Equation of State for Adsorption of Gases and Their Mixtures in Porous Materials

ALAN L. MYERS
*Department of Chemical and Biomolecular Engineering, University of Pennsylvania,
Philadelphia, PA 19104, USA*
amyers@seas.upenn.edu

Abstract. Desorption functions (G, H, S) are useful for adsorbent characterization, phase equilibria, and enthalpy and entropy balances. Adsorption isotherms, enthalpy, and entropy are temperature and pressure derivatives of the free energy, so that $G(T, P)$ is an adsorption equation-of-state which contains complete thermodynamic information about the system. The free energy of desorption is the minimum isothermal work necessary to regenerate the adsorbent. The free energy of desorption also determines the selectivity of an adsorbent for different gases. The ideal enthalpy of desorption for a mixture $(H = \sum_i n_i h_i^\circ)$ is a simple function of the enthalpies of desorption for the individual components. Sample calculations of the free energy, enthalpy, and entropy desorption functions are provided for pure components and mixtures.

Keywords: adsorption, gas, mixture, micropore, enthalpy, entropy

Introduction

Previous work on the thermodynamics of adsorption of mixtures has been concentrated on the measurement, simulation, and prediction of the amount adsorbed, the differential enthalpy (isosteric heat), and the differential entropy of adsorption. Since the differential entropy is infinite at zero loading and both differential functions have mathematical singularities at high loading, the physical significance and interpretation of differential variables is problematic.

This paper is based upon the idea that the desorption free energy $G(T, P, y)$ is an adsorption equation of state whose derivatives provide a complete thermodynamic description of the system. This approach deviates significantly from the usual treatment of adsorption. First, the nomenclature is different. The desorption free energy has been called in the past: (1) the product of spreading pressure and surface area (ΠA) (Adamson and Gast, 1997); (2) the free energy of immersion (Myers, 2002); (3) the grand potential

(Myers and Monson, 2002). All of these quantities have the same numerical value but the desorption free energy and (ΠA) are positive quantities; the free energy of immersion and the grand potential are negative quantities. Spreading pressure is a variable for two-dimensional films; the other names apply to porous materials. The grand potential (Ω) arises in statistical thermodynamics because of its relationship to the grand canonical partition function $(\Omega = -kT \ln \Xi)$ (Nicholson and Parsonage, 1982). The proliferation of different names for the same physical quantity is confusing at first. Whatever name is preferred, the two-dimensional spreading pressure is inappropriate for porous materials because it cannot be defined theoretically or measured experimentally. The free energy of immersion of the clean adsorbent, or its absolute value, the desorption free energy, is well defined and straightforward to measure experimentally or calculate theoretically.

The scope of this paper extends beyond arguments about the proper terminology for adsorption in porous

materials. The standard treatment of adsorption is based upon the spreading pressure and surface area variables for two-dimensional films (Ruthven, 1984; Yang, 1987). The misapplication of two-dimensional films to adsorption in porous materials has already led to unnecessary complications and confusion. The historical preoccupation with differential quantities such as isosteric heat, which exhibits a singularity (Salem et al., 1998), has obscured the significance of the integral enthalpy of the adsorbed phase, which is smooth in all derivatives with respect to pressure. It is suggested that the integral functions (enthalpy, free energy, and entropy) are easier to understand and more useful for theoretical and experimental characterization of adsorption in porous materials.

