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Phenomenological Sorption Thermodynamics

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The thermodynamics of sorption of pure substances and of mixtures from the vapour or the liquid phase on sorbents of different types are discussed. The stoichiometric theory of adsorption and the osmotic theory (based on the vacancy solution model) are analysed in detail, as well as the most recent advances in the theory of volume filling of micropores. The following problems are examined: the validation of the model, and of the choice of components of the sorption solution, the methods of calculating the appropriate activity coefficients, the internal thermodynamic consistency of data on adsorption from the vapour and the liquid phase, and the prediction of equilibrium adsorption characteristics from the smallest possible amount of experimental data. Capillary phenomena are examined from the standpoint of maximising the information on the pore structure of the adsorbent. 80 references.

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I. INTRODUCTION

The increasingly wide application of sorption processes in chemical industry has been responsible for recent developments in the study of adsorption, and in particular of the thermodynamic theory of adsorption. The control and optimisation of these processes, the preparation of adsorbents offering the required selectivity towards certain components of the mixture, and the identification of the mechanism of adsorption–catalytic processes have created a need for still further developments in theoretical studies of adsorption.

One of the most important theoretical problems is to develop methods of predicting the equilibrium characteristics of adsorption in one-component and multi-component systems, because the empirical approach to achieving selectivity in adsorption systems (and thus making the systems more effective and economically attractive) is laborious and impractical when the number of mixtures to be extracted, purified, or separated is very large. In principle this problem can be solved by molecular–statistical thermodynamics.

Many recent experimental and theoretical papers have dealt with intermolecular interactions in sorption systems, and with the study of the physical and physicochemical

properties of adsorbents and adsorbed molecules by modern methods of analysis. However, the complexity of the problem is such that rapid progress cannot be expected by this approach. Far more useful advances have been made in the developments of a strict phenomenological theory of adsorption thermodynamics usable in conjunction with empirical rules or non-thermodynamic considerations suggested by simple, approximate models of sorption systems.

In this review we shall examine recent achievements in that type of work. No attempt will be made to cover the literature exhaustively, but we shall try instead to clarify the present position of the thermodynamic theory of adsorption by referring to published information as required.

The symbols used in this review have their conventional meaning (unless accompanied by a statement to the contrary). We shall also use the following additional symbols:

n_i, c_i, x_i, γ_i are the number of moles, the concentration (mole litre^{-1}), the mole fraction, and the activity coefficient of the stated component in the bulk phase (the tilde sign ~ denoting the liquid solution when a vapour and a liquid bulk phase can coexist, e.g. $\tilde{c}_i$, etc.);

$\bar{n}_i$, $\bar{c}_i$, $\bar{x}_i$, θ_i, $\bar{\gamma}_i$, $\bar{\varphi}_i$, are the number of moles, the concentration (mole kg^{-1}), the mole fraction, the surface coverage, the activity coefficient, and the full chemical potential of the components of the sorption solution (the subscript R denotes the adsorbent, for example $\bar{c}_R$ is the concentration of the adsorbent); c_{is}, γ_{is}, $\tilde{c}_{0i}$, $\bar{c}_{0i}$ are the concentration (mole litre^{-1}) and the activity coefficient of the saturated vapour and of the pure liquid component and the concentration (mole kg^{-1}) of the sorption solution when saturated with the stated component; s_i, s_R, and s are the molar volumes or areas of the components of the sorption solution;

σ is the surface tension or internal pressure;

W *and* W_0 are the surface (or volume) and the specific surface (or volume) of the macroporous or microporous sorbents;

$\bar{v}_{0i}$ is the molar volume of the liquid adsorbate at the given temperature;

K_i and $\bar{K}_i$ are the equilibrium coefficient and the thermodynamic equilibrium constant for the adsorption of the i-th component;

α, K, and $\bar{K}$ are the separation coefficient, the equilibrium coefficient, and the thermodynamic equilibrium constant for the adsorption of a binary mixture;

g_i is the osmotic coefficient of component i in the sorption solution;

β_i, β, and $\beta_{i(af)}$ are the stoichiometric coefficients for the individual and the exchange adsorption, and the affinity coefficient of the theory of volume filling of micropores (TVFM);

α_i is the thermal expansion coefficient of the components of the sorption solution in the TVFM;

E_0 is the characteristic free energy of adsorption of the standard vapour in the TVFM;

r is the equivalent radius of the mesopores;

t and t_e are the mean square thickness of the adsorption layer in the mesopores without and with the correction (respectively) for the effect of the sorption field of the sorbent;

ω is the parameter of Tolman's equation.

II. THE SORPTION SOLUTION MODEL

Two methods of describing adsorption systems thermodynamically are known: the Gibbs surface excess method[1] and the finite thickness layer method (or, more exactly, the total content method)[2]. In the Gibbs method the real structure of the adsorption phase is ignored. Therefore the thermodynamic functions determined from the experimentally measured excess quantities apply to the sorption system as a whole and cannot be used to analyse the distribution of volume phase and of sorption phase in the adsorbents, and the thermodynamic properties of the latter. For this reason modern theories of adsorption have tended to rely on the finite thickness layer method.

In the thermodynamic analysis of sorption systems a distinction is often made between adsorption in the surface layer (macroporous sorbents) and in the volume of micropores (microporous sorbents). In a critical analysis of this approach[3] a new function (Φ) was introduced to describe both processes within the same thermodynamic model. As the present writer recently pointed out[4], the properties of both these sorption phases are similar in many ways[3,4], though they differ very substantially from those of ordinary bulk phases: the pressure in the plane of the surface layer of the bulk sorption phase is different (at least, in some directions) from the total pressure P in the system. Hence, in both cases[1,4,5] the fundamental equations should include the term σdW to allow for the additional work of formation of the surface layer (where σ is the surface tension and W is the area of the surface) or of the "volume" sorption phase in the micropores (where σ is the internal pressure and W is the volume of the sorption phase):

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i + \sum_i \bar{\varphi}_i\,\mathrm{d}\bar{n}_i + \sigma\,\mathrm{d}W, \tag{1}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_i \mu_i\,\mathrm{d}n_i + \sum_i \bar{\varphi}_i\,\mathrm{d}\bar{n}_i + \sigma\,\mathrm{d}W \tag{2}$$

so that

$$-S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_i n_i\,\mathrm{d}\bar{\varphi}_i + W\,\mathrm{d}\sigma = 0. \tag{3}$$

The full chemical potentials of the components of the sorption solution should be written[1,5] as

$$\bar{\varphi}_i = \bar{\mu}_i^0(T, P) + RT\ln\bar{c}_i\bar{\gamma}_i - \int_0^{\sigma} s_i\,\mathrm{d}\sigma = \bar{\mu}_i - s_i\sigma, \tag{4}$$

$$\bar{\varphi}_i = \bar{\mu}_i^0(T, P) + RT\ln\bar{x}_i\bar{\gamma}_{ix} - \int_0^{\sigma} s_i\,\mathrm{d}\sigma = \bar{\mu}_i - s_i\sigma. \tag{5}$$

The molar areas or volumes (s_i) of the components of the sorption solution depend (in general) on the composition of the solution. However, since the dependence is usually not very marked, and the form of the relevant function is not known, we can adopt the rigid sorption solution model (i.e. $s_i = \text{const}$) without affecting the thermodynamic validity of the argument. Any deviation from the assumed model can be allowed for by choosing an appropriate activity coefficient. By this approach (which is currently favoured by most workers) correct use can be made of the right-hand side Eqns.(4) and (5). We note that in the calculation of $\bar{\gamma}_i$ and $\bar{\gamma}_{ix}$ reference (standard) states differing by a factor of $\bar{c}_{0i}$ are usually used:

$$\bar{\gamma}_i,\ \bar{\gamma}_{ix} \to 1 \text{ for } \bar{c}_i \to \bar{c}_{0i}, \text{ i.e. } \bar{x}_i \to 1, \tag{6}$$

whereas $\bar{\gamma}_{ix} = \bar{\gamma}_i\bar{c}_0$ (where $\bar{c}_0$ is the total concentration of the solution), which leads to a formal difference between the numerical values of the standard parts of the chemical

potentials and of the standard thermodynamic functions derived from them[6-8].

