphite crystallites provided an almost ideal substrate for physically adsorbed films
whose properties could be used to test theoretical ideas concerning systems of two
dimensions. Before long, a large international conference on ordering in two dimensions
(ref. 4) was held. Currently, helpful general articles for the uninitiated are beginning
to appear (refs. 5 and 6).

It will soon be evident that physically adsorbed films – even of the rare gases – have
complex phase diagrams. Some also have phases which have no counterparts in bulk systems.
Actual structures are known for only a minor fraction of the phases and thus any physical
techniques such as calorimetry which can elucidate elements of the phase diagrams are of
great value. Beyond that, it is possible to measure directly calorimetrically energies
of interaction between gas molecules and solid substrates. The energies are basic
quantities needed for theoretical interpretation of adsorption phenomena.

INFORMATION ABOUT PHASE DIAGRAMS FROM ADSORPTION ISOTHERM DATA

The chemical potential of an adsorbed phase, referred to a convenient reference state, is
readily computed from adsorption isotherm data (surface coverage as a function of the
equilibrium gas pressure at constant temperature). However, the adsorption data them-
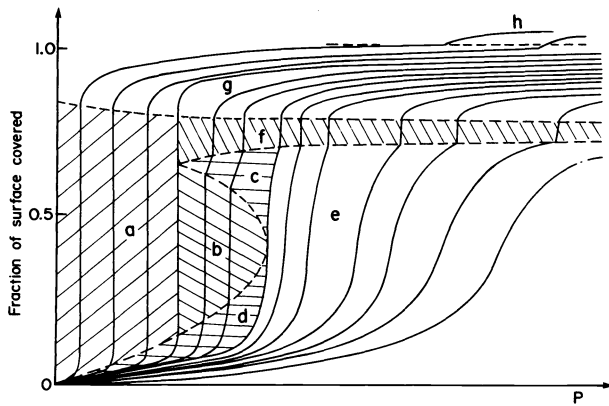selves reveal much about the phase diagram – especially at surface coverages of the

Fig. 1. Schematic diagram of adsorption
isotherms for simple gases on graph-
ite. The temperature increases to
the right. a – 2D gas + 2D solid I;
b – 2D gas + 2D liquid; c – 2D
liquid; d – 2D gas; e – 2D hyper-
critical phase; f – 2D liquid + 2D
solid I; g – 2D solid I; h – 2D
solid II. (ref. 3).

equivalent of a monolayer or less. Thomy and Duval (ref. 3), and many others subsequently,
have observed steps and kinks in isotherms which are associated with regions where two
surface phases coexist or with passage across a phase boundary. A schematic composite
diagram of adsorption isotherms is shown in Fig. 1. It represents the phase behaviour of
systems of several simple molecules, – e.g. rare gases, methane, nitrogen – adsorbed on
graphite.

As in a bulk system, there is a well-defined solid-liquid melting temperature and a liquid-
gas critical temperature. In general, these temperatures turn out to be approximately 0.6
and 0.4 respectively of those for bulk phases (ref. 5). The appearance of two solid
surface phases should be commented upon because of a special aspect of an adsorbing system.
Depending upon the size of the adsorbed molecules, the periodicity of the structure of the
substrate can induce the formation of new solid surface phases. To anticipate some later
discussion, 2D solid I which is designated in Fig. 1 has a structure which is commensurate
with that of the basal plane of graphite (ref. 6).

To summarize this short section: adsorption isotherms yield thermodynamic data which can
be combined with values of other quantities to yield a thermodynamic (meaning macroscopic)
description of an adsorbing system. Since, however, isotherms can often be measured
quickly and easily, they are frequently used to delineate the system for efficient experi-
mental study by techniques which yield information about the microscopic composition and
behaviour of the system.

HEATS OF ADSORPTION

The fundamental quantities which are needed to describe physical adsorption are admolecule-
substrate and admolecule-admolecule interaction potentials. While the exact form of the
potentials is unlikely to be gleaned soon, the admolecule-substrate potential is often
constructed from the sum of pairwise atom-atom potentials of the form of the common
Lennard-Jones 12-6 function (ref. 7). Admolecule-admolecule potentials are taken, where
possible, to be those which give sensible results for properties of the adsorbate in bulk.