Adsorption Equations for Experimental or Simulated Data

Adsorption of a pure gas is a function of temperature and pressure and is normally reported as a series of adsorption isotherms. A typical example is shown by Fig. 1 for ethylene on NaX zeolite. These experimental data are *excess* adsorption. Theoretical calculations yield *absolute* adsorption. The distinction between absolute and excess adsorption is negligible in the low (sub-atmospheric) pressure region discussed in this paper. Methods for converting absolute variables to ex-
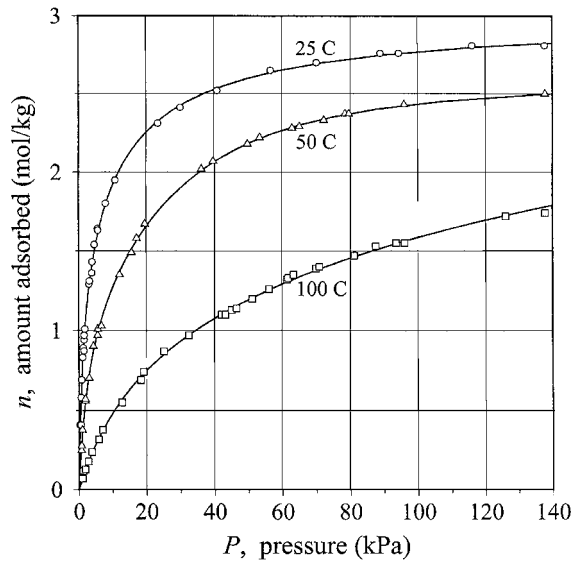
Table 1. Constants of Eq. (1) for C_2H_4 on NaX (Hyun and Danner, 1982).

T (K)	K (mol/kg kPa)	m (mol/kg)	C_1 (kg/mol)	C_2 (kg/mol)^2	C_3 (kg/mol)^3
298.15	1.9155	2.9997	0.841	−0.06311	−0.009415
323.15	0.5543	2.6644	0.7537	0.03866	−0.096189
373.15	0.07794	–	0.9494	0.03408	0

cess variables at higher pressure are covered elsewhere (Myers and Monson, 2002).

The calculation of thermodynamic functions such as enthalpy is facilitated by fitting the data with an adsorption equation. The two-constant Langmuir equation is usually incapable of describing adsorption isotherms over several decades of pressure from very low loading up to saturation. The three-constant LUD and Toth equations (Valenzuela and Myers, 1989) give good fits of adsorption isotherms like those on Fig. 1 but do not provide analytical equations for thermodynamic functions. The Langmuir-virial equation:

$$P = \frac{n}{K}\left[\frac{m}{m-n}\right]\exp[C_1 n + C_2 n^2 + C_3 n^3 + \cdots] \quad (1)$$

contains the Henry constant (K), the saturation capacity (m), and as many constants of the virial series ($C_1, C_2, \ldots$) as required to fit the data points. Equation (1) is plotted on Fig. 1 using the set of constants in Table 1. Plots of $\ln(P/n)$ shown in Fig. 2 are
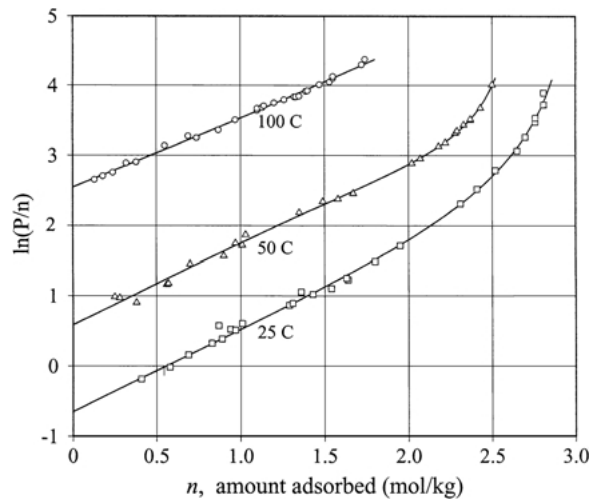

Figure 1. Adsorption isotherms for ethylene on NaX (Hyun and Danner, 1982). Solid lines are Eq. (1).

Figure 2. Logarithm of (P/n) plots of experimental data (Hyun and Danner, 1982) for adsorption of ethylene on NaX. Solid lines are Eq. (1).

useful for examining the behavior of the isotherm at low pressure. The solid lines in Fig. 2 are Eq. (1); the *y*-intercept at the limit of zero loading is the logarithm of the reciprocal of the Henry constant. Normally data points on a $\ln(P/n)$ plot exhibit increased scatter as $n \to 0$ and should either be discarded or multiplied by weighting functions for accurate determination of the Henry constant. The other limit on the isotherm is the saturation capacity at high pressure. Since the saturation capacity for the isotherm at 100°C was not established, that isotherm was fitted with the virial equation without the $m/(m-n)$ factor in Eq. (1). The extrapolation to zero pressure for the Henry constant is satisfactory for all three isotherms.