Another important property of the sorption phase is its finite size (implicit in the finite thickness layer model). Thus, the sorption solution is a phase of limited capacity with respect to the overall combination of components of the solution. Since the inhomogeneous region at the contact between two phases extends, strictly speaking, to the whole volume[5], the fundamental problem in the total content method is a thermodynamically correct choice of the size of the sorption phase (thickness, in the case of adsorption on macroporous systems, and volume, in the case of sorption in micropores).

In the sorption of gases or vapours the excess adsorption quantities are almost identical to the corresponding total contents of components in the sorption phase. Hence the model phase can be chosen with adequate precision on the basis of the adsorption isotherm and of physically acceptable data on the effective size of the adsorbed molecules (monlayer thickness for the sorption of gases on macroporous sorbents, and micropore volume for the sorption of gases and vapours in micropores). The sorption of vapours in macropores is complicated by multimolecular adsorption and capillary condensation phenomena, and requires a special thermodynamic analysis.

Sorption from liquid solutions is a far more complex problem, because in this case the experimental data can be used reliably to calculate only the minimum capacity of the sorption phase[5,9], and this cannot be a basis for a correct choice of the size of the phase[9,10]. An interesting method for the thermodynamically correct choice of a sorption phase model in this case was proposed by Larionov[9].

1. The monolayer capacity $\bar{c}_{i(M)}$ or micropore volume $\bar{c}_{i(W)}$ is determined experimentally. Critical studies[9,10] of the methods of determining these quantities for the sorption of vapours and of liquid solutions suggest that the most reliable results are obtained by comparing data for the sorption of pure vapours with data for the sorption of their binary liquid solutions.

2. The size of the sorption phase is obtained by multiplying the $\bar{c}_{i(M)}$ or $\bar{c}_{i(W)}$ values thus obtained by the arbitrarily chosen factor k.

3. Using the experimental excess sorption isotherm of the binary liquid solution the changes in σ or in the thermodynamic wetting functions attending the transfer of the sorbent wetted with one of the components to a solution of composition $\tilde{x}_1$ are calculated by the Gibbs and the total content method. The Gibbs method, being free from any model assumptions, yields the true values of the change in the thermodynamic functions of the sorption system. In the calculation by the total content method the result obtained depends on the chosen model, i.e. on the value of k. By varying k so as to make the two sets of results coincide a thermodynamically correct model of the sorption solution is obtained.

Larionov applied this method of analysis to a large number of adsorption systems[9,11,12], and he showed that in the case of microporous sorbents the volume of the micropores is a good approximation to the volume of the sorption phase. With macroporous sorbents the best approximation is given by the monolayer volume, or occasionally by the volume of two or three layers. Thus, even in the case of sorption from liquid solutions the model of a rigid layer of finite thickness is thermodynamically justified.

The choice of components of the sorption solution is an important part of the construction of the model of the sorption phase[3,4,6,13-17]. The problem consists in defining, within the thermodynamic meaning of the term, a set of components which allows the required thermodynamic relationships to be set up in the simplest way for different sorption systems (both one-component and multi-component).

If the components of the sorption solution are identified with the substances in the bulk phase (A, B, ...), and the sorbent is not explicitly treated as a component of the sorption solution, the role of the sorbent is limited to the creation of an adsorption force field. In this case the equilibrium conditions in a closed system become (P, T = const)

$$\bar{\varphi}_i = \mu_i. \tag{7}$$

This choice of components is thermodynamically correct, but not always convenient. For example, from (5) and (7) we obtain the adsorption isotherm equation

$$\bar{c}_i\bar{\gamma}_i = c_i\gamma_i \exp[(\mu_i^0 - \bar{\mu}_i^0 + s_i\sigma)/RT], \tag{8}$$

which contains the experimentally inaccessible quantity σ. Of course, by solving Eqn.(8) simultaneously with the Gibbs adsorption equation for a layer of finite thickness

$$\sigma = -\frac{RT}{W_0}\int_0^{c_i}\sum_i \bar{c}_i\, d\ln c_i\gamma_i, \tag{9}$$

we can eliminate σ from Eqn.(8) and obtain a general form of the adsorption isotherm equation. However, this approach presents mathematical difficulties, due to the complicated dependence of σ on the composition of a multi-component sorption solution containing molecules of different size, and to the absence of an analytical expression of the type of $\bar{c}_i = f(c_i\gamma_i)$.

Complications can arise also in the analysis of systems showing evidence of chemisorption, since in this case we cannot assume that the component remains chemically identical in the two phases in equilibrium. We should stress that the stipulation commonly made in this case that the sorbent must be "inert" (i.e. that $\bar{\phi}_R$ = const) is thermodynamically incorrect, since [as we see from Eqns.(4) and (5)] σ varies during sorption. The errors caused by this assumption are discussed in Ref.14.

In the thermodynamic stoichiometric theory of adsorption (STA) developed by the present writer[4,6,13,18-22] the components of the sorption phase are taken to be the complexes formed by the adsorbate species with the sorption centres and the free sorption centres of the sorbent (AR_{s_A/s_R}, BR_{s_B/s_R}, R), whose mass is divided into the number of moles ($\bar{n}_R$) so that a molar surface or volume (s_i, s_R) can be associated with each mole of the components, and for W = const we have

$$s_i = W/\bar{n}_{0i} = W_0/\bar{c}_{0i},\quad s_R = W/\bar{n}_{0R} = W_0/\bar{c}_{0R}, \tag{10}$$

and since the sorption solution is always saturated with the sum of the components we also have

$$\sum_i s_i\bar{n}_i + s_R\bar{n}_R = W, \tag{11}$$

$$\sum_i s_i\, d\bar{n}_i + s_R\, d\bar{n}_R = 0. \tag{12}$$

[Since the value of $\bar{c}_{0R}$ is unknown we cannot evaluate s_R numerically from the expressions (10)].

This choice of components is consistent with the physically possible occupancy of several sorption centres by a sorbate molecule, it treats the adsorbent explicitly as one of the components of the system, and it is thermodynamically strict, whatever the magnitude of the adsorbate–absorbent interaction (i.e. it is equally correct whether the adsorption energy is close to the energy of a chemical bond, as in

chemisorption, or whether it is a weak dispersion interaction as in the adsorption of inert gases on graphitised carbon). It allows a fairly simple description of adsorption equilibria in different sorption systems (involving localised or delocalised physisorption or chemisorption) for the one-component or multi-component sorption of molecules of different size from bulk phases of any kind.

We should stress that Eqns.(11) and (12) apply when all the sorption centres are equally accessible to the adsorbate molecules, i.e. when molecular sieve effects are absent. If, on the other hand, in a two-component adsorption system the sorption volume W_A is available to A molecules and the sorption volume W_B to B molecules, with $W_B > W_A$, Eqns.(11) and (12) will apply only to the volume W_A, and similar expressions can be written for the adsorption of component B in the volume $W_B - W_A$.[18,21]

Simultaneous solution of Eqn.(2) (for P, T = const) and Eqn.(12) gives the basic equations of the STA:[4,6,13]

$$(\bar{\varphi}_A - \mu_A)/s_A = (\bar{\varphi}_B - \mu_B)/s_B = \ldots = \bar{\varphi}_R/s_R, \qquad (13)$$

or, using Eqn.(5)

$$(\bar{\mu}_A - \mu_A)/s_A = (\bar{\mu}_B - \mu_B)/s_B = \ldots = \bar{\mu}_R/s_R. \qquad (14)$$

Thus the choice of components for the sorption solution adopted in the STA allows us to treat adsorption processes as quasi-chemical addition reactions ($\beta_i = s_R/s_i$):

$$\beta_A A + R \rightleftarrows \beta_A AR_{1/\beta_A} \text{ etc.} \qquad (15)$$

or exchange reactions ($\beta = s_A/s_B = \beta_B/\beta_A$):

$$A + \beta BR_{1/\beta_B} \rightleftarrows AR_{1/\beta_A} + \beta B \text{ etc.} \qquad (16)$$

and therefore it makes the well developed methods of chemical thermodynamics available for the thermodynamic description of adsorption processes. On the other hand the properties of sorption solutions can be discussed in terms of the most recent advances in the theory of solutions of different-sized particles.