For an ideal homogeneous surface, the energy minimum of the interaction potential for an
atom on a surface is given by (ref. 8):

$$\varepsilon_0 = 1/2 \; RT - q_{st}(0) \tag{1}$$

for mobile adsorption and

$$\varepsilon_0 = - 1/2 \; RT - q_{st}(0) \tag{2}$$

for localized adsorption. Here, $q_{st}(0)$ is the isosteric heat (or enthalpy) of adsorption
at zero surface coverage and q_{st} is defined by

$$\left(\frac{\partial \ln P}{\partial T}\right)_n = \frac{q_{st}}{RT^2} \quad , \tag{3}$$

where the subscript n denotes that the derivative is taken at constant amount adsorbed.

The isosteric heat of adsorption can usually be obtained more sensitively and accurately
from calorimetric measurements in which increments of gas are admitted successively to a
calorimeter which contains the solid substrate and the energy released is measured. Care

must be taken, however, to connect correctly the measured quantities with the thermo-
dynamic properties desired. The connection depends upon how the calorimeter is operated –
e.g. isothermally, adiabatically, etc. Alternatively, the calorimeter may be operated with
continuous admission of gas. The different possible situations have been analysed care-
fully by Rouquerol, et al. (ref. 9).

While, strictly speaking, the adsorbing system contains two components, the adsorbate and
the substrate, the surface of the substrate is normally assumed to be unperturbed by
physical adsorption on it. In effect, the surface is simply taken to provide a force field
to which the gas molecules are attracted. Thus, all of the changes measured by means of
a calorimeter are assigned to the adsorbate which is then treated as a one component
system. Parenthetically, it should be remarked that the thermodynamics remains the same
but the names and the interpretation of the thermodynamic quantities change. We should
also note that, in contrast to bulk systems, the molar properties (e.g. X/n) of the
adsorbed phase vary with the amount adsorbed.

Recently, a careful study was reported (ref. 10) of slow equilibration of a calorimeter
containing different graphite substrates and adsorbed films of He and Ne. The long
relaxation times are interpreted as being associated with small readjustments in the
substrate surfaces as a result of thermoelastic stresses. Further investigation of the
effects seems warranted because of their possible consequence to the assumption that solid
surfaces are unperturbed by physical adsorption on them.

A simple but very useful type of calorimeter for measuring heats of adsorption was designed
by R.A. Beebe many years ago (ref. 11). An example of valuable results obtained with it
is illustrated in Fig. 2. Here, the heat of adsorption of argon at T = 78 K was measured
as a function of the amount adsorbed on carbon blacks which had been graphitized at a
series of successively higher temperatures (ref. 12). The small graphs contain a surpris-
ing amount of fundamental information. First, the decrease in the heat of adsorption at
low surface coverages, shows that graphitization at T $\geq$ 2000°C produces a solid surface
which is more homogeneous energetically. Second, the subsequent increase in the heat of
adsorption followed by a sharp fall becomes independent of the prior treatment of the
substrate. It is now known that the increase results from interactions between the adatoms
and that the fall marks the completion of an adsorbed monolayer. Third, the broad peaks
in the heat of adsorption at the higher surface coverages are caused by interactions
between the adatoms in the second layer.

Several calorimeter assemblies of greater precision and accuracy have been constructed to
measure heats of adsorption as well as heat capacities of physically adsorbed layers (refs.
13, 14, 15, 16). The heat capacity will be dealt with in the next section. Here, we shall
be concerned with what can be learned about surfaces and films adsorbed on them from
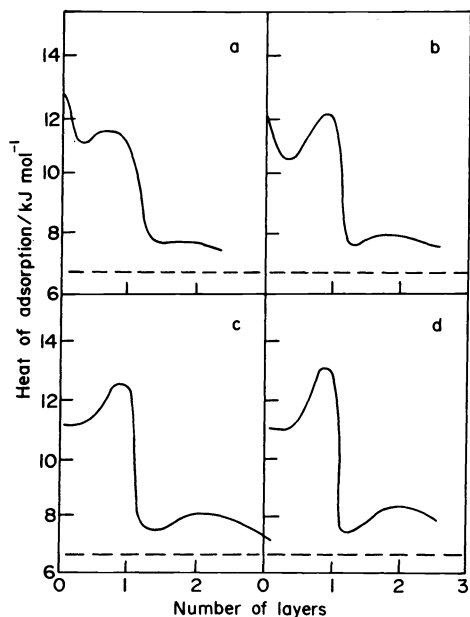accurate measurements of heats of adsorption.