Except for its correct asymptotic behavior at high and low loading for porous materials, the theoretical basis for the Langmuir-virial equation is weak. Its selection is based upon empirical evidence of its ability to fit experimental data for adsorption in porous materials. Equation (1) fails to describe multilayer adsorption and other phenomena such as adsorption hysteresis.

Temperature Coefficient of Adsorption

Interpolation of adsorption isotherms is based upon the differential enthalpy of desorption (Myers, 2002):

$$\bar{h} = -R\left[\frac{\partial \ln P}{\partial(1/T)}\right]_n \qquad (2)$$

The fact that the differential enthalpy (isosteric heat) is a weak function of temperature at constant loading (Shen et al., 2000) permits interpolation or modest extrapolation of adsorption isotherms using the integrated form of Eq. (2):

$$\ln\left[\frac{P}{P^*}\right] = \frac{\bar{h}}{R}\left[\frac{1}{T^*} - \frac{1}{T}\right] \quad \text{(constant } n\text{)} \qquad (3)$$

which provides the temperature dependence $P(T)$ given a reference point $P^*(T^*)$ at the same loading.

Figure 3 shows differential enthalpies calculated numerically by Eq. (2) using the fitted data (solid lines) in Fig. 1. The difference between the two curves in Fig. 3 indicates that the differential enthalpy is a strong and complex function of temperature. However, the error associated with differentiating the isotherms is the main source of the difference between the two curves. The best estimate of the differential enthalpy over the range from 25 to 100°C is an average of the two curves on Fig. 3.
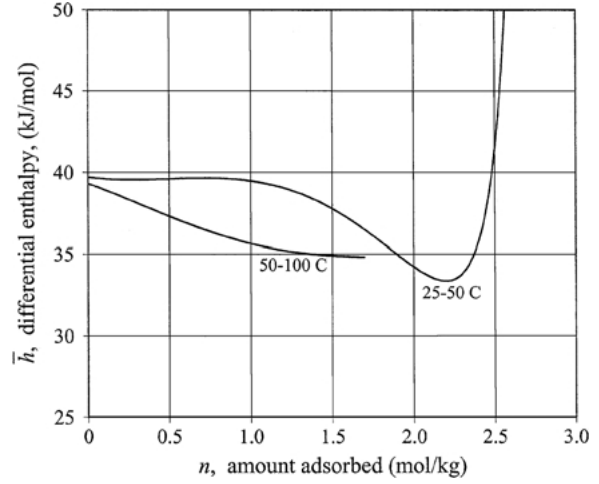

Figure 3. Differential enthalpies (isosteric heat) calculated by Eq. (2) from the solid lines plotted in Fig. 1.

At high loading near saturation, the differential enthalpy has a limit of infinity as shown on Fig. 3 for the 25–50°C temperature interval. This singularity at high loading is a standard feature of differential enthalpy and differential entropy. Therefore the interpolation and extrapolation of adsorption isotherms based upon the assumption of a temperature-independent differential enthalpy is limited to loadings well below the saturation capacity.

Although the standard name for the differential enthalpy of desorption is the isosteric heat (q_{st}), the enthalpy terminology is a reminder that the isosteric heat is actually a state function.

Equation of State for Adsorption of Single Gases

The terminology and notation for thermodynamic functions has not been standardized in the adsorption literature. Here, G refers to the change in Gibbs free energy for complete desorption of the solid adsorbent at the imposed conditions of temperature and pressure. The units of G are kJ/kg of adsorbent. H is the enthalpy of desorption and S is the entropy of desorption.

The reverse of the desorption process is complete immersion of clean adsorbent in the gas. The free energy of immersion is $-G$, the enthalpy of immersion is $-H$, etc. Normally the free energy, enthalpy, and entropy of immersion are all negative quantities because adsorption is an exothermic, spontaneous process. Conversely, the desorption functions (G, H, S) are normally positive in sign.

In treatments of surface thermodynamics presented in textbooks (Ruthven, 1984; Yang, 1987), the free energy of desorption is called the ΠA product, where Π is spreading pressure and A is specific surface area. In terms of solution thermodynamics, the free energy of immersion $(-G)$ is the chemical potential of the solid adsorbent relative to its clean state at the same temperature (Myers, 2002). The desorption free energy (G), a positive quantity, conveys the nature of the physical property more clearly than the product of the spreading pressure and the surface area.