In the osmotic theory of adsorption (OTA) developed by Bering, Serpinskii, and others[15-17] the components of the sorption solution are adsorbate molecules and vacancies, which are identified with elements of free space in the sorption volume of micropores or in a surface layer of finite thickness. This choice of components is in many ways analogous to the previous variant, but in this case the equilibrium phases contain at least two components, which allows the methods of the osmotic theory of solutions to be applied to the analysis of one-component adsorption. Since the model assumes that in the sorption of pure substances $s_i = s_* = W_0/c'_{i,\max}$ (where s_* is the molar volume of the vacancies) on changing to multi-component adsorption we have $s_* \neq$ const, and Eqn.(12) for W = const is replaced by

$$\sum_i s_i \, d\bar{n}_i + s_* \, d\bar{n}_* + \bar{n}_* \, ds_* = 0, \qquad (17)$$

where the variations ds_* are many-valued functions of the composition of the sorption solution. This makes necessary the use of special algorithms in the thermodynamic analysis of these systems.

We also note that in the case of one-component adsorption imposing the condition $s_i = s_*$ on the model may perturb the real physical description of the solution, since according to the general statistical theory of binary solutions[6] we can write for $\bar{\gamma}_i$

$$RT \ln \bar{\gamma}_i = RT\bar{c}'_R(s_R - s_i) + (\bar{c}'_R)^2 s_R (s_R s_i)^{1/2} \Delta U_{i-R} \qquad (18)$$

(where $\bar{c}'_R$ is in mole litre^{-1}, and the subscript R is analogous to $*$), and any deviation from ideality (i.e. any deviation of $\bar{\gamma}_i$ from unity) should be associated with changes in the intermolecular interactions in solution ΔU_{i-R}, whereas such deviations could result simply from the difference in size of the component molecules with $\Delta U_{i-R} = 0$. The latter feature is, of course, entirely irrelevant to a formal thermodynamic analysis.

A very important aspect of this model is the fact that the vacancy solutions are in a state of osmotic equilibrium, i.e. the chemical potential of the solvent (vacancies) in the sorption phase is equal to the chemical potential of the pure solvent (vacancies in a vacuum). Therefore, using (5), we have[15,16]

$$\mu_* = \bar{\mu}^0_*(T, P) + RT \ln \bar{x}_* \bar{\gamma}_* - s_* \sigma = \mu^0_*(T, P). \qquad (19)$$

Since $\bar{\mu}^0_* = \mu^0_*$, and $\bar{x}_* = \bar{c}_*/\bar{c}_{i,\max} = \bar{\theta}_* = 1 - \bar{\theta}_i$, it follows from (19) and (10) that for one-component adsorption

$$\sigma W_0 = \bar{c}_{i,\max} RT \ln [(1 - \bar{\theta}_i)\bar{\gamma}_*]. \qquad (20)$$

The advantage of the OTA vacancy model is not only that the theory of bulk solutions can be applied to the sorption phase, but also that a general adsorption isotherm equation can be obtained relatively simply (without the need to integrate the Gibbs adsorption equation) by solving Eqns.(20) and (7) simultaneously after writing the latter in a form appropriate to the adsorbate A:[17]

$$\mu^0_A + RT \ln c_A \gamma_A = \bar{\mu}^0_A + RT \ln \bar{x}_A \bar{\gamma}_A - s_A \sigma. \qquad (21)$$

We note that the chemical potential of the sorbent changes during sorption, but $\bar{\phi}_*$ according to (19) remains constant for all values of $\bar{\theta}_i$. Therefore the vacancies cannot be treated as formally analogous to the sorbent, and the latter is not one of the components of the sorption solution in the OTA model.

To conclude this discussion of the model of the sorption solution we need to examine the precise definition of the limiting adsorption value.

If the $\bar{c}_{0i}$ values are found by extrapolating the linearised adsorption isotherm equations to $c_i \to \infty$ (for gases) or to $c_i = c_{is}$ (for a saturated vapour) they give only an approximate indication of the limiting adsorption under the given conditions, since the equations do not apply for $\bar{\theta}_i \to 1$. These values are termed apparent limiting adsorptions to distinguish them from the true values ($\bar{c}'_{0i}$) obtained by direct physical measurements (for example, at $c_i = c_{is}$). The latter values are of the utmost importance in studies of the physical properties of sorption solutions. In the case of delocalised adsorption both $\bar{c}_{0i}$ and $\bar{c}'_{0i}$ are, of course, functions of temperature.

The proponents of the osmotic theory of solutions[14-17] suggest that the limiting adsorption of a gas, vapour, or liquid should be treated as the maximum achievable adsorption, consisting of the maximum possible number of sorbate molecules close-packed in the sorption volume:

$$\bar{c}_{i,\max} = W_0/\bar{v}_{i,\min}. \qquad (22)$$

An obvious disadvantage of introducing $\bar{c}_{i,\max}$ is the need to evaluate this quantity from adsorption measurements. This difficulty was satisfactorily overcome[17], however, by calculating the molar volume of the substance subjected to maximum compression ($\bar{v}_{i,\min}$) from the parameter σ_∞ (the intermolecular interaction potential).

The use of the maximum adsorption values offers the obvious advantage that these quantities are independent of temperature, but the calculation of $\bar{c}_{i,\max}$ by Eqn.(22) is complicated and indeterminate to some extent, and the worth-whileness of introducing the quantity $\bar{c}_{i,\max}$ into the analysis of conventional adsorption equilibria requires

further discussion. Of course, the validity of the thermodynamic analysis is unaffected by whether the chosen model of the sorption solution does or does not rely on the quantities $\bar{c}_{0i}$ and $\bar{c}_{i,\max}$.

We shall now briefly examine recent developments in the thermodynamic theories of sorption based on different models of the sorption solution.

III. THE STOICHIOMETRIC THEORY OF ADSORPTION

1. Adsorption of Pure Substances

From Eqn.(13) or (14), using Eqn.(4), we can easily obtain a general isotherm equation for one-component adsorption[6,22]:

$$\bar{K}_A = \beta_A (\bar{c}_A\gamma_A)^{\beta_A}/(c_A\gamma_A)^{\beta_A}(\bar{c}_{0A} - \bar{c}_A)\,\bar{\gamma}_R = \bar{K}'_A\bar{\gamma}_A^{\beta_A}/\bar{\gamma}_R. \qquad (23)$$

Since $d\bar{c}_A = -\beta_A d\bar{c}_R$, we can write (for P, T = const)

$$\bar{c}_A\, d\ln\bar{\gamma}_A + \bar{c}_R\, d\ln\bar{\gamma}_R + (1 - 1/\beta_A)\, d\bar{c}_A = 0 \qquad (24)$$

and eliminate $\bar{\gamma}_R$ from (23):

$$\left(\frac{\bar{K}_A}{\beta_A\bar{c}_{0A}^{\beta_A-1}}\right)^{1/\beta_A} = \bar{K}'_A = \frac{\bar{c}_A\bar{\gamma}_A}{c_A\gamma_A(\bar{c}_{0A} - \bar{c}_A)}\exp\left[\int_0^{\bar{c}_A}\left(\frac{\bar{c}_A}{\bar{c}_{0A} - \bar{c}_A}\right) d\ln\bar{\gamma}_A\right]. \qquad (25)$$

From the general equations (23) and (25) we can obtain special formulae for specific types of $\bar{\gamma}_i = f(c_i)$ relationship, chosen on the basis of various theories of solutions (e.g. the Hill equation, the Fowler and Guggenheim equation, etc.[22]). The following three cases are the most interesting.

1. For ideal adsorption (γ_A, $\bar{\gamma}_A$, $\bar{\gamma}_R = 1$, and therefore $\beta_A = 1$) Eqns.(23) and (25) reduce to the Langmuir equation.

2. If the sorption solution consists of non-interacting particles of equal size [$\Delta U_{i-j} = 0$, Eqn.(18)] we have

$$\bar{\gamma}_A = \exp\left[\frac{\bar{c}_R(s_R - s_A)}{W_0}\right] = \exp\left[\frac{\beta_A - 1}{\beta_A\bar{c}_{0A}}(\bar{c}_{0A} - \bar{c}_A)\right], \qquad (26)$$

and Eqn.(25) reduces to

$$\bar{K}'_A = \bar{K}_A \exp\left[\frac{\beta_A - 1}{\beta_A}\right] \Big/ \beta_A = \bar{c}_A^{\beta_A}/(c_A\gamma_A)^{\beta_A}(\bar{c}_{0A} - \bar{c}_A), \qquad (27)$$

which can be linearised (for $\gamma_A = 1$) in order to evaluate β_A.

