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Thermodynamics of Adsorption on Deformable Adsorbents

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Abstract—A new approach to constructing adsorption thermodynamics that provides the derivation of rigorous thermodynamic relationships for any adsorption system, particularly for a system with a deformable adsorbent, is proposed. Expressions for the thermodynamic functions of an adsorption system in the form of an arbitrary control volume containing the adsorbent and the adsorbed gas are derived. In the derived expressions, the role of adsorption is played by the total adsorbate content in the system. If the control volume boundaries are set appropriately, this quantity is identical to absolute adsorption.

INTRODUCTION

During adsorption, all adsorbents undergo deformation [1–3]. In some cases, deformations can be considerable and must be accounted in thermodynamic descriptions of adsorption systems [4–6]. Although this fact has long been known [7, 8], an adequate thermodynamic theory at the present time is absent. Conventional approaches to constructing adsorption thermodynamics are based on the assumption that the adsorbent is undeformable [9–11].

A new approach to constructing adsorption thermodynamics is proposed in this work. The approach allows to obtain all thermodynamic characteristics of an arbitrary adsorption system, particularly one with a deformable adsorbent. At the heart of the approach is a passage to independent differentials in the initial fundamental equation. For example, suppose that the initial equation is the Helmholtz free energy equation

$$dF = -SdT - PdV + \mu dn. \tag{1}$$

Since the adsorption layer is in equilibrium with the gas phase, differentials dT, dV, and dn are not independent here. Therefore, considering the volume as a function of T and n, we rewrite this equation in the form

$$dF = -\left(S + P\frac{\partial V}{\partial T}\right)dT + \left(\mu - P\frac{\partial V}{\partial n}\right)dn. \tag{2}$$

All required relationships are then derived using standard methods.

Another difference between the proposed approach and conventional approaches is that the initial equation does not contain a term describing the change in thermodynamic functions caused by altering the surface area or weight of the adsorbent. The initial equation is thus absolutely rigorous and can be applied to every adsorption system without exception. All of the resulting relationships are the same as in the conventional approaches. If, by analogy with conventional approaches, an additional term is included in the initial equation, the applicability of this equation becomes limited. In particular, if the adsorbent surface area is used as an additional external variable, this equation cannot be applied to systems in which the surface area is not determined exactly (e.g., systems with a microporous adsorbent). If the adsorbent weight is used as an additional external variable, this equation cannot be applied to systems in which the condensed phase cannot be treated as a solution (e.g., systems with a macroporous adsorbent).

SINGLE-COMPONENT ADSORBATE

The thermodynamic system under discussion is an arbitrary control volume that contains adsorbent and the adsorbed gas. The distance of the control volume boundaries from the adsorbent should be sufficient to exclude the effect of the adsorption field on the gas molecules. The pressure at the system boundary will in this case be identical to gas pressure P at a distance from the adsorbent (assuming that only the adsorbate exerts pressure on the condensed phase). Suppose that the system is open with respect to changes in the amount of the adsorbate and closed with respect to changes in the amount of the adsorbent. The com-

bined equation of the first and second laws of thermodynamics for this system is

$$dE = TdS - PdV + \mu dn. \tag{3}$$

Here, E, S, V, and T are the system energy, entropy, volume, and temperature, respectively; μ is the chemical potential of the gas; and n is the number of gas moles in the system.

In some particular cases, the system boundaries must be specified so as to meet two conditions, whenever possible. First, since the point at issue is adsorption, it is necessary to ensure a minimal amount of nonadsorbed gas in the system. Second, the system volume as a function of temperature and pressure should be available for experimental determination. It is not always possible to meet these two conditions simultaneously. For example, if the adsorbent is a continuous microporous solid, we may assume that the system boundary is the outer boundary of the adsorbent. In this case, both conditions are met: the amount of adsorbate n in the adsorption system is almost identical to the absolute adsorption and the system volume is measurable. If the adsorbent contains macropores, the system boundary cannot be specified so as to meet both conditions. If the outer boundary of the adsorbent is assumed to be the only boundary, the first condition will not be met because the macropores will contain a significant amount of nonadsorbed gas. If macropores are not included in the system's composition, the second condition will not be met because the macropore volume as a function of temperature and pressure cannot be experimentally determined for a deformable adsorbent. The decision of what to do in these situations must be made separately in each particular case. Whatever decision is made (i.e., whatever the specified system boundaries are), initial Eq. (3), along with all subsequent equations, remains unchanged. Only the numerical values of functions appearing in the equations will depend on the specified boundaries. The only requirement for the boundary to ensure the validity of the equations is the identity of the pressure at the boundary to the pressure in the gas volume.