Given adsorption equilibrium at a given value of temperature and pressure of the gas, the free energy of desorption is the minimum isothermal work necessary to clean the adsorbent. Most of the operating cost of adsorptive separations is associated with degassing the adsorbent in preparation for the next cycle.

An advantage of the Langmuir-virial equation is that the free energy of desorption can be calculated analytically (Siperstein and Myers, 2001):

$$G = RT \int_0^P \frac{n}{P} dP = RT \left[-m \ln \left(1 - \frac{n}{m} \right) \right.$$
$$\left. + \frac{1}{2} C_1 n^2 + \frac{2}{3} C_2 n^3 + \frac{3}{4} C_3 n^4 + \cdots \right] \quad (4)$$

Equation (4) is written specifically for the Langmuir-virial equation, for which the functionality $n(T, P)$ and $G(T, P)$ is implicit. The following equations show that the desorption free energy $G(T, P)$ may be viewed more generally as a master equation for thermodynamic functions. The enthalpy of desorption is obtained from the Gibbs-Helmholtz equation:

$$H = \left[\frac{\partial(G/T)}{\partial(1/T)} \right]_P \quad (5)$$

or by integrating the differential enthalpy:

$$H = \int_0^n \bar{h} \, dn \quad (6)$$

Finally, the entropy of desorption is:

$$S = -\left[\frac{\partial G}{\partial T} \right]_P = \frac{H - G}{T} \quad (7)$$

The free energy function $G(T, P)$ is a general equation of state for the adsorption of a single gas because its temperature coefficient yields the enthalpy and entropy
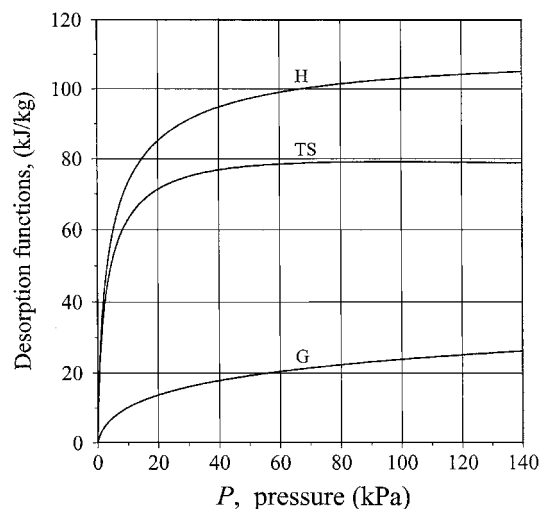

Figure 4. Desorption properties for ethylene on NaX at 25°C.

functions and the pressure coefficient is the adsorption isotherm:

$$n = \frac{1}{RT} \left[\frac{\partial G}{\partial \ln P} \right]_T \quad (8)$$

The desorption functions calculated for ethylene in NaX from the adsorption isotherms in Fig. 1 are plotted on Fig. 4. The enthalpy of desorption approaches a saturation value of about 110 kJ/kg and (TS) has a maximum of about 80 kJ/kg. Plots of the desorption functions of other gases in microporous adsorbents are similar in form to Fig. 4.

The desorption functions shown on Fig. 4 are recommended for characterizing and comparing the performance of different adsorbents in terms of their capacity, enthalpy, and entropy at a standard temperature in a reference gas.

Equation of State for Adsorption of Mixtures

Selectivity

The desorption functions play a critical role in describing the equilibrium behavior of mixtures. The following development is written for ideal adsorbed solutions (IAS). Activity coefficients for nonideal solutions are covered elsewhere (Siperstein and Myers, 2001). Figure 5 shows the free energy of desorption of NaX for several gases at 20°C. The free energy of desorption is the standard state for the vapor pressures
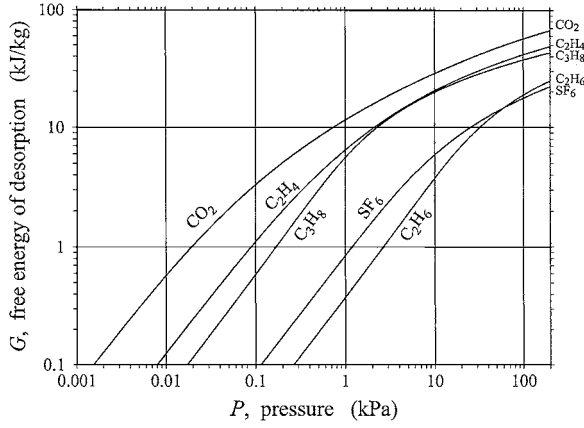
Figure 5. Free energies of desorption of various gases from NaX at 25°C.