Eqn.(27) has been applied[19] to published data claimed to be in satisfactory agreement with the Langmuir isotherm. Values of β_A differing significantly from unity were obtained, and it was shown that Eqn.(27) offers a better description of the experimental results. Exactly as required by Eqn.(10), the quantities $\beta_A : \beta_B : \beta_i$ were found to be in the same ratio as $\bar{c}_{0A} : \bar{c}_{0B} : \bar{c}_{0i}$, a positive confirmation of the validity of the basic assumptions of the STA. Hence the β_i values could be calculated from the expressions

$$\beta_i = \beta_j\bar{c}_{0i}/\bar{c}_{0j}. \qquad (28)$$

If an adsorbate to which Eqn.(27) is strictly applicable on the given sorbent cannot be found, the parameter β_j for any adsorbate is evaluated approximately by Eqn.(27) and all the other β_i values are found by Eqn.(28).

3. As was pointed out by Bering and Serpinskii[15], in the sorption of various adsorbates on microporous adsorbents the $\bar{\gamma}_i = f(\bar{c}_i)$ relationship can often be written

$$\bar{\gamma}_A = \bar{c}_A^{g_A-1}, \quad \bar{\gamma}_R = \bar{c}_R^{g_R-1}, \qquad (29)$$

where g_A and g_R are constant for $0 < \bar{c}_i < \bar{c}_{0i}$, and $g_i \to 1$ for $\bar{c}_i \to \bar{c}_{0i}$. Inserting (29) into (25) leads to the Kisarov equation[22] [since according to Eqn.(24) $g_R = \beta_A g_A$]:

$$\bar{c}_A = (\bar{K}_A/\beta_A)^{1/g_R}\bar{c}_{0A}c_A^{1/g_A}/[1 + (K_A/\beta_A)^{1/g_R}c_A^{1/g_A}], \qquad (30)$$

and after replacing $\bar{c}_{0A}$ by $\bar{c}_{A,\max}$ it leads to the corresponding equation of the osmotic theory of adsorption[15]. In spite of a statement to the contrary in Ref.15, Eqn.(30) describes a more general case of sorption solution, with components of unequal size ($\beta_A \neq 1$).

If the special forms of Eqn.(25) cannot be applied satisfactorily to specific experimental results it becomes necessary, in order to use (23) or (25), not only to determine β_i from Eqn.(27) or (28) but also to evaluate $\bar{\gamma}_i(\bar{c}_i)$ and $\bar{K}_i$ from the experimental data. This problem has been resolved[8] by simultaneous solution of (23) and (24) using Eqn.(6) for the standard states.

If the temperature dependence of the adsorption is known over small temperature ranges, in which β_i can be assumed to be independent of T, full thermodynamic information on the sorption system can be extracted from the conventional equations of chemical thermodynamics. In this case it is advantageous to replace $\bar{c}_{0i}$ by $\bar{c}_{i,\max}$ in Eqn.(10) and in the following equations, thus making β_i strictly independent of temperature.

2. Adsorption of Mixtures

To simplify the treatment we shall confine the discussion to the adsorption of binary mixtures. In this case we obtain from (13) or (14) and (4) general adsorption isotherm equations in the form of[6,22]

$$\bar{K} = \frac{\bar{c}_A\bar{\gamma}_A(c_B\gamma_B)^{\beta}}{c_A\gamma_A(\bar{c}_B\bar{\gamma}_B)^{\beta}} = K\frac{\bar{\gamma}_A\bar{\gamma}_B^{\beta}}{\gamma_A\bar{\gamma}_B^{\beta}} = K'\frac{\bar{\gamma}_A}{\bar{\gamma}_B^{\beta}}, \qquad (31)$$

$$\bar{K}_A = \frac{(\bar{c}_A\bar{\gamma}_A)^{\beta_A}}{(c_A\gamma_A)^{\beta_A}(\bar{c}_{0A}/\beta_A - \bar{c}_A/\beta_A - \bar{c}_B/\beta_B)\,\bar{\gamma}_R}. \qquad (32)$$

The parameter β is easily determined according to (10) or (16):

$$\beta = \bar{c}_{0B}/\bar{c}_{0A}. \qquad (33)$$

If molecular sieve effects are present we proceed as in Refs.18 and 21. We should stress that Eqn.(31) applies for any level of coverage of the sorbent by the sum of the adsorbates ($\bar{\theta}_{A+B}$), and also for multi-component adsorption. In the latter case it offers greater generality than other similar equations proposed earlier by various authors for the sorption of binary liquid solutions (i.e. for $\bar{\theta}_{A+B} = 1$). For specific types of $\bar{\gamma}_i = f(\bar{c}_i, \bar{c}_j)$ relationship we can easily obtain from (31) or (32) the isotherms for adsorption from binary mixtures proposed by Frumkin, Damaskin, and others[22].

In the special case of non-interacting particles of different size [$\Delta U_{i-j} = 0$ in an equation analogous to (18)] the quantities $\bar{\gamma}_i$ in a three-component sorption solution can be defined by analogy with (26), and Eqn.(32) then becomes

$$\bar{K}'_A = \bar{K}_A e^{\beta_A - 1} = \bar{c}_A^{\beta_A}/(c_A\gamma_A)^{\beta_A}(\bar{c}_{0A}/\beta_A - \bar{c}_A/\beta_A - \bar{c}_B/\beta_B), \qquad (34)$$

which can be treated as a generalisation of the Langmuir equation for delocalised adsorption of molecules of different size, reducing to the Langmuir equation when the mixture being sorbed consists of molecules of equal size with $\beta_A = \beta_B = 1$ and $\gamma_A = 1$.

Since in binary adsorption $\bar{\gamma}_i = f(\bar{c}_i, \bar{c}_j)$, the calculation of $\bar{\gamma}_i$ from experimental data is carried out most simply along the $\bar{\theta}_R$ = const. sections. Equations obtained as described above for any value of $\bar{\theta}_R$ = const. are given in Ref.8. In that work[8] all the calculations were carried out from the $\ln K' = f(\bar{\theta}_A)_{\bar{\theta}_R = \text{const}}$ relationship and from the adsorption isotherms of the individual components. We note that the $\bar{K}$ values [which are independent of $\bar{\theta}_R$ under the chosen

standard conditions (6)] can be calculated only from the individual sorption isotherms, since according to (15) and (16) we have

$$\overline{K} = (\overline{K}_A/\overline{K}_B)^{1/\beta_A} \quad (35)$$

or in principle they can be calculated by any analogous method[20].

Since the parameter β (unlike β_A) is practically independent of temperature[18] the temperature dependence of $\overline{K}$ or K can be used to obtain full thermodynamic information on the sorption systems of interest by applying the conventional equations of chemical thermodynamics.

IV. THE OSMOTIC THEORY OF ADSORPTION

1. Adsorption of Pure Substances

By using the concept of an osmotic equilibrium[15-17] we can easily obtain a general isotherm for individual adsorption. This involves inserting into (21) the expression for σ from (20):

$$\overline{K}_A = \bar{c}_A\bar{\gamma}_A/c_A\gamma_A(\bar{c}_{A,max} - \bar{c}_A)\,\bar{\gamma}_*. \quad (36)$$

By comparing this equation with (23) we note that (36) is a special case of (23) for $\beta_A = 1$. This is a direct consequence of the greater generality of the sorption solution model used in the STA.

Using (24) to eliminate $\overline{\gamma}_A$ (with $\beta_A = 1$) we can rewrite Eqn.(36) as[17]

$$c_A\gamma_A = \frac{\bar{\theta}_A}{\overline{K}_A(1-\bar{\theta}_A)}\exp\left[-\frac{\ln\bar{\gamma}_*}{\bar{\theta}_A} - \int_0^{\bar{\theta}_A}\frac{\ln\bar{\gamma}_*}{\bar{\theta}_A^2}\,d\bar{\theta}_A\right], \quad (37)$$

which is identical to the corresponding Eqn.(25) of the STA if $\overline{\gamma}_*$ is replaced by $\overline{\gamma}_A$ in Eqn.(37) and allowance is made for the fact that $\overline{\gamma}_A$ is referred to different concentration scales in Eqns.(25) and (37) [see Eqn.(6)].

We shall examine three special cases.