Fig. 2. The heat of adsorption at
T = 78 K of argon on carbon blacks
graphitized at different tempera-
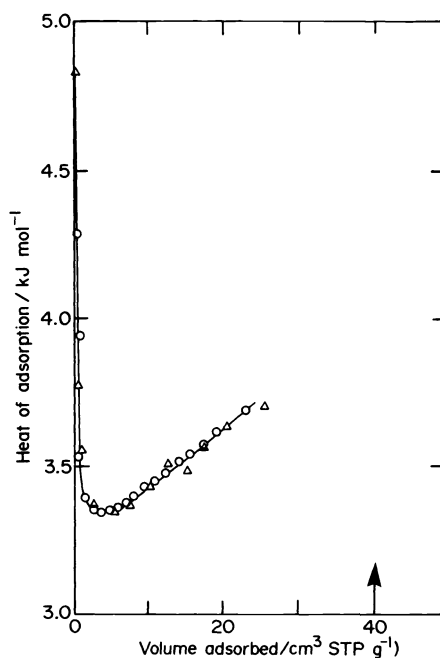tures. a – 1000°C; b – 1500°C;
c – 2000°C; d – 2700°C. (ref. 12).

Fig. 3. The heat of adsorption of
neon on graphitized carbon black
at T = 29 K as a function of
surface coverage in the region
less than a monolayer (marked by
the arrow). (ref. 14).

Fig. 3 shows results of measurements of the isosteric heat of adsorption of neon on
graphitized carbon black at T = 29 K and for surface coverages less than 0.6 of a mono-
layer (ref. 14). The high precision is evident from the good agreement (to better than
± 0.5%) between the duplicate sets of results. That precision has also allowed measure-
ments to be made to surface coverages lower than those accessible to the Beebe type
calorimeter. We see that the carbon black used here, which had been graphitized at
T = 2700°C, still has a small proportion of adsorption sites of higher energy.

Many of the later calorimetric studies have been made with exfoliated graphite, much of
which carries the trade names Papyex (Le Carbone Lorraine) or Grafoil (Union Carbide Corp.).
It can be obtained with bulk densities in the range 0.1 to 1.1 g cm^{-3}. Some of the
available materials have been characterized by X-ray diffraction (ref. 17). It turns out
that, as gauged through measurements of heats of adsorption of simple molecules, the
different exfoliated graphites present very similar surfaces for physical adsorption (ref.
18). All seem to show a small amount of surface heterogeneity of the kind deduced from
the results displayed in Fig. 3.

When the amount of heterogeneity is small, as in the example in Fig. 3, an estimate of the
heat of adsorption of a single molecule on an energetically homogeneous graphite surface
can be obtained by smooth extrapolation of the data for higher coverages (in this case for
the region 0.6 to 0.12 of a monolayer) to zero coverage. For this example, $q_{st}(0)$ =
3.26 kJ mol^{-1}. The same procedure has been applied to similar data for the xenon/graphite
system at T = 195.5 K (ref. 19), but extended through use of equations (1) and (2) to
yield estimates of the energy minimum of the xenon–carbon interaction potential. The
results are ε_0 = 16.49 or ε_0 = 18.11 kJ mol^{-1} depending upon whether the model for the
adsorption is chosen to be mobile or localized. A recent theoretical study of interaction
potentials between rare gases and surfaces yields ε_0 = 15.90 kJ mol^{-1} for xenon–carbon.
Since it is more probable that the adsorbed film of xenon is mobile, we conclude that the
experimental and theoretical estimates of the well depth of the potential agree well.
Similar comparisons have been made for nitrogen (ref. 16) and carbon monoxide (ref. 8(b))
adsorbed on graphite and agreement found to within 10% or better.