Equation (3) holds true if the adsorbent–adsorbate interface area undergoes changes during an adsorption experiment. The validity of this statement can be illustrated using a simple example. Suppose that the adsorbent is a sphere. In terms of the theory of capillarity, we know that in this case, the combined equation of the first and the second laws should be

$$dE = TdS - P'dV' - P''dV'' + \gamma dA + \mu dn, \tag{4}$$

where P' is the pressure inside the adsorbent, $P'' = P$ is the pressure in the gas phase, V' is the adsorbent volume, V'' is the gas phase volume, γ is the surface tension, and A is the surface area of the adsorbent. If the volume of the sphere is altered under the action of surface tension forces during adsorption–desorption, then differentials dV', dV'', and dA will be interrelated:

$$dV' + dV'' = dV, \tag{5}$$

$$dA = \frac{2}{r}dV', \tag{6}$$

where r is the sphere's radius and V is the total system volume. In addition, the Laplace equation describing the mechanical equilibrium condition must be met:

$$P' - P'' = \frac{2\gamma}{r}. \tag{7}$$

Substituting relationships (5)–(7) into Eq. (4), we obtain Eq. (3). It is evident that the assumption of the spherical shape of the adsorbent is immaterial. Equation (3) holds true for any type of adsorbent because the work of surface tension forces and the work of deformation of the adsorbent will annihilate each other in any case. These two types of works are performed on some parts of the adsorption system by other parts, rather than by external forces. These types of work do not lead to an exchange of energy with the environment, so they make no contribution to the energy balance equation for the entire system.

Using the Helmholtz free energy ($F = E - TS$) as a thermodynamic potential, we pass from Eq. (3) to the equation

$$dF = -SdT - PdV + \mu dn. \tag{8}$$

Here, the right-hand side contains three differentials. However, since the studied system is in equilibrium with the gas phase, the system's state is clearly determined by two parameters. Hence, to derive an equation with independent differentials, one of the differentials must be eliminated. If the temperature and number of moles are taken as independent parameters, after eliminating the volume differential we obtain

$$dF = -\left(S + P\frac{\partial V}{\partial T}\bigg|_n\right)dT + \left(\mu - P\frac{\partial V}{\partial n}\bigg|_T\right)dn. \tag{9}$$

Since this expression is a total differential, the coefficients preceding dT and dn are partial derivatives of F with respect to T and n, respectively.

To find the integral quantities, Eq. (9) must be integrated at a constant temperature:

$$F = F^0 + \int_0^n \mu dn - \int_{V^0}^V PdV. \tag{10}$$

Here, $F^0 = F(T, n = 0)$ and $V^0 = V(T, n = 0)$. Differentiating this relationship with respect to temperature at constant n and considering that $\frac{\partial F}{\partial T}\bigg|_n = -S - P\frac{\partial V}{\partial T}\bigg|_n$, we obtain the expression for entropy:

$$S = -\frac{\partial F^0}{\partial T} - \int_0^n \left.\frac{\partial \mu}{\partial T}\right|_n dn + \left.\frac{\partial}{\partial T}\right|_n \int_{V^0}^V P dV - P \left.\frac{\partial V}{\partial T}\right|_n. \quad (11)$$

The penultimate term in the right-hand side is transformed using the identical equation

$$\left.\frac{\partial f}{\partial T}\right|_n = \left.\frac{\partial f}{\partial T}\right|_V + \left.\frac{\partial V}{\partial T}\right|_n \left.\frac{\partial f}{\partial V}\right|_T, \quad (12)$$

which is valid for arbitrary function f. Since $P(T, V^0) = 0$, we obtain

$$S = -\frac{\partial F^0}{\partial T} - \int_0^n \left.\frac{\partial \mu}{\partial T}\right|_n dn + \int_{V^0}^V \left.\frac{\partial P}{\partial T}\right|_V dV. \quad (13)$$