1. For ideal adsorption $\overline{\gamma}_* = 1$, and Eqn.(37) reduces to the Langmuir equation ($\gamma_A = 1$).

2. If the vacancy solution is regular, we can write from the theory of regular solutions $\ln\overline{\gamma}_* = \bar{\alpha}\bar{\theta}_A^2$ (where α is a constant), and (37) simplifies to the Fowler-Guggenheim equation

$$c_A\gamma_A = \frac{\bar{\theta}_A}{\overline{K}_A(1-\bar{\theta}_A)}\exp[-2\alpha\bar{\theta}_A]. \quad (38)$$

3. The most widely used equation is derived from (37) as described above by using Eqn.(29) (since $s_A = s_*$, it follows that $g_* = g_A$):[15,16]

$$c_A\gamma_A = \bar{c}_A^{g_*}/\overline{K}_A(\bar{c}_{i,max} - \bar{c}_A)^{g_*}, \quad (39)$$

This equation was first obtained in the OTA[15,16] by a strict thermodynamic argument. For adsorption from an ideal gas phase Eqn.(39) can be recast as

$$\ln P_A = \ln P_{A(\bar{\theta}_A=0,5)} + g_A\ln\frac{\bar{\theta}_A}{(1-\bar{\theta}_A)}, \quad (40)$$

which allows the parameters to be determined from the experimental isotherm[15,16]. As was pointed out above, Eqns.(30), (39), and (40) accurately describe the individual adsorption isotherms of many substances on microporous sorbents.

An important and interesting application of the OTA of a single substance was the successful development of a thermodynamic theory of the change in size of microporous adsorbents resulting from sorption[14,23-25]. Correctly denying the thermodynamic validity of Bangham's theory, based on the assumption that $\bar{\phi}_R = \text{const}$, Bering and coworkers[23-25] obtained some fairly strict expressions predicting both an increase and a decrease in the particle size of adsorbents as a result of adsorption.

2. Adsorption of Mixtures

The application of the OTA to mixtures causes a number of difficulties arising from the chosen model of the sorption solution. Thus, in the simplest case of binary sorption the molar volume of a vacancy [see Eqn.(17)] varies as follows with the composition of the sorption solution[17,26,27]:

$$s_*(\bar{z}) = s_A\frac{\bar{c}_A}{\bar{c}_A+\bar{c}_B} + s_B\frac{\bar{c}_B}{\bar{c}_A+\bar{c}_B} = s_A\bar{z}_A + s_B\bar{z}_B. \quad (41)$$

The desired isotherm equation is obtained by solving Eqns.(20) and (21) simultaneously[17]. In this case Eqn.(20) can be combined with (41) to give, for a solution of constant composition $\bar{z}_A$,[27]

$$\sigma W_0 = \frac{W_0}{s_A\bar{z}_A + s_B\bar{z}_B}RT\ln\bar{x}_*\bar{\gamma}_* = \bar{c}_*^0(\bar{z})\,RT\ln[(1-\bar{\theta}_A-\bar{\theta}_B)\,\bar{\gamma}_*], \quad (42)$$

where $\bar{c}_*^0$ is the limiting concentration of vacancies in the sorbent, with a molar volume corresponding to the composition $\bar{z}_A$.

Inserting σ from (42) into (21) yields the adsorption isotherm equation[17], which can be written as

$$\overline{K}_A = \bar{c}_A\bar{\gamma}_A\bar{c}_{0A}/c_A\gamma_A[(1-\bar{\theta}_A-\bar{\theta}_B)\,\bar{\gamma}_*]^{1/\beta_A(\bar{z})}\cdot\bar{c}_*^0(\bar{z}), \quad (43)$$

where $\bar{c}_*^0(\bar{z})$ and $\beta_A(\bar{z})$ depend on the composition ($\bar{z}$) of the sorption solution. Eqn.(43) is formally analogous to the corresponding Eqn.(32) of the STA (allowing for the fact that the $\overline{\gamma}_i$ values are referred to different concentration scales), but it is less convenient than the latter in that it depends on the variables $\beta_A(\bar{z})$ and $\bar{c}_*^0(\bar{z})$, which complicates its practical application even when the $\overline{\gamma}_i = f(\bar{x}_A, \bar{x}_B)$ relationships are known. We note that since $\beta_A(\bar{z})$ and $\beta_B(\bar{z})$ have identical dependences on $\bar{z}$ we can obtain Eqn.(31) by dividing the two equations (43) written for A and B respectively by each other, since $\beta_B(\bar{z})/\beta_A(\bar{z}) = \beta = \text{const}$.

General methods of finding the activity coefficients of the components of the sorption solution are not discussed in the OTA papers, but they are exactly analogous to the methods described above for the STA. The application of the OTA to the general case of adsorption from a multi-component mixture could be greatly simplified by abandoning the conditions $s_* = s_A$, $s_* = s_B$ for one-component adsorption and by assuming (as in the STA) that $s_* = \text{const} \neq s_A \neq s_B$. In particular, Eqn.(43) would correspond exactly to Eqn.(32).

V. ADSORPTION AND THE ENERGY NON-UNIFORMITY OF THE SORPTION CENTRES OF THE SORBENT

In the previous sections we have discussed adsorption equilibria in general, using the activity method to allow (in terms of the activity coefficients of the components of the sorption solution) for molecular interactions and for the energy non-uniformity of the sorption centres of the sorbent. It would be very useful, however, to have a sorption isotherm equation free from the constraints of the activity method. One variant of this approach, proposed by Zel'dovich[28] in 1935, has been examined intensively in recent years (see, for example, Refs.29–39). The basic concept is to set up a general isotherm for the adsorption of one substance

[$\theta(P)$] from local adsorption isotherms applying to energetically uniform sorption centres [$\phi(P, \varepsilon)$] together with a distribution function of the adsorption centres in free energy of adsorption [$\chi(\varepsilon)$]. In the case of a discrete distribution[29,30] we can write

$$\bar{\theta}(P) = \sum_i f_i \varphi_i(P, \varepsilon_i), \tag{44}$$

where f_i is the fractional number of centres having an energy ε_i.

If the function $\chi(\varepsilon)$ is assumed to be continuous we replace (44) by the equation[28-32]

$$\bar{\theta}(P) = \int_0^\infty \varphi(P, \varepsilon)\chi(\varepsilon)\,d\varepsilon. \tag{45}$$

Lastly, for the adsorption of a mixture of i components we have[33-35,38,39]

$$\sum_{i=1}^{i} \bar{\theta}_i(P_n) = \int_{\Delta(n)} \sum_{i=1}^{i} \varphi_i(P_n, \varepsilon)\chi(\varepsilon)\,d\varepsilon, \tag{46}$$

where $n = 1, 2, 3, \ldots, i$, integration is carried out in i-dimensional space, $\sum_{i=1}^{i}$ denotes the total and the local isotherm for the adsorption of the i components of the mixture, and $\bar{\theta}_i$ and ϕ_i are the total and the local adsorption isotherm of the i-th component.

Unfortunately, the solution of the problem in a general form meets a number of fundamental difficulties[29,34]. Since only the total isotherm [$\bar{\theta}(P)$] is available to the investigator Eqns.(44) and (45) do not offer a unique solution of the problem, because a given $\bar{\theta}(P)$ relationship can be obtained by combining $\phi(P, \varepsilon)$ functions of different types, and hence by combining different $\chi(\varepsilon)$ distribution functions. For example, a given $\bar{\theta}(P)$ isotherm can be interpreted as the the sum of a number of Langmuir isotherms for a non-uniform surface, or as an adsorption isotherm for substantial intermolecular interactions on a practically uniform surface. The distribution function $\chi(\varepsilon)$ characterises the adsorbate–adsorbent system rather than the adsorbent. Therefore Eqn.(45) cannot be used to calculate the adsorption isotherms of several adsorbates from the $\chi(\varepsilon)$ function obtained for any one adsorbate. The general solution of (46) is extremely complex[34], and therefore the problem is often simplified by considering the case of a constant difference between the free energies of the adsorbates on the different types of adsorption centre ($\varepsilon_i - \varepsilon_j = \text{const}$).[30,33,34]

Because of these difficulties the approach is usually confined to systems in which the adsorption is obviously localised and the local isotherm can be described with reasonable accuracy by the ideal Langmuir equation. In this case the form of the $\chi(\varepsilon)$ function can be established with great confidence, and the method can be used to solve various problems[35-37]. For example, an interesting application was the derivation of a general equation for the localised adsorption of a mixture on a non-uniform surface and its use in a formal kinetic analysis of heterogeneous catalytic reactions[37,39].