of the adsorbates. The selectivity of the adsorbent for any pair of adsorbates is:

$$\alpha_{i,j} = \frac{x_i/y_i}{x_j/y_j} = \frac{P_j^\circ}{P_i^\circ} \qquad (9)$$

For example, at $G = 0.1$ kJ/kg, the ideal selectivity of NaX for CO_2 relative to C_2H_6 is $\alpha_{1,2} = 0.2647/0.001546 = 171$. It is apparent from Fig. 5 that the the selectivity normally decreases with pressure and in some cases exhibits a reversal characterized by the formation of azeotropes. At constant pressure, the difference in pure-component free energies obeys the integral equation (Sircar and Myers, 1971):

$$G_2 - G_1 = RT \int_0^1 \left[\frac{n_1}{y_1} - \frac{n_2}{y_2} \right] dy_1 \approx \bar{n} RT \ln(\bar{\alpha}_{1,2}) \qquad (10)$$

Equation (10), which is useful at high pressure, shows that the mean selectivity ($\bar{\alpha}_{1,2}$) at constant pressure and temperature is given by $\ln(\bar{\alpha}_{1,2}) = (G_2 - G_1)/RT\bar{n}$, where $\bar{n}$ is the average total loading. For example, at 20°C and 100 kPa where the average loading is 2.9 mol/kg, the mean selectivity of NaX for C_3H_8 relative to SF_6 is given approximately by:

$$\bar{\alpha}_{1,2} = \exp\left[\frac{(37.54 - 17.72)(1000)}{(8.3145)(293.15)(2.9)} \right] = 16.5 \quad (11)$$

Adsorption-Vapor Equilibrium

Diagrams like Fig. (5) are useful for choosing the optimum adsorbent for a particular separation. Equations for calculating the various thermodynamic functions (free energy, enthalpy, and entropy) for mixtures are developed next.

The free energy of desorption is the standard state for forming adsorbed solutions from the pure components. Given the pressure (P), temperature (T), and mole fraction of component 1 in the gas phase (y_1) for a binary mixture, three equations are solved simultaneously to establish the standard-state loadings (n_1°, n_2°) for a binary mixture:

$$P y_1 = P_1^\circ(n_1^\circ) x_1$$
$$P y_2 = P_2^\circ(n_2^\circ) x_2 \qquad (12)$$
$$G_1^\circ(n_1^\circ) = G_2^\circ(n_2^\circ)$$

The three unknowns are $(n_1^\circ, n_2^\circ, x_1)$, where $x_2 = 1 - x_1$. For multicomponent mixtures, each additional component adds two equations and two unknowns (n_i°, x_i).

Solution of Eq. (12) fixes the standard state and the composition of the adsorbed solution (x_1) for the specified state (T, P, y_1). The total loading (n) is:

$$\frac{1}{n} = \sum_i \frac{x_i}{n_i^\circ} \qquad (13)$$

and individual loadings are:

$$n_i = n x_i \qquad (14)$$

Thermodynamic Functions for Mixtures

The equilibrium calculation described above yields the loadings of the individual components. The calculation of the free energy of desorption from Eq. (12) is necessary to establish the standard state for vapor-adsorption equilibrium but its connection to enthalpy and entropy has not been recognized. This misunderstanding is encouraged by the (ΠA) notation used for the free energy of immersion.

The solution of Eq. (12) yields the free energy of desorption ($G = G_1^\circ = G_2^\circ$). The free energy of desorption is the change in Gibbs free energy corresponding to complete degassing of the adsorbent at the equilibrium

conditions. The ideal enthalpy of desorption is then obtained from the enthalpies of the single gases by:

$$H = \sum_i n_i h_i^\circ \qquad (15)$$

where the pure-component molar enthalpy of desorption (h_i°) is fixed by the standard state of that component (n_i° or P_i°). n_i is the actual adsorption of ith component from Eq. (14). The simplicity of Eq. (15) for the integral enthalpy should be compared with the complicated equation for differential enthalpy (Siperstein and Myers, 2001), which calls for the slope of the adsorption isotherm and the differential and integral enthalpies of the single gases in their standard states.