The expression for energy ($E = F + TS$) is

$$E = E^0 + \int_0^n \left(\mu - T \left.\frac{\partial \mu}{\partial T}\right|_n \right) dn - \int_{V^0}^V \left(P - T \left.\frac{\partial P}{\partial T}\right|_V \right) dV, \quad (14)$$

where $E^0 = F^0 + T \frac{\partial F^0}{\partial T}$. Enthalpy ($H = E + PV$) is written in the form

$$\begin{aligned}
H = E^0 &+ \int_0^n \left(\mu - T \left.\frac{\partial \mu}{\partial T}\right|_n \right) dn \\
&+ \int_0^P V dP + \int_{V^0}^V T \left.\frac{\partial P}{\partial T}\right|_V dV.
\end{aligned} \quad (15)$$

Differential quantities are found by differentiating the integral quantities with respect to n at a constant temperature:

$$\left.\frac{\partial F}{\partial n}\right|_T = \mu - P \left.\frac{\partial V}{\partial n}\right|_T, \quad (16)$$

$$\left.\frac{\partial S}{\partial n}\right|_T = -\left.\frac{\partial \mu}{\partial T}\right|_n + \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial n}\right|_T, \quad (17)$$

$$\left.\frac{\partial E}{\partial n}\right|_T = \mu - T \left.\frac{\partial \mu}{\partial T}\right|_n + T \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial n}\right|_T - P \left.\frac{\partial V}{\partial n}\right|_T, \quad (18)$$

$$\left.\frac{\partial H}{\partial n}\right|_T = \mu - T \left.\frac{\partial \mu}{\partial T}\right|_n + T \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial n}\right|_T + V \left.\frac{\partial P}{\partial n}\right|_T. \quad (19)$$

Subtracting the molar enthalpy of the gas $\left(h^g = \mu - T \left.\frac{\partial \mu}{\partial T}\right|_P \right)$ from both sides of the last relation, we obtain the following expression for isosteric heat of adsorption $\left(q^{st} = h^g - \left.\frac{\partial H}{\partial n}\right|_T \right)$:

$$q^{st} = T \left(\left.\frac{\partial \mu}{\partial T}\right|_n - \left.\frac{\partial \mu}{\partial T}\right|_P \right) - T \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial n}\right|_T - V \left.\frac{\partial P}{\partial n}\right|_T. \quad (20)$$

Transforming difference $\left.\frac{\partial \mu}{\partial T}\right|_P - \left.\frac{\partial \mu}{\partial T}\right|_n$ using identical equations

$$\left.\frac{\partial \mu}{\partial T}\right|_n = \left.\frac{\partial \mu}{\partial T}\right|_P + \left.\frac{\partial P}{\partial T}\right|_n \left.\frac{\partial \mu}{\partial P}\right|_T \quad (21)$$

and

$$\left.\frac{\partial \mu}{\partial P}\right|_T = v^g, \quad (22)$$

where v^g is the molar volume of the gas, we obtain

$$q^{st} = T v^g \left.\frac{\partial P}{\partial T}\right|_n - T \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial n}\right|_T - V \left.\frac{\partial P}{\partial n}\right|_T. \quad (23)$$

Using the identical equation

$$\left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial P}{\partial T}\right|_n - \left.\frac{\partial P}{\partial n}\right|_T \left.\frac{\partial V}{\partial T}\right|_n \left.\frac{\partial n}{\partial V}\right|_T, \quad (24)$$

this expression can be transformed as

$$q^{st} = T \left(v^g - \left.\frac{\partial V}{\partial n}\right|_T \right) \left.\frac{\partial P}{\partial T}\right|_n - \left.\frac{\partial P}{\partial n}\right|_T \left(V - T \left.\frac{\partial V}{\partial T}\right|_n \right). \quad (25)$$

This expression was derived earlier using the approach proposed by Bakaev in [12, 13]. It can also be derived in terms of conventional approaches (see Appendix A).

If we start from the equation for Gibbs free energy ($G = F + PV$),

$$dG = -S dT + V dP + \mu dn, \quad (26)$$

passing to an equation with independent differentials

$$dG = -\left(S - V \frac{\partial P}{\partial T} \right) dT + \left(\mu + V \frac{\partial P}{\partial n} \right) dn, \quad (27)$$

and acting similarly, we obtain expressions for thermodynamic functions that are equivalent to the previous expressions, yet have another form. Some of these are

$$G = F^0 + \int_0^n \mu \, dn + \int_0^P V \, dP, \quad (28)$$

$$S = -\frac{\partial F^0}{\partial T} - \int_0^n \left.\frac{\partial \mu}{\partial T}\right|_n dn - \int_0^P \left.\frac{\partial V}{\partial T}\right|_P dP, \quad (29)$$