Nevertheless, the wide application of this approach in the description and calculation of sorption equilibria and in the determination of $\chi(\varepsilon)$ functions still presents many problems, and requires substantial further developments.

VI. CALCULATION OF THE EQUILIBRIUM SORPTION CHARACTERISTICS FROM THE MINIMUM AMOUNT OF EXPERIMENTAL INFORMATION

In addition to the strict thermodynamic analysis of adsorption equilibria, another important function of the theory is to develop methods of calculating sorption equilibria for many different systems from the smallest possible volume of experimental information. As we have already pointed out the problem could be solved, in principle, by the methods of molecular–statistical thermodynamics, but unfortunately the difficulties are such as to limit the practical application of these methods to the simplest systems for the time being. Therefore the practical solution of problems usually involves additional, non-thermodynamic relationships derived from experimental data or from very simple (and therefore approximate) physical models of the system of interest. The most successful applications of this approach have been in adsorption from a one-component gas or vapour phase.

1. Calculation of Individual Adsorption Isotherms

The most important advances in the description of isotherms for the individual adsorption of vapours on microporous sorbents were achieved by the theory of volume filling of micropores (TVFM), developed by Dubinin and his coworkers[40-42]. This theory is founded on the temperature-independence of the characteristic free energy of adsorption (E): a thermodynamic analysis shows that this condition can obtain only if the entropy of adsorption is negative, and this restricts the region of validity of the theory to coverages $\bar{\theta}_i > 0.1$.[42]

Within these limitations the equations of the TVFM, applied to monodisperse microporous sorbents and ignoring the non-ideality of the vapour phase, have the form[42-44]

$$\lg \bar{c}_i = \lg \bar{c}_{0i} - \frac{BT^n}{\beta_{i(\mathrm{af})}^n}[\lg(P_{is}/P_i)]^n, \tag{47}$$

where

$$B = (2.303R/E_0)^n; \quad \bar{c}_{0i} = W_0/\bar{v}_{0i} = \bar{c}_{0i}^0 \exp[-\alpha_i(T - T_0)] \tag{48}$$

($\bar{c}_{0i}^0$ is the limiting adsorption at $T = T_0$).

If the adsorbent has a wide distribution of pore radii (carbon sorbents) or of adsorption energies (zeolites used for small adsorbate molecules) an approximate solution is obtained by aggregating two structures with different values of the parameters n and E_0 [40-42] (corresponding to the subscripts 1 and 2):

$$\bar{c}_i = \bar{c}_{0i(1)} \exp\left[-\frac{RT \ln P_{is}/P_i}{\beta_{i(\mathrm{af})}E_{01}}\right]^{n_1} + \bar{c}_{0i(2)} \exp\left[-\frac{RT \ln P_{is}/P_i}{\beta_{i(\mathrm{af})}E_{02}}\right]^{n_2}. \tag{49}$$

For normal micropores of different size $n_1 = n_2 = 2$; for a combination of normal and super-micropores $n_1 = 2$, $n_2 = 3$; for the sorption of small molecules on type A and X zeolites $n_1 = 2$ and $n_2 = 3$ or 4.[41] The n values in (47) undergo similar changes.

Since

$$\beta_{i(\mathrm{af})} = E_i/E_0, \tag{50}$$

where E_0 is the characteristic free energy for vapour adsorption taken as a standard ($\beta_{0(\mathrm{af})} = 1$), it follows that the adsorption isotherms of a substance for various temperatures (lower than T_{cr}) can be calculated by the TVFM from the isotherm measured at a single temperature: hence the thermodynamic adsorption functions and the adsorption isotherms of other adsorbates at different temperatures can also be calculated if $\beta_{i(\mathrm{af})}$ is determined by Eqn.(50).

For calculations of the highest precision $\beta_{i(\mathrm{af})}$ should be obtained from experimental data. For this we need one point on the isotherm of the i-th adsorbate. In a somewhat rougher approximation the $\beta_{i(\mathrm{af})}$ values for microporous carbons can be expressed as the ratio of the parachors of the i-th and the standard adsorbate[43].

Since Eqns.(47) and (30) describe the same experimental data[44], the TVFM can be regarded as a special case of the STA, applicable to systems in which the $\bar{\gamma}_i = f(\bar{c}_i)$ relationships are described by Eqns.(29) with $g_i = g_R = \text{const}$. Under these conditions $\beta_{i(af)}$ allows for the difference not only in the size of the adsorbate molecules but also in the energy of their interaction with the adsorbent [through Eqn.(50)]. Hence[22]

$$1/\beta_{i(af)} = \beta_i \beta_{en} / \beta_j, \qquad (51)$$

where β_j is the stoichiometric coefficient for the standard substance, and the coefficient β_{en} characterises the difference in interaction energy between the two adsorbates and is close to unity for the sorption of substances of the same type. In this case the $\beta_{i(af)}$ values can be calculated by Eqn.(28), as confirmed by existing experimental data. We note that in systems of this type the $\bar{\gamma}_R = f(\bar{c}_R)$ relationship is the same for all adsorbates.

Dubinin and coworkers[40-42] have discussed in detail the methods of finding the parameters of Eqns.(47) and (49), and have given several examples illustrating the wide applications of the TVFM to the calculation of individual adsorption isotherms and of the corresponding thermodynamic functions. More recently[45] the possibility of extrapolating the results by 50–60 K (to the region of $T > T_{cr}$) was demonstrated.

We must stress that the TVFM offers important information on the structure of the micropores (W_0) and on the adsorption energy (E_0) for microporous adsorbents of different types. This is shown most clearly in studies of adsorption on zeolites, when an independent determination of W_0 by X-ray methods is possible.

The ability of the TVFM to describe experimental data has been improved[46,47] by using n as a variable parameter in Eqns.(47) and (49), but Dubinin showed that this approach is unsatisfactory[48,49]. In the case of carbons the agreement between experimental and calculated isotherms is worse for n values other than $n = 2$: the values of W_0 and E_0 are no longer constant, and the calculated differential heats of adsorption are very different from those measured calorimetrically.

Industrial carbon adsorbents can have a polydisperse micropore structure. Stoeckli[50] tried to apply Eqn.(47) to sorbents of this type, assuming a normal gaussian distribution to describe the distribution of micropore volumes with respect to the parameter B of Eqn.(47). However, experimental data for the sorption of nitrogen, xenon, benzene, and n-butane at different temperatures on E-02 active carbon[50] were shown[48] to be described with equal precision by the Stoeckli equation and by Eqn.(49) with $n_1 = n_2 = 2$, and therefore the two-term equation (49) of the TVFM is a fully acceptable approximation.

Several workers have pointed out that the fundamental postulates of the TVFM are also satisfied (to different extents) for equilibria in other adsorption systems. Thus, Eqn.(47) with $n = 2$ was shown[51-54] to be applicable to adsorption on carbons from aqueous solutions of sparingly soluble organic compounds if P_{is}/P_i is replaced by $\tilde{c}_{is}/\tilde{c}_i$ (where $\tilde{c}_{is}$ is the solubility at the given temperature). A method of determining the micropore volume from adsorption data for systems of this type was developed on this basis[52].

Gur'yanov and coworkers[55,56] have shown that Eqn.(47) can be used to describe multimolecular adsorption and to determine the monolayer capacity. With swelling (polymeric) sorbents Eqn.(47) again gives a satisfactory description of the adsorption isotherms, but the parameter n decreases[57,58] as the degree of crystallinity of the polymer decreases from 0.7 to 0.5 (and even to 0.33), and the temperature-independence of the characteristic free energy is retained in the temperature ranges where the structure of the polymeric sorbent remains substantially constant[58]. These results indicate that the basic postulates of the theory of volume filling are more generally applicable than the variant adopted in the classical TVFM, though further experimental and theoretical work is needed to explain in detail and to justify such a generalisation of the theory.