The entropy of desorption may be obtained by an equation similar to Eq. (15):

$$S = \sum_i n_i s_i^\circ \qquad (16)$$

s_i° is the molar entropy of desorption in the standard state. Surprisingly, a term for the entropy of mixing does not appear in Eq. (16). The total entropy of the adsorbate mixture relative to its pure, perfect-gas reference state includes a separate term for mixing and compressing the adsorbate gas to its equilibrium state (T, P, y_1).

Finally, the three desorption functions are related by the familiar thermodynamic equation:

$$G = H - TS \qquad (17)$$

Differential Functions

The desorption functions (G, H, S) are integral functions and the corresponding differential functions may be obtained from their definition. For the differential enthalpy of desorption (isosteric heat):

$$\bar{h}_i = \left[\frac{\partial H}{\partial n_i} \right]_{T, n_j} \qquad (18)$$

This derivative can be evaluated numerically. Holding the adsorption of one component fixed while varying the adsorption of the other component requires that the amounts adsorbed (n_i) be independently variable. For this purpose, Eq. (12) is replaced by:

$$\frac{1}{n} = \frac{x_1}{n_1^\circ} + \frac{x_2}{n_2^\circ}$$
$$G_1^\circ(n_1^\circ) = G_2^\circ(n_2^\circ) \qquad (19)$$

where $n = (n_1 + n_2)$, $x_1 = (n_1/n)$, and $x_2 = (1 - x_1)$ are known and the two equations are solved for standard-state values of n_1° and n_2°. These standard states are needed for the numerical determination of the enthalpy increment ΔH by Eq. (15). An increment of $\Delta n_i = 0.01$ mole is small enough to obtain an accurate value of the derivative in Eq. (18). Actually, this procedure mimics the experimental determination of the differential enthalpy by calorimetry (Siperstein et al., 1999).

The differential entropy may be evaluated numerically by an equation similar to Eq. (18) or from:

$$\mu_i = \bar{h}_i - T\bar{s}_i \qquad (20)$$

The overline notation used to identify differential variables is omitted for the chemical potential since its differential character is understood.

The relationship between integral and differential enthalpy for a binary mixture is

$$H = \int_{n_1=0}^{n_1} \bar{h}_1 dn_1 + \int_{n_2=0}^{n_2} \bar{h}_2 dn_2 \qquad (21)$$

Since H is a state function, the integral is independent of the path selected for the integration through (n_1, n_2) space. Similar equations can be written for the integral free energy and integral entropy functions. This property of independence of path provides a basis for testing experimental mixture data for thermodynamic consistency, usually by integrating the free energy of desorption over a closed path for which the sum of the integrals must be equal to zero (Sircar and Myers, 1971).

Example

The calculation of thermodynamic properties is illustrated for the particular case of adsorption of C_2H_4 (1) and C_2H_6 (2) in NaX (Siperstein and Myers, 2001). For the individual gases, the constants of the Langmuir-virial equation are listed in Table 2 and the constants for the differential enthalpy of desorption (isosteric heat) are in Table 3 for the equation:

$$\bar{h} = \sum_{i=0}^{4} D_i n^i \qquad (22)$$

The molar enthalpy of desorption is then:

$$h = \frac{1}{n} \int_0^n \bar{h} dn = \sum_{i=0}^{4} \left[\frac{D_i}{i+1} \right] n^i \qquad (23)$$

Table 2. Constants of Eq. (1) for adsorption on NaX at 293.15 K (Siperstein and Myers, 2001).

Gas	K (mol/kg kPa)	m (mol/kg)	C_1 (kg/mol)	C_2 (kg/mol)^2	C_3 (kg/mol)^3	C_4 (kg/mol)^4
C_2H_4	5.2039	4.5341	0.3850	0.0075	0.0012	0.0012
C_2H_6	0.1545	3.8937	−0.2670	−0.0499	0.0192	0.0

Table 3. Constants of Eq. (22) for differential enthalpy (isosteric heat) of adsorption on NaX at 293.15 K (Siperstein and Myers, 2001).