$$H = E^0 + \int_0^n \left(\mu - T \left.\frac{\partial \mu}{\partial T}\right|_n \right) dn + \int_0^P \left(V - T \left.\frac{\partial V}{\partial T}\right|_P \right) dP, \quad (30)$$

$$\left.\frac{\partial G}{\partial n}\right|_T = \mu + V \left.\frac{\partial P}{\partial n}\right|_T, \quad (31)$$

$$\left.\frac{\partial S}{\partial n}\right|_T = -\left.\frac{\partial \mu}{\partial T}\right|_n - \left.\frac{\partial V}{\partial T}\right|_P \left.\frac{\partial P}{\partial n}\right|_T, \quad (32)$$

$$\left.\frac{\partial H}{\partial n}\right|_T = \mu - T \left.\frac{\partial \mu}{\partial T}\right|_n - T \left.\frac{\partial V}{\partial T}\right|_P \left.\frac{\partial P}{\partial n}\right|_T + V \left.\frac{\partial P}{\partial n}\right|_T, \quad (33)$$

$$q^{st} = T v^g \left.\frac{\partial P}{\partial T}\right|_n - \left.\frac{\partial P}{\partial n}\right|_T \left(V - T \left.\frac{\partial V}{\partial T}\right|_P\right). \quad (34)$$

Expressions for other functions obviously follow from the above equations. In particular, the correct expression for the $\Omega_{os} = G - n\mu$ function (the osmotic potential) is

$$\Omega_{os} = F^0 - \int_{-\infty}^{\mu} n d\mu + \int_0^P V dP$$
$$= F^0 - \int_0^P \left(n v^g - V\right) dP. \quad (35)$$

The expression used by some authors [14−16],

$$\Omega_{os} = F^0 - \int_0^P n v^g dP + PV, \quad (36)$$

holds true only for a constant volume V. If the volume undergoes changes, the equation is not valid. This is evident when we consider a case where an adsorbent is not included in the system, i.e., when $\Omega_{os} = 0$, $F^0 = 0$, and $V = n v^g$.

A MULTICOMPONENT ADSORBATE

With multicomponent gas adsorption, the Helmholtz free energy differential is written as

$$dF = -SdT - PdV + \sum_{i=1}^{k} \mu_i dn_i, \quad (37)$$

where k is the number of components in the gas mixture. By considering the volume as a function of temperature and number of moles n_i of the components, we can rewrite this equation in the form

$$dF = -\left(S + P \left.\frac{\partial V}{\partial T}\right|_n\right) dT + \sum_{i=1}^{k} \left(\mu_i - P \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}\right) dn_i. \quad (38)$$

(Here, subscript n means that all numbers of moles are constant during differentiation. Subscript n_j means that all numbers of moles, except for the number with respect to which differentiation is performed, are constant.) This equation yields expressions for the partial derivatives:

$$\left.\frac{\partial F}{\partial n_i}\right|_{T,n_j} = \mu_i - P \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}, \quad (39)$$

$$\left.\frac{\partial F}{\partial T}\right|_n = -S - P \left.\frac{\partial V}{\partial T}\right|_n. \quad (40)$$

Differentiating Eq. (39) with respect to T and Eq. (40) with respect to n_i, and equating the results, we find the differential entropy:

$$\left.\frac{\partial S}{\partial n_i}\right|_{T,n_j} = -\left.\frac{\partial \mu_i}{\partial T}\right|_n + \left.\frac{\partial P}{\partial T}\right|_n \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j} - \left.\frac{\partial P}{\partial n_i}\right|_{T,n_j} \left.\frac{\partial V}{\partial T}\right|_n. \quad (41)$$

Combining Eqs. (39) and (41), we obtain the differential energy:

$$\left.\frac{\partial E}{\partial n_i}\right|_{T,n_j} = \mu_i - T \left.\frac{\partial \mu_i}{\partial T}\right|_n$$
$$- \left(P - T \left.\frac{\partial P}{\partial T}\right|_n\right) \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j} - T \left.\frac{\partial P}{\partial n_i}\right|_{T,n_j} \left.\frac{\partial V}{\partial T}\right|_n. \quad (42)$$