In the STA and the OTA, which do not stipulate a temperature-invariant characteristic energy of adsorption, thermal adsorption equations can be obtained, in principle, for any temperature range, and in particular for $T \gg T_{cr}$, where the equations of the TVFM are not applicable. This problem was analysed in detail in the original papers on the OTA, and the special forms (39) and (40) of the general OTA equation were shown to describe with good precision the adsorption isotherms for microporous sorbents[15-17]. We should point out that the possibility of determining $c_{i,max}$ by Eqn.(22) was realised relatively recently[17]. In the earlier papers from the same laboratory[49,59-61] the quantity $\bar{c}_{i,max}$ was determined as an empirical parameter ($\bar{c}_{i,emp}$) from the experimental adsorption isotherm plotted as $\ln P_i$ against $\bar{c}_i$, which according to Eqn.(40) has an inflection at the point $(\ln P_{i(\bar{\theta}_i = 0.5)}, \bar{c}_{i,emp}/2)$. The temperature independence of $\bar{c}_{i,emp}$, first established experimentally[60], was later proved by a strict thermodynamic argument. Therefore the thermal equation of the OTA is easily obtained from Eqn.(40), since $\ln P_{i(\bar{\theta}_i = 0.5)}$ is the thermodynamic equilibrium constant of the adsorption, and the function $g(T)$ should be the same as in $\ln \bar{\gamma}_*$:[59]

$$\ln P_i \gamma_i = a + a' \ln\left(\frac{\bar{c}_i}{\bar{c}_{i,emp} - \bar{c}_i}\right) - \left[b + b' \ln\left(\frac{\bar{c}_i}{\bar{c}_{i,emp} - \bar{c}_i}\right)\right] T^{-1}. \qquad (52)$$

When $\bar{c}_i = \text{const}$ Eqn.(52) gives the adsorption isostere equation:

$$\ln P_i \gamma_i = \bar{a} - \bar{b} T^{-1}. \qquad (53)$$

The determination of the five parameters of Eqn.(52) (a, a', b, b', $\bar{c}_{i,emp}$) is discussed in Refs.49 and 59. We know[59-61] that the replacement of $\ln P_i \gamma_i$ by $\ln P_i$ in Eqns.(52) and (53) extends the application of (53) to a large number of systems over a wide temperature range, in spite of the temperature dependence of the enthalpy of adsorption. This fact justifies calculation of the effect of temperature on adsorption over wide temperature ranges, as was demonstrated[59-61] for the adsorption of Ar and Xe on NaX zeolite at 150 K $\leq T \leq$ 600 K. Eqn.(52) can describe, in principle, systems in which the heat of adsorption decreases or increases with coverage, though the latter case is not covered by the equations of the TVFM.

Thus the thermal equations of the TVFM and of the OTA are mutually complementary, and depending on the specific features of the practical problem the effect of temperature on the sorption can be calculated by one of the equations given above. We note that the adsorption isotherms of several adsorbates can be calculated, in principle, from the adsorption isotherm of one substance within the framework of the STA. Appropriate methods of realising this possibility are currently being developed.

2. Calculation of the Equilibrium Characteristics of the Adsorption of Binary Mixtures

Studies of the calculation of adsorption equilibria in multicomponent mixtures have been confined almost entirely to binary systems. Many papers have dealt with the possibility

of calculating the isotherm for adsorption from a binary mixture, i.e.

$$\bar{c}_i = f(c_1, c_2) \tag{54}$$

from the experimental isotherms for the adsorption of the individual components

$$\bar{c}_1 = f_1(c_1), \quad \bar{c}_2 = f_2(c_2). \tag{55}$$

Progress in this direction has been discussed in recent review articles[62-64], and we shall not dwell on that work: we shall only mention that in the final analysis a solution of the problem (54), (55) can be found only for ideal sorption solutions or for solutions in which $\Delta U_{i-j} = 0$.[19] In the general case we need additional information on the adsorption of the binary mixture itself. One variant of this approach was recently examined in the OTA for the special case of $g = \text{const}$ when $z = \text{const}$[17,26,27]. The present writer favours a solution of the problem on the basis of experimental information on the sorption of one, two, or three standard mixtures on the given sorbent, i.e. calculation by Eqn.(31) of the values

$$K = f(\bar{c}_A, \bar{c}_B) \tag{56}$$

for a large number of different mixtures of adsorbates from the experimental relationships [Eqn.(56)] for one–three systems and from some properties of the adsorbates (molar volume, dipole moment, polarisability, etc.). Work in this direction is only just beginning, and is limited so far to the accumulation of experimental information and its analysis[6,8,11,12,20,65-68], but the results to date suggest that a solution of the problem (56) will be found.

We should mention two results obtained by the STA which should greatly decrease the need for exploratory experimental work. The first concerns the comparative evaluation of data on the adsorption of binary mixtures from the vapour phase and from the liquid phase on microporous sorbents[20,69].

As we have shown[20], under the standard conditions (6) the thermodynamic constants ($\bar{K}$) and the equilibrium coefficients (K) for sorption from the vapour and the liquid phase are related by the expressions

$$\bar{K}_{vap} = \bar{K}_{(liq)} \frac{\tilde{c}_{0A} (c_{Bs}\gamma_{Bs})^{\beta}}{\tilde{c}_{0B} (c_{As}\gamma_{As})} = \bar{K}_{liq} \frac{K^{\beta}_{B,evap}}{K_{A,evap}}, \tag{57}$$

(where $K_{i,evap}$ are the equilibrium constants for the evaporation of the pure liquids), and

$$K_{vap} = K_{liq} \frac{\tilde{c}_{0A} (c_{Bs}\gamma_{Bs})^{\beta}}{\tilde{c}_{0B} (c_{As}\gamma_{As})} \cdot \frac{\gamma_A \tilde{\gamma}^{\beta}_B}{\tilde{\gamma}_A \gamma^{\beta}_B}, \tag{58}$$

which allow us to calculate $\bar{K}$ and $K = f(\bar{x}_A)$ for sorption from the vapour phase from data for sorption from the liquid phase, and *vice versa*, since γ_i and $\tilde{\gamma}_i$ are usually known or can easily be determined if necessary. We note that calculation by (58) is legitimate, strictly speaking, if $\bar{\theta}_{A+B} = 1$ for sorption from the vapour phase. However, in most cases the $K = f(\bar{x}_A)$ relationships are almost indistinguishable for $\bar{\theta}_{A+B} > 0.8$–0.9,[20,65] and therefore we can use (58) to calculate equilibria in real, practical vapour–adsorbent systems with $\bar{\theta}_{A+B} > 0.8$. From (57) we can easily obtain an equation for reciprocal calculations of the temperature dependence of sorption (for $\bar{\theta}_{A+B} > 0.8$):[20]

$$\Delta H^0_{vap} = \Delta H^0_{liq} + \beta \Delta H^0_{B,evap} - \Delta H^0_{A,evap}. \tag{59}$$

We can easily show, also, that if the separation coefficients (α) are determined for the equilibrium compositions of the phases we have[69]

$$\alpha_{vap} = \frac{\bar{c}_A c_B}{c_A \bar{c}_B} = \frac{\tilde{c}_A c_B}{c_A \tilde{c}_B} \cdot \frac{\bar{c}_A \tilde{c}_B}{\tilde{c}_A \bar{c}_B} = \alpha^{vap}_{liq} \alpha_{liq}. \tag{60}$$

In Refs.20 and 69 Eqns.(57)–(60) are tested on the sorption of several binary mixtures on active carbon and on zeolites, and satisfactory agreement between calculation and experiment is obtained. Thus these expressions offer a substantial reduction in the amount of experimentation needed to optimise the separation and purification of particular mixtures by sorption methods.

According to the STA [see (31) and (60)] the separation coefficient α, which is very important in practice because it characterises the selectivity of the sorbent towards the given mixture of adsorbates, is related to the equilibrium coefficient K by the expression

$$\alpha = K(c_B/\bar{c}_B)^{1-\beta}. \tag{61}$$

Therefore, when K is independent of $\bar{\theta}_{A+B}$ (as is usually the case for $\bar{\theta}_{A+B} > 0.5$–0.8) the separation coefficient can be increased to a useful extent by varying the concentration of the components in the bulk phase. In this case the α values can be calculated over a wide range of pressure. Furthermore, if one of the components (say, A) is present in trace amounts we find[70,71] that for $c_B/\bar{c}_B = \text{const}$

$$\ln \alpha = a + bm, \tag{62}$$

where m is the number of carbon atoms in the molecules of homologues present as trace components, and a and b are constants determined from experimental data for two homologues.

The validity of Eqns.(61) (and hence of the basic assumptions of the STA) and (62) was tested experimentally in a number of sorption systems[65,70,71]. Their use can substantially lighten the task of optimising empirically the conditions of separation by sorption. Of course, the calculation of adsorption equilibria for binary and for multi-component mixtures is a complex problem, still not fully resolved. However, the need to solve this problem has been highlighted by the increasing penetration of sorption methods of extracting, separating, and purifying mixtures in industrial practice, and research in this direction has been intensified.