A different direct comparison between theory and experiment can be made through the
dependence of the heat of adsorption upon surface coverage in the region where adatom-
adatom interactions become significant. In the first examples to be discussed, the
quantity to be determined is the integral heat of adsorption rather than q_{st}. From the
experimental side, adiabatic calorimeters in which increments of gas are introduced
successively (e.g. ref. 16) measure changes in the integral heat of adsorption

$$\Delta Q = C_{system} \times \Delta T - V_{cal} \times \Delta P \quad . \tag{4}$$

Thus, the integral heat of adsorption at any surface coverage is obtained by summing ΔQ
from zero coverage. This will, of course, include a contribution from surface hetero-
geneity, but it can be estimated as long as a value can be found for the effective heat
of adsorption of a single molecule on a homogeneous surface. Some details of the mechanics
are given in ref. 8(b).

From the theoretical side, the calculation to be performed is the determination of Q for
a homogeneous surface by means of Monte Carlo simulation with the assumption of a specific
adatom–adatom potential. In the examples to be cited of nitrogen and carbon monoxide
adsorbed on graphite, molecule–molecule interaction potentials which account reasonably
well for properties of the bulk solids were transformed to atom–atom potentials for the
detailed calculations. Substrate screening of the interactions was also included. The
detailed results are summarized in Table 1. The magnitudes of the changes in the calcul-
ated and measured values of Q are comparable but quantitative agreement cannot be claimed.
A subsequent extension of the calculations in a study of structures of adsorbed phases of
nitrogen and carbon monoxide, concluded that refinements were still required for the inter-
action potentials, especially for that for carbon monoxide (ref. 20).

TABLE 1.   A comparison of integral heats of adsorption of N_2 and CO on
            graphite at T = 79.3 K[*].

Fraction of surface covered	Q (kJ mol^{-1})			
	nitrogen		carbon monoxide	
	calculated	measured	calculated	measured
0	(10.4)	10.4 ± 0.1	(10.9)	10.9 ± 0.1
0.5	11.6	11.1	11.96	11.6
0.75	12.0	11.4	12.46	11.9

[*]refs. 8(b) and 16.

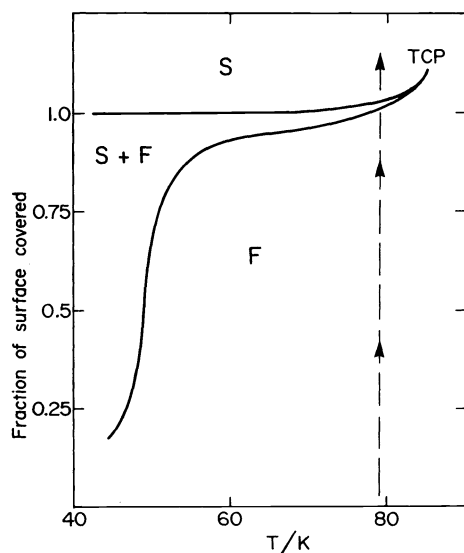Fig. 5. The isosteric heat of adsorption of nitrogen on graphite at T = 79.3 K (ref. 16).

Fig. 4. A portion of the phase diagram for nitrogen adsorbed on graphite (ref. 25).
    S – commensurate solid;
    F – fluid;
 S + F – coexistence region;
  TCP – tri-critical point.
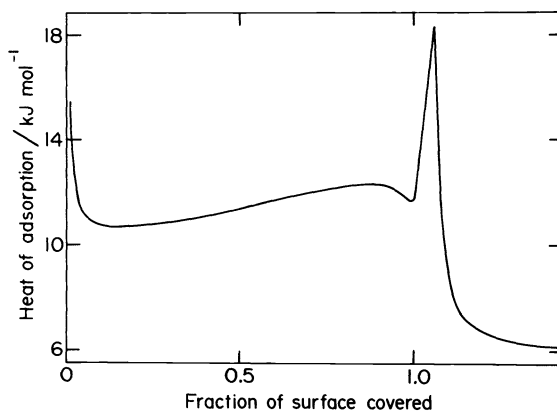– → – → path of measurements of heats of adsorption at T = 79.3 K.

Such a refinement has recently been accomplished for the example of nitrogen and a comparison made of calculated and measured isosteric heats of adsorption over a range of surface coverages (ref. 21). The agreement found is quantitative which encourages the conclusion that heats of adsorption measured calorimetrically can provide critical information about interaction potentials for physically adsorbed films. The potential model devised for nitrogen/graphite is now being applied to multilayers (ref. 22).