Adding $\left.\dfrac{\partial (PV)}{\partial n_i}\right|_{T,n_j}$, we obtain the differential enthalpy:

$$\left.\frac{\partial H}{\partial n_i}\right|_{T,n_j} = \mu_i - T \left.\frac{\partial \mu_i}{\partial T}\right|_n$$
$$+ \left(V - T \left.\frac{\partial V}{\partial T}\right|_n\right) \left.\frac{\partial P}{\partial n_i}\right|_{T,n_j} + T \left.\frac{\partial P}{\partial T}\right|_n \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}. \quad (43)$$

Expression $\mu_i - T \left.\dfrac{\partial \mu_i}{\partial T}\right|_n$ can be defined concretely. If the chemical potential of the ith component of the gas mixture is written in the form

$$\mu_i = \mu_i^0 (T) + RT \ln (f_i), \quad (44)$$

then

$$\left.\frac{\partial H}{\partial n_i}\right|_{T,n_j} = h_i^0 - RT^2 \left.\frac{\partial \ln f_i}{\partial T}\right|_n$$
$$+ \left(V - T \left.\frac{\partial V}{\partial T}\right|_n\right) \left.\frac{\partial P}{\partial n_i}\right|_{T,n_j} + T \left.\frac{\partial P}{\partial T}\right|_n \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}. \quad (45)$$

Here, f_i is the fugacity, μ_i^0 is the chemical potential of an ideal gas in the standard state at temperature T and $f_i = 1$ bar, and h_i^0 is the enthalpy of an ideal gas in the standard state:

$$h_i^0 = -T^2 \frac{d}{dT}\left(\frac{\mu_i^0}{T}\right). \quad (46)$$

If the gas is an ideal mixture, f_i is equal to partial pressure p_i, while h_i^0 is equal to partial enthalpy h_i^g. Equation (45) is in this case transformed into

$$q_i^{st} = RT^2 \left.\frac{\partial \ln p_i}{\partial T}\right|_n$$
$$- \left(V - T \left.\frac{\partial V}{\partial T}\right|_n\right) \left.\frac{\partial P}{\partial n_i}\right|_{T,n_j} - T \left.\frac{\partial P}{\partial T}\right|_n \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}, \quad (47)$$

where $q_i^{st} = h_i^g - \left.\dfrac{\partial H}{\partial n_i}\right|_{T,n_j}$ is the partial isosteric heat of adsorption. At a constant volume, Eqs. (45) and (47)

reduce to the familiar relationships given in [10] and in [17, 18], respectively.

The expression that relates derivative $\left.\dfrac{\partial P}{\partial T}\right|_n$ to partial isosteric heats of adsorption is of considerable practical interest [17, 18]. In the simplest case, when the gas is an ideal mixture, we have $p_i = x_i P$. Hence,

$$\left.\frac{\partial \ln P}{\partial T}\right|_n = \sum_{i=1}^{k} x_i \left.\frac{\partial \ln p_i}{\partial T}\right|_n . \tag{48}$$

Here, x_i is the mole fraction of the ith component of the gas mixture. Using Eq. (47) to eliminate $\left.\dfrac{\partial \ln p_i}{\partial T}\right|_n$, we obtain

$$T\left(v^g - \sum_{i=1}^{k} x_i \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}\right) \left.\frac{\partial P}{\partial T}\right|_n$$
$$= \sum_{i=1}^{k} x_i \left[q_i^{st} + \left(V - T\left.\frac{\partial V}{\partial T}\right|_n\right)\left.\frac{\partial P}{\partial n_i}\right|_{T,n_j}\right]. \tag{49}$$

In general case, the corresponding relationship is derived from equilibrium conditions $\mu_i = \mu_i^g$ and $d\mu_i = d\mu_i^g$. Considering equality $\mu_i = h_i^g - Ts_i^g$, Eq. (43) can be rewritten as

$$q_i^{st} = T\left(s_i^g + \left.\frac{\partial \mu_i}{\partial T}\right|_n\right)$$
$$- \left(V - T\left.\frac{\partial V}{\partial T}\right|_n\right)\left.\frac{\partial P}{\partial n_i}\right|_{T,n_j} - T\left.\frac{\partial P}{\partial T}\right|_n \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}. \tag{50}$$