VII. CAPILLARY PHENOMENA AND INFORMATION ON THE PORE STRUCTURE OF THE ADSORBENT

As was stated above, the thermodynamic analysis of multimolecular adsorption processes (which include the transition from pure sorption processes with a sorption volume of limited capacity to condensation processes) is still an unsolved problem. Nevertheless, detailed studies of multi-molecular adsorption and capillary condensation in mesopores (15 Å < r < 2000 Å) have been applied to the characterisation of the structure of mesopores. The theory of this phenomenon was originally developed by Deryagin in 1940; in 1967 de Boer and Broekhoff introduced an approximate correction for the effect of the adsorption field of the pore walls on the chemical potential of the sorbate in their derivation of a modified Kelvin equation; Brunauer and coworkers followed a somewhat different approach. A detailed discussion of that work, with comprehensive lists of references, can be found in Refs.72–75.

The Deryagin–Broekhoff–de Boer method has been recently improved by Dubinin and coworkers, who also allowed for the dependence of the surface tension on the mean radius of curvature of the liquid meniscus[74,75], and used a more universal form of the equation for the t-curve (which describes the dependence of the mean-square thickness (t) of the adsorption layer in the mesopores on the equilibrium relative pressure P/P_s [76,77]).

Solution of this problem requires an assumption as to the geometrical shape of the pores. Attempts to identify the geometry of the pores from the type of hysteresis loop in the isotherm produced by capillary condensation gave ambiguous results[72,73], and therefore the concept of equivalent cylindrical pores is adopted in most calculations. The problem is formulated in such a way that identical capillary evaporation isotherms are obtained for the real adsorbent (with a complex pore structure) and the equivalent adsorbent (with cylindrical pores). The equivalent pore radius (r) is usually defined as double the ratio of the normal cross-sectional area of the pore to the perimeter of the pore.

The classical method (method I) of analysing the distribution of cylindrical mesopore radii is based on the Kelvin equation

$$r_c = 2\sigma \bar{V}_{ol}/RT \ln (P_{is}/P_i), \quad (63)$$

where r_c is the radius of curvature of the spherical meniscus of the liquid adsorbate, formed in the area between the adsorption layers on the walls of a mesopore of radius r. The thickness (t) of the layers is assumed to be independent of r, and is expressed through the t-curve equation, based on the Harkins and Jura adsorption isotherm[73,74,76]:

$$\ln (P_{is}/P_i) = Mt^{-2} - \varphi(t) \quad (64)$$

where M is a constant parameter and $\phi(t)$ is a correction which can be either constant or weakly dependent on t. Hence, in this model

$$r = r_c + t. \quad (65)$$

In the Deryagin–Broekhoff–de Boer method (method II) the effect of adsorption on capillary evaporation from cylindrical pores is allowed for by the function

$$F(t_e) = \bar{\mu}_t - \tilde{\mu}_t, \quad (66)$$

the chemical potential of the adsorbate being assumed to be a function of the distance (t_e) of the liquid–vapour interface from the pore wall, with the function $F(t_e)$ defined by the t-curve (64). The surface tension of the adsorbate is assumed to be independent of the radius of curvature of the liquid meniscus.

In the method developed by Dubinin and coworkers[73–75] (method III) an additional allowance is made for the dependence of σ on r_c by using the Tolman equation (which can also be obtained by molecular statistics[74])

$$\sigma/\sigma_0 = (1 - 2\omega/\rho)^{-1}, \quad (67)$$

in which σ_0 is the surface tension of the planar liquid surface and ρ is the average effective radius of curvature of the meniscus in a cylindrical pore:

$$\rho = r - t_e. \quad (68)$$

However, a detailed analysis by Dubinin[76] of the capillary evaporation isotherm has shown that whereas all three methods should give the same value of r and $t_e \to t$ for $P_i/P_{is} \to 1$, there is a large difference between the radii calculated by methods I, II, and III for the pores from which desorption occurs under the stated conditions (up to 100–150% [79]), and also between the corresponding values of t_e and t. Calculations by methods II and III gave consistent results in this case. It was also shown[76] that the lack of agreement of calculations for $P_i/P_{is} \to 1$ is due to inadequate description of the adsorption in mesopores by the t-curve (64), and that in many systems it would be better to use a more rational equation of the Halsey type

$$\ln (P_{is}/P_i) = \bar{M} t^{-m}, \quad (69)$$

where $\bar{M}$ and m are constant parameters. By replacing (64) by (69) the discrepancy between calculations by methods I, II, and III at $P_i/P_{is} \to 1$ could be eliminated[76,77].

The equations of method III in this case become[76,77]

$$\ln (P_{is}/P_i) - \bar{M} t_e^{-m} - \sigma_0 \bar{V}_{ol}/RT (r - t_e - \omega) = 0, \quad (70)$$

$$r - t_e = \frac{2\sigma_0 \bar{V}_{ol} (r - t_e)}{RT (r - t_e - 2\omega) \ln (P_{is}/P_i)} + \frac{2\bar{M}}{(r - t_e) \ln (P_{is}/P_i)} \left[\frac{r^{2-m}}{(1-m)(2-m)} - \frac{r t_e^{1-m}}{(1-m)} + \frac{t_e^{2-m}}{(2-m)} \right]. \quad (71)$$

The calculations, described in detail in Refs.74–79, were taken as far as a minimum pore size of 16–17 Å. In the case of these micro-mesoporous sorbents the specific surface area of mesopores ($\bar{S}$, $m^2\ g^{-1}$) was determined independently by the "t/F method", developed and proposed in Refs.79 and 80. Essentially, the method consists in calculating the sorption in micropores by Eqn.(47), subtracting the adsorption calculated by the TVFM from the total adsorption experimentally observed, and thus arriving at the sorption in mesopores only. With other adsorbents $\bar{S}$ was determined also by the BET method.

The total volumes of mesopores calculated by the three methods are almost indistinguishable, but the mesopore surfaces are given more accurately by methods II and III. However, the basic difference between these three methods is in the distribution of mesopore volumes with respect to radius. The effect arises[74] from differences in the dependence of P_i/P_{is}, t, and t_e on the mesopore radius in the three methods of calculation. Thus, for $r > 150$–200 Å the P_i/P_{is} values do not differ significantly in the three methods, but the t_e values in methods II and III are similar but different from t (method I). This means that the correction for the $\sigma(\rho)$ variation (method III) is significant only for $r < 150$–100 Å. The intermediate mesopore region (radii from 100 to 50 Å) is characterised by large differences between the t_e and P_i/P_{is} values calculated by the three methods, the effects becoming even more marked for $r < 50$ Å. In this range of mesopore radii the $\sigma(\rho)$ dependence makes a substantial contribution to the final result and must obviously be included in the calculation. The correction makes the t_e values given by method III smaller than the other values. On changing from method I to method III the mesopore volume distribution curve shifts towards larger radii. The differences are large, and they give rise to large changes in the porosity characteristics which cannot be ignored, even to a rough approximation.

Thus Dubinin's variant of the calculation of the structural characteristics of mesopores is an important development of the method, though it is only a first step in the required direction and needs to be made more precise, especially in the region of 16 Å $< r <$ 30 Å. Furthermore, allowance for the real structure of the mesopores (flat, cylindrical, spherical) may also result in significant changes of the pore radius distribution function[75]. Therefore the structural characteristics obtained by methods I–III are arbitrary to a greater or lesser extent, and allowance for the real structure of the mesopores has become the most pressing of the theoretical problems.

* * *

This brief review of the present state of the thermodynamic theory of adsorption shows that substantial progress has been made in recent years towards the development of a strict thermodynamic theory of sorption. A full

thermodynamic analysis of various sorption systems is possible by the OTA, and even more so by the STA.

The TVFM, and also the OTA and the STA, have led to successful developments of methods of calculating sorption equilibria for individual adsorption from a single experimental isotherm. Important advances in this direction have been made also for the adsorption of mixtures.

Progress in methods of calculating mesopore structures from capillary condensation phenomena has been substantial.

Nevertheless the increasing application of sorption methods in the chemical industry has created a need for even greater scientific efforts in the study of two-component and multi-component adsorption. In this context the development of methods of calculating adsorption equilibria in multi-component systems from the minimum amount of experimental information becomes a major objective of the theory of adsorption.

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