Several different properties of physically adsorbed films have been measured in studies aimed at delineating two-dimensional phase diagrams: vapour pressure, structure (by LEED, neutron or X-ray diffraction), heat capacity. Until relatively recently, heats of adsorption were not much used to provide information about the diagrams but they turn out to be very sensitive to phase boundaries and two phase regions. This seems first to have been noted by Rouquerol, et al. (refs. 23, 24) for argon and nitrogen adsorbed on graphite. The only limitation is that the vapour pressure of the adsorbed film should be appreciable in the region chosen for calorimetric measurements.

Figure 4 is a schematic diagram of a portion of the phase diagram for nitrogen/graphite in a region where commensurate solid (S) and fluid (F) surface phases coexist. It is based on the results of heat capacity and vapour pressure measurements (ref. 25). The vertical dashed line at T = 79.3 K marks the path along which the isosteric heat of adsorption has been measured with the result shown in Fig. 5 (ref. 16). The solid-fluid coexistence region is clearly marked by the large spike in the heat of adsorption. Similar observarions have been made for carbon monoxide/graphite (ref. 8(b)) and methane/graphite (ref. 18) systems. In these two examples, measurements of the heats of adsorption at different temperatures provided some quantitative information on the temperature dependence of the coexistence region leading up to the tricritical point which is marked by TCP in Fig. 4. In another system which has been studied, multilayers of ethylene adsorbed on graphite, a coexistence region has been detected by a sharp and large decrease in the heat of adsorption that was measured calorimetrically (ref. 26).

HEAT CAPACITIES OF ADSORBED FILMS

Direct measurements of the heat capacities of adsorbed films with conventional style calorimeters are difficult to make accurately because the mass of the film will usually be a small fraction of the total mass of the calorimeter system. Nevertheless, a number of such measurements has been made (refs. 13, 14, 27) and the results analysed in terms of simple models for the adsorbed phase. There is, however, the difficulty – which also exists for the interpretation of heat capacities of bulk systems – that unambiguous deductions about the state of the adsorbed atoms or molecules can rarely be made from heat

capacities. On the other hand, the heat capacity undergoes marked changes at phase transitions, and measurements in these regions have proven to be interesting and informative. Some examples of studies of melting of physically adsorbed films are the following: nitrogen on titanium dioxide (ref. 28); helium on graphite (ref. 29); methane on graphite (ref. 27). A very early study was made of heat capacity anomalies in helium films on jeweller's rouge in the region of the superfluid transition (ref. 30).

Except for the example of graphite (ref. 27), the other substrates probably presented surfaces that were highly non-uniform. On them, the heat capacity anomalies at melting and at the superfluid transition broadened and were displaced to lower temperatures as the thickness of the adsorbed layers decreased. Anomalies were not detected for films less than about two layers thick. By contrast, melting of methane on graphite remained sharp for surface coverages greater than the equivalent of two layers. Similarly, the breadth and mean temperature of the heat capacity anomaly for the superfluid transition in helium films on graphite was found to be independent of film thickness (ref. 31).

In a radical departure in design, Chan, et al, (ref. 32) have developed a calorimeter in which the fractional contribution of the adsorbed film is greatly increased. The substrate - an expanded form of exfoliated graphite called Grafoam - in the form of a small cylinder is bonded to two sapphire disks which carry a heater and a thermometer (Fig. 6). The assembly is suspended from fine wires in a sample chamber into which adsorbing gases can be admitted. In a variation of the technique, the heat capacity of helium films on a single flake of graphite has been measured (ref. 33).

The calorimetric method is especially suited for determining the heat capacity of submono-layer adsorbed films because of its high resolution - of the magnitude of 0.2% of the total heat capacity. Its main disadvantages are two. Because the substrate specimen is so small, contamination of the surface is a more serious problem than it is for the much larger specimens used in conventional calorimetry. Also, the method becomes much less accurate in the regime when the equilibrium vapour pressure of the adsorbed film is significant. The "dead" volume of the calorimeter system is relatively large with the result that corrections for desorption become large when the temperature is increased.