Gas	D_0	D_1	D_2	D_3	D_4
C_2H_4	41.836	−0.3215	1.2203	−0.9452	0.1576
C_2H_4	26.893	1.1719	−0.0328	0.1195	0.0

Enthalpy given in units of kJ/mol for n in mol/kg.

Table 4. Comparison of IAS theory with experiment for adsorption of mixture of ethylene (1) and ethane (2) in NaX.

	P (kPa)	T (K)	y_1	x_1	n (mol/kg)
Theory	26.52	293.15	0.185	0.741	3.097
Exper.	26.52	297.46	0.185	0.692	3.106

Table 6. Desorption properties for a mixture of ethylene and ethane in NaX. Equilibrium gas conditions: 26.52 kPa, 297.46 K, 18.5 mol% ethylene.

	H (kJ/kg)	G (kJ/kg)	S (kJ/kg-K)
Theory	118.5	17.6	0.344
Exper.	125.4	18.4	0.360

for handling and even for predicting nonidealities in the adsorbed phase, but much more work is needed before mixed-gas nonidealities can be predicted with confidence.

The differential enthalpies (isosteric heats) $\bar{h}_1 = 40.2$ kJ/mol and $\bar{h}_2 = 29.1$ kJ/mol were obtained using an increment of 0.01 mol/kg of each component at the prescribed state ($T = 293.15°C$, $P = 26.52$ kPa, $y_1 = 0.185$) by Eq. (18). These values of differential enthalpy agree exactly with values calculated for an ideal solution using the explicit equation mentioned in the section on differential functions. These differential enthalpies for an ideal solution are compared with experiment in Table 5.

From Eq. (15), the enthalpy of desorption $H = (2.294)(41.18) + (0.803)(29.93) = 118.5$ kJ/kg, which agrees exactly with the value obtained by numerical integration using Eq. (21), either along the path of preloading pure ethylene or along the path for preloading pure ethane before adding the second component.

The entropy of desorption is $TS = (H − G) = (118.5 − 17.59) = 100.9$ kJ/kg, which agrees with the result calculated from Eq. (16). Results for the desorption properties are summarized and compared with experiment in Table 6.

Specifically, consider the mixture state at $T = 293.15$ K, $P = 26.52$ kPa, and $y_1 = 0.185$. Solution of Eq. (12) yields $n_1^\circ = 3.004$, $n_2^\circ = 3.399$, and $x_1 = 0.741$. The free energy of desorption in the standard state is $G = G_1^\circ = G_2^\circ = 17.59$ kJ/kg. At this standard state, the molar enthalpies of desorption from Eq. (23) are $h_1^\circ = 41.18$ kJ/mol and $h_2^\circ = 29.93$ kJ/mol. From Eqs. (13) and (14), $n = 3.097$ mol/kg, $n_1 = 2.294$ mol/kg, and $n_2 = 0.803$ mol/kg.

Table 4 shows a comparison of the IAS calculation with the experimental data. Although the temperatures differ by about 4°C, the main source of the difference between theory and experiment is nonideal behavior in the adsorbed phase: mixtures of ethylene and ethane on NaX exhibit negative deviations from Raoult's law. Methods are available (Siperstein and Myers, 2001)

Table 5. Differential properties for a mixture of ethylene (1) and ethane (2) in NaX. Standard state is perfect gas at 1 bar and same temperature.

	P (kPa)	T (K)	y_1	$\bar{h}_1$	$\bar{h}_2$	μ_1	μ_2	$\bar{s}_1$	$\bar{s}_2$
				(kJ mol^{-1})				(kJ mol^{-1} K^{-1})	
Theory	26.52	293.15	0.185	40.21	29.07	7.380	3.766	0.1120	0.0863
Exper.	26.52	297.61	0.185	40.40	32.50	7.492	3.823	0.1106	0.0964

This particular example shows the effect of nonidealities in adsorbed solutions at high loading. All mixtures approach ideal behavior at low loading.