At constant numbers of moles n_j, conditions $d\mu_i = d\mu_i^g$ reduce to

$$\left.\frac{\partial \mu_i}{\partial T}\right|_n dT = -s_i^g dT$$
$$+ v_i^g dP + \sum_{i=1}^{k-1} \frac{\partial \mu_i^g}{\partial x_j} dx_j \quad (i = 1, 2, \ldots, k), \tag{51}$$

where s_i^g and v_i^g are the partial entropy and partial volume of the ith component of the gas mixture, respectively. Multiplication of these conditions by x_i and summation yield the formula

$$\sum_{i=1}^{k} x_i v_i^g \left.\frac{\partial P}{\partial T}\right|_n = \sum_{i=1}^{k} x_i \left(s_i^g + \left.\frac{\partial \mu_i}{\partial T}\right|_n\right). \tag{52}$$

(The term containing partial derivatives with respect to x_j vanishes in accordance with the Gibbs–Duhem relationship.) Multiplicating Eqs. (50) by x_i and summing with allowance for (52), we arrive at the equation

$$T\sum_{i=1}^{k} x_i \left(v_i^g - \left.\frac{\partial V}{\partial n_i}\right|_{T,n_j}\right) \left.\frac{\partial P}{\partial T}\right|_n$$
$$= \sum_{i=1}^{k} x_i \left[q_i^{st} + \left(V - T\left.\frac{\partial V}{\partial T}\right|_n\right)\left.\frac{\partial P}{\partial n_i}\right|_{T,n_j}\right]. \tag{53}$$

This formula is valid in the general case of adsorption of a nonideal gas mixture by a deformable adsorbent. It is a generalization of the familiar formula that is valid for the adsorption of an ideal mixture by a non-deformable adsorbent [18]. If all partial volumes are identical, this formula reduces to (49). With a single-component adsorbate, it reduces to (25).

RESULTS AND DISCUSSION

The approach proposed in this work is similar to the one proposed by Guggenheim [19] and developed by Bakaev [12, 13]. In both approaches, the adsorbent and the adsorbate are treated as a single thermodynamic system. The difference between the approaches lies in the method used to derive thermodynamic relationships. In the Guggenheim–Bakaev approach, relationships for an expanded system that includes the entire content of the adsorption vessel are written first; we can then pass to the relationships for the system under study. The pass is made possible by algebraic relationships, meaning that the thermodynamic functions for the expanded system are equal to the sum of functions for the system under study and for the non-adsorbed gas. In the approach proposed here, the thermodynamic relationships for the system under study are derived directly from the basic equation of thermodynamics written for this system. This approach allows the systematic determination of all the characteristics of the adsorption system, particularly for the case of a multicomponent adsorbate.

The relationships derived in this work describe a system composed of an adsorbent and an adsorbate. If the adsorbent is deformable, it is impossible to derive relationships that refer only to the adsorption layer, since the effect the adsorbent has on this layer is unknown. However, if the adsorbent is inert (i.e., if the effect of the adsorbent on the adsorption layer does not depend on the magnitude of adsorption), the thermodynamic functions of the adsorption layer satisfy Eq. (3), and all of the derived relationships can be applied to the adsorption layer. There is then no need to include the adsorbent in the composition of the adsorption system. The system volume will vary only because of the growth of the adsorption layer. Regardless of how correct the determination of the layer volume, all of the derived relationships hold true if the condition of the pressure at the layer boundary being equal to the pressure in the gas volume is met. Since all

thermodynamic functions in this case correspond to the adsorbate, we must assume the quantities corresponding to the adsorbent in the formulas (e.g., E^0, F^0, etc.) are zero.

With an inert adsorbent, the derived relationships can be used to obtain expressions for excess quantities. We must first subtract the equation for the nonadsorbed gas occupying volume $V^g = V - V^s$,

$$dF^g = -S^g dT - PdV^g + \mu dn^g \qquad (54)$$

and the equation for the adsorbent,

$$dF^s = -S^s dT - PdV^s \qquad (55)$$

from Eq. (8). The result is an equation for the excess quantities corresponding to the two-dimensional Gibbs phase:

$$dF^e = -S^e dT + \mu dn^e. \qquad (56)$$

This equation can be formally obtained from Eq. (8) if each thermodynamic quantity Z is replaced by excess quantity Z^e ($Z^e = Z - Z^s - Z^g$) and it is assumed that $V^e = 0$. Hence, all the thermodynamic relationships describing the two-dimensional Gibbs phase can also be obtained from the relationships derived here after the above substitutions. Equation (25) in particular can thus be transformed into the familiar relationship

$$h^g - \left.\frac{\partial H^e}{\partial n^e}\right|_T = T v^g \left.\frac{\partial P}{\partial T}\right|_{n^e}. \qquad (57)$$

Although the relationships for excess quantities are derived as a particular case from relationships for absolute values, the former and the latter contain the same amount of information. This is because the excess quantities and the quantities characterizing the adsorption layer are clearly interrelated ($Z^e = Z - \frac{V}{v^g} z^g$). This relation allows some relationships to be transformed into others. Equation (57) in particular can be transformed into Eq. (25) (see Appendix B).

