CHAPTER 21

Thermodynamics of Adsorption

ALAN L. MYERS

1 Introduction

The attachment of molecules to the surface of a solid by adsorption is a broad subject. This chapter is focused on the adsorption of gases in high-capacity solid adsorbents such as active carbon [1] or zeolites.[2] These commercial adsorbents owe their enormous capacity to an extensive network of nanopores of various shapes (cylinders, slits) with specific volumes in the range from 100 to 1000 $\mathrm{cm^3\,kg^{-1}}$. Applications of adsorption exploit the ability of nanoporous materials to adsorb one component of a gas preferentially. For example, the preferential adsorption of nitrogen from air passed through an adsorption column packed with zeolite creates a product stream of nearly pure oxygen.

Thermodynamics has the remarkable ability to connect seemingly unrelated properties. For example, the temperature coefficient of adsorption is directly proportional to the heat of immersion of the solid adsorbent in the gas. The most important application of thermodynamics to adsorption is the calculation of phase equilibrium between a gaseous mixture and a solid adsorbent.

The basis for thermodynamic calculations is the adsorption isotherm, which gives the amount of gas adsorbed in the nanopores as a function of the external pressure. Adsorption isotherms are measured experimentally or calculated from theory using molecular simulations.[3] Potential functions are used to construct a detailed molecular model for atom–atom interactions and a distribution of point charges is used to reproduce the polarity of the solid material and the adsorbing molecules. Recently, *ab initio* quantum chemistry has been applied to the theoretical determination of these potentials, as discussed in another chapter of this book.

Thermodynamics applies only to equilibrium adsorption isotherms. Equilibrium means that any point can be reached from either direction by raising (adsorption) or lowering (desorption) the pressure at constant temperature. If the desorption isotherm does not coincide with the adsorption isotherm, then equilibrium has not been achieved and the usual thermodynamic equations do not apply. The mismatch of adsorption and desorption, which is called hysteresis, does not occur in pores smaller than 2 nm but is observed[1] when the pores are large enough for the adsorbing molecules to condense to a liquid. For adsorption of supercritical gases or for adsorption of subcritical vapors in nanopores, most experiments and simulations yield equilibrium isotherms with no evidence of hysteresis.

Molecular simulations yield *absolute* adsorption or the actual number of molecules in the nanopores. Experiments measure *excess* adsorption, which is the number of molecules in the nanopores in excess of the amount that would be present in the pore volume at the equilibrium density of the bulk gas. The difference between absolute and excess adsorption is negligible at the sub-atmospheric pressures of greatest interest. For supercritical gases adsorbed at high pressure (*e.g.* 100 bar), the difference between absolute and excess adsorption is too large to ignore.[4]

2 Adsorption Isotherm and Equation of State

Whether the adsorption isotherm has been determined experimentally or theoretically from molecular simulation, the data points must be fitted with analytical equations for interpolation, extrapolation, and for the calculation of thermodynamic properties by numerical integration or differentiation. The adsorption isotherm for a pure gas is the relation between the specific amount adsorbed n (moles of gas per kilogram of solid) and P, the external pressure in the gas phase. For now, the discussion is restricted to adsorption of a pure gas; mixtures will be discussed later. A typical set of adsorption isotherms is shown in Figure 1. Most supercritical isotherms, including these, may be fit accurately by a modified virial equation.[5]

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

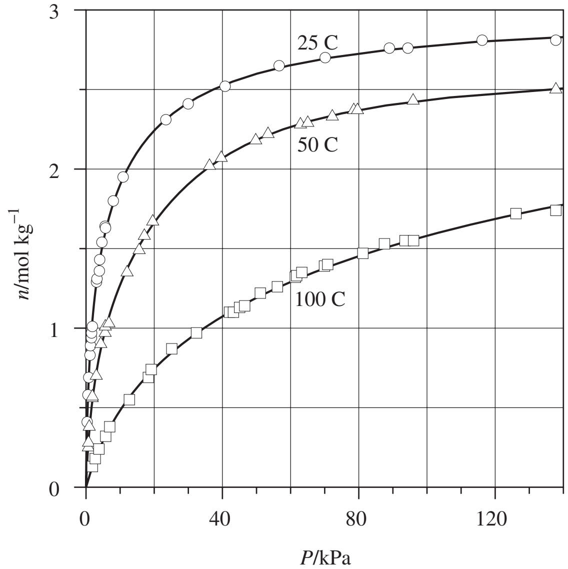

Figure 1 *Adsorption isotherms of C_2H_4 in NaX (zeolite structure FAU), where n is the amount absorbed and P is the pressure. Points indicate experimental data.[6] Solid lines indicate Equation (1)*

where K is the Henry's constant, or the slope of adsorption isotherm $\mathrm{d}n/\mathrm{d}P$ at the limit of zero pressure, m is the saturation capacity (mol kg^{-1}), and the C_i are virial coefficients, three of which usually suffice to fit the data within experimental error. If the virial coefficients are all zero, Equation (1) reduces to the well-known Langmuir equation.[1] Equation (1) has the form $P(n)$ so that the inverse function $n(P)$ is implicit. This slight inconvenience is offset by the fact that the implicit form can be integrated analytically for the thermodynamic functions (see below).

The determination of an accurate value for Henry's constant (K) is essential for the calculation of thermodynamic properties and for mixture calculations. According to Equation (1), a plot of $\ln(P/n)$ as a function of n intersects the y-axis at $1/K$. If the scatter of the data at low pressure is so large that an accurate value of K is impossible to determine, then Henry's constant should be measured at a higher temperature. It is difficult to obtain reliable values of Henry's constants from gravimetric measurements because the amount of gas adsorbed at low pressure is given by the difference of two weight measurements that differ by an infinitesimal amount. Volumetric measurements are preferred for