One of the studies performed with the calorimeter has already been referred to, viz. the determination of a portion of the phase diagram for nitrogen adsorbed on graphite (refs. 25 and 32) (Fig. 4). In addition, evidence has been found for a transition in monolayer adsorbed nitrogen that involves orientational ordering-disordering of the nitrogen molecules (ref. 34). Similar studies have been made for the systems argon/graphite (ref. 35), carbon tetrafluoride/graphite (ref. 36) and ethylene/graphite (ref. 37). Some of the solid phases proposed to account for transitions attributed to observed peaks in the heat capacity are consistent with structures deduced from X-ray and neutron diffraction measurements.

In a somewhat different application of the calorimetry, the profile of the two dimensional liquid-vapour equilibrium curve has been examined and an order parameter found which describes it for methane adsorbed on graphite (ref. 38). Other heat capacity measurements (ref. 39) and NMR results (ref. 40) yield somewhat different estimates of the liquid-vapour critical temperature and suggest that the shape of the equilibrium curve may not be so symmetric as is illustrated in Fig. 7. However, as Fisher has pointed out (ref. 41), the determination of the exact shape of a coexistence curve in the region of the critical temperature is difficult even for a bulk system. For two dimensions, the heat capacity should in principle give the least ambiguous measure of the critical temperature and the order parameter.
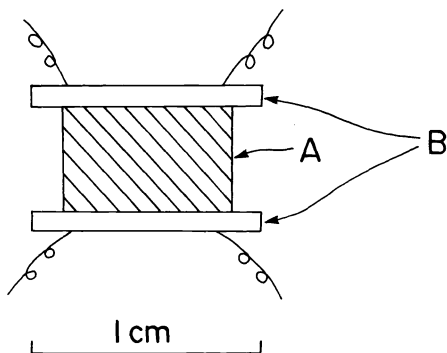

Fig. 6. Schematic sketch of the essential elements of the calori-meter of Chan, et al. (ref. 32). A - Grafoam; B - sapphire disks.
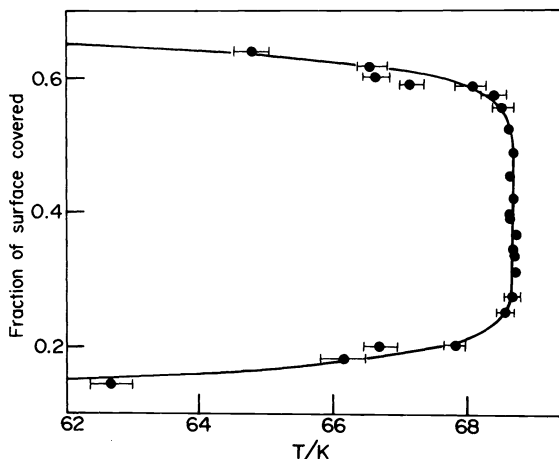

Fig. 7. Two dimensional liquid-vapour co-existence curve deduced from observed peaks in the heat capacity of methane adsorbed on graphite (ref. 38).

A further example is provided by the system of ethylene adsorbed on graphite for which heat capacity (ref. 37), heat of adsorption (ref. 26) and structural (ref. 42) measurements have been made in the submonolayer region. While the results of the different kinds of measurements agree in the identification of a two dimensional liquid-vapour coexistence region, the estimates of the critical temperature differ markedly.

To conclude the discussion of calorimetry in the study of physical adsorption, a brief account will be given of a current problem which is engendering much interest. It is now well established (ref. 5) that, below a particular temperature, certain adsorbing systems will form only a limited number of layers. Any additional gas added forms bulk solid. The phenomenon is called incomplete wetting and it is characterized by a wetting temperature T_w. Above T_w, adsorption proceeds without limit and the properties of the adsorbed film approach those of the adsorbate in bulk. One of the first examples discovered was of ethylene adsorbed on graphite through measurements of adsorption isotherms (ref. 43), and it has since been fully verified by neutron and X-ray diffraction studies (refs. 42, 44, 45). In this example, T_w has been found to be very close to the melting temperature of ethylene. While extensive theoretical work has been done with the object in part of predicting wetting temperatures for particular systems (refs. 46 and 47), it appears that, at present, laborious experimental investigation of individual systems is still necessary. In a study to be published shortly (ref. 48), calorimetry has been used to investigate layering, melting and layer critical transitions in multilayer films of ethylene on graphite.

Acknowledgement

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