If the adsorbent is deformable, for the experimental determination of changes in the thermodynamic functions upon switching from the vacuum state to the target state ($\Delta Z = Z(T, P) - Z^0(T)$), we must know, in addition to the adsorption isotherm, the dependence of volume on temperature and pressure. This requirement somewhat complicates the task of the experimentalist. On the other hand, we need not measure the dead volume if this relationship is known. The amount of the adsorbate in the system (n) is in this

case found as the difference between the total amount of the adsorbate in the adsorption vessel and the amount of the gas in the volume: $V^{\text{vessel}} - V$, where V^{vessel} is the vessel volume.

It should be noted that the conventional thermodynamic consistency tests for experimental data are not applicable to a deformable absorbent. These tests are typically derived from the Gibbs adsorption equation [20, 21]

$$d\Omega = -SdT - \sum_{i=1}^{k} n_i d\mu_i. \qquad (58)$$

(where Ω is the grand potential: $\Omega = F - \sum_{i=1}^{k} n_i \mu_i$). With a deformable adsorbent, the analog of this equation can be written as

$$d\Omega = -\left(S + P\frac{\partial V}{\partial T}\right)dT - \sum_{i=1}^{k}\left(n_i + P\frac{\partial V}{\partial \mu_i}\right)d\mu_i. \quad (59)$$

Respective tests must be derived from this.

A specific example showing that deformations of the adsorbent (in this case, the sorbent) can have a considerable thermodynamic effect can be provided using the experimental data of [22] on the sorption of carbon dioxide by a polycarbonate sorbent. The author of [22] gave analytical expressions for sorption isotherms and the magnitude of sorption deformation. The sorption isotherm corresponding to $T = 308$ K in the pressure range of 1.5−6.5 MPa is described by the equation $n = \frac{aKP}{1 + KP}$, where $a = 0.28$ g/g and $K = 1.22 \times 10^{-7}$ Pa^{-1}. The relative deformation in the temperature range of 308−318 K and the pressure range of 1.5−6.5 MPa is described by the equation $\frac{V - V_0}{V_0} = D\exp\left(\frac{E}{RT}\right)P$, where $E = 40.4$ kJ/mol and $D = 5.76 \times 10^{-15}$ Pa^{-1}. The temperature dependence of volume V_0 is weaker than exponential dependence $\exp\left(\frac{E}{RT}\right)$. These data can be used to calculate the contribution from the deformation of the sorbent to differential energy (18). When $T = 308$ K and $P = 6.5$ MPa, expression $\left(T\left.\frac{\partial P}{\partial T}\right|_V - P\right)\left.\frac{\partial V}{\partial n}\right|_T$ in (18) gives ~13 kJ/mol; in order of magnitude, this value is comparable to the isosteric heat of sorption calculated in [22] (~40 kJ/mol).

CONCLUSIONS

A new approach to constructing adsorption thermodynamics has been proposed. The adsorbent, the adsorbed gas, and the gas enclosed in the spaces between the adsorbent's particles are treated as a single

thermodynamic system. The condition of equilibrium between the condensed phase and the gas is used to eliminate the redundant variable in the fundamental equation. The proposed approach is rigorous; it can be applied to any adsorption system. In particular, it allows the derivation of expressions for the thermodynamic functions of an adsorption system with a deformable adsorbent. Expressions for integral and differential functions were derived for a single-component adsorbate. Expressions for the partial isosteric heats of adsorption and an expression relating the $\left.\dfrac{\partial P}{\partial T}\right|_n$ derivative to the partial isosteric heats of adsorption were derived for a multicomponent adsorbate.