Conclusions

The desorption properties (G, H, S) introduced in this paper are integral functions whose values are independent of the integration path. The values of these desorption properties are linearly related to the corresponding properties for the single gases, as shown by Eq. (15) for the enthalpy of desorption (H). The free energy of desorption (G) determines the standard state for the thermodynamic analysis of adsorbed mixtures. The differential enthalpy (isosteric heat) may be calculated numerically from the enthalpy of desorption in a manner which mimics its measurement by calorimetry.

The free energy of desorption function for a single gas exemplified by Eq. (4) provides a equation of state for the complete thermodynamic description of the system, with the enthalpy and entropy functions related to its isobaric temperature coefficient and the adsorption isotherm related to its isothermal pressure coefficient.

Nomenclature

C_i Constant, Eq. (1) (kg^i mol^{-i})
D_i Constant, Eq. (22)
G Gibbs free energy of desorption (kJ kg^{-1})
h Molar enthalpy of desorption (kJ mol^{-1})
$\bar{h}$ Differential enthalpy of desorption (kJ mol^{-1})
H Enthalpy of desorption (kJ kg^{-1})
K Henry constant, Eq. (1) (mol kg^{-1} kPa^{-1})
m Saturation capacity (mol kg^{-1})
n Amount adsorbed (mol kg^{-1})
P Pressure (Pa)
R Gas constant, 8.3145 J mol^{-1} K^{-1}
s Molar entropy of desorption (kJ mol^{-1} K^{-1})
$\bar{s}$ Differential entropy of desorption (kJ mol^{-1} K^{-1})
S Entropy of desorption (kJ kg^{-1} K^{-1})
T Temperature (K)
x_i Mole fraction of component i in adsorbed phase
y_i Mole fraction of component i in vapor phase

Greek Letters

$\alpha_{i,j}$ Selectivity of component i relative to component j, Eq. (9)

μ Chemical potential (kJ mol^{-1})
Ξ Grand canonical partition function
Ω Grand potential (kJ kg^{-1})

Subscripts

i Refers to component i

Superscripts

$\circ$ Refers to standard state for adsorbed mixture

Acknowledgment

References

Adamson, A.W. and A.P. Gast, *Physical Chemistry of Surfaces*, 6th Edition, Wiley, New York, 1997.

Hyun, S.H. and R.P. Danner, *J. Chem. Eng. Data*, **27**, 196 (1982).

Myers, A.L., "Thermodynamics of Adsorption in Porous Materials," *AIChE J.*, **48**, 145–160 (2002).

Myers, A.L. and P.A. Monson, "Adsorption in Porous Materials at High Pressure: Theory and Experiment," *Langmuir*, **18**, 10261–10273 (2002).

Nicholson, D. and N.G. Parsonage, *Computer Simulation and the Statistical Mechanics of Adsorption*, Academic Press, London, 1982.

Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, pp. 65–85, John Wiley & Sons, New York, 1984.

Salem, M.M.K., P. Braeuer, M.V. Szombathely, H. Heuchel, P. Harting, and K. Quitzsch, "Thermodynamics of High Pressure Adsorption of Argon, Nitrogen, and Methane on Microporous Adsorbents," *Langmuir*, **14**, 3376 (1998).

Shen, D., M. Bülow, F. Siperstein, M. Engelhard, and A.L. Myers, "Comparison of Experimental Techniques for Measuring Isosteric Heat of Adsorption," *Adsorption*, **6**, 275 (2000).

Siperstein, F. and A.L. Myers, "Mixed-Gas Adsorption," *AIChE J.*, **47**, 1141–1159 (2001).

Siperstein, F., R.J. Gorte, and A.L. Myers, "A New Calorimeter for Simultaneous Measurements of Loading and Heats of Adsorption from Gaseous Mixtures," *Langmuir*, **15**, 169–176 (1999).

Sircar, S. and A.L. Myers, "A Thermodynamic Consistency Test for Adsorption of Binary Liquid Mixtures on Solids," *AIChE J.*, **17**, 186–190 (1971).

Valenzuela, D.P. and A.L. Myers, *Adsorption Equilibrium Data Handbook*, Prentice-Hall, Englewood Cliffs, N.J., 1989.

Yang, R.T., *Gas Separation by Adsorption Processes*, Butterworths, London, 1987.