APPENDIX A

In the conventional approach to adsorption thermodynamics, the following expression for the change of differential enthalpy has been derived [17]:

$$h^g - \left.\frac{\partial H}{\partial n}\right|_{T,P} = T\left(v^g - \left.\frac{\partial V}{\partial n}\right|_{T,P}\right)\left.\frac{\partial P}{\partial T}\right|_n. \qquad (A1)$$

This formula is correct; however, it contains partial derivatives with respect to n at constant T and P, while in an adsorption experiment, pressure is not an independent variable; it is related to n and T by the adsorption isotherm equation. It is generally assumed that the properties of the condensed phase depend weakly on pressure, so the partial derivatives at constant T and P are therefore replaced with partial derivatives at constant T. This approach is justified at low pressures. To derive an expression that is valid at high pressures, we must transform former partial derivatives into letter using the exact formulas

$$\left.\frac{\partial H}{\partial n}\right|_T = \left.\frac{\partial H}{\partial n}\right|_{T,P} + \left.\frac{\partial P}{\partial n}\right|_T\left(V - T\left.\frac{\partial V}{\partial T}\right|_{n,P}\right), \qquad (A2)$$

$$\left.\frac{\partial V}{\partial n}\right|_T = \left.\frac{\partial V}{\partial n}\right|_{T,P} + \left.\frac{\partial V}{\partial P}\right|_{T,n}\left.\frac{\partial P}{\partial n}\right|_T, \qquad (A3)$$

$$\left.\frac{\partial V}{\partial T}\right|_n = \left.\frac{\partial V}{\partial T}\right|_{n,P} + \left.\frac{\partial V}{\partial P}\right|_{T,n}\left.\frac{\partial P}{\partial T}\right|_n. \qquad (A4)$$

The substitution of these formulas in (A1) yields Eq. (25). Relationship (A2) is derived using the equations

$$\left.\frac{\partial H}{\partial n}\right|_T = \left.\frac{\partial H}{\partial n}\right|_{T,P} + \left.\frac{\partial H}{\partial P}\right|_{T,n}\left.\frac{\partial P}{\partial n}\right|_T, \qquad (A5)$$

$$\left.\frac{\partial H}{\partial P}\right|_{T,n} = V + T\left.\frac{\partial S}{\partial P}\right|_{T,n}, \qquad (A6)$$

$$\left.\frac{\partial S}{\partial P}\right|_{T,n} = -\left.\frac{\partial V}{\partial T}\right|_{n,P}. \qquad (A7)$$

APPENDIX B

The following relationships between partial derivatives hold true for arbitrary function f:

$$\left.\frac{\partial f}{\partial n}\right|_T = \left.\frac{\partial f}{\partial n^e}\right|_T\left.\frac{\partial n^e}{\partial n}\right|_T, \qquad (B1)$$

$$\left.\frac{\partial f}{\partial T}\right|_n = \left.\frac{\partial f}{\partial T}\right|_{n^e} + \left.\frac{\partial f}{\partial n^e}\right|_T\left.\frac{\partial n^e}{\partial T}\right|_n. \qquad (B2)$$

In this particular case, $n^e = n - \dfrac{V}{v^g}$; so from (B1) and (B2), we obtain

$$\left.\frac{\partial H^e}{\partial n^e}\right|_T = \left.\frac{\partial H^e}{\partial n}\right|_T\bigg/\left[1 - \left.\frac{\partial}{\partial n}\right|_T\left(\frac{V}{v^g}\right)\right], \qquad (B3)$$

$$\left.\frac{\partial P}{\partial T}\right|_{n^e} = \left.\frac{\partial P}{\partial T}\right|_n + \left.\frac{\partial P}{\partial n}\right|_T\left.\frac{\partial}{\partial T}\right|_n\left(\frac{V}{v^g}\right)\bigg/\left[1 - \left.\frac{\partial}{\partial n}\right|_T\left(\frac{V}{v^g}\right)\right]. (B4)$$

Since

$$H^e = H - \frac{V}{v^g}h^g, \qquad (B5)$$

$$\left.\frac{\partial h^g}{\partial n}\right|_T = v^g - T\left.\frac{\partial v^g}{\partial T}\right|_P, \qquad (B6)$$

$$\left.\frac{\partial v^g}{\partial T}\right|_n = \left.\frac{\partial v^g}{\partial T}\right|_P + \left.\frac{\partial v^g}{\partial n}\right|_T\left.\frac{\partial P}{\partial T}\right|_n\left.\frac{\partial n}{\partial P}\right|_T, \qquad (B7)$$

by substituting relationships (B3) and (B4) in (57) we obtain (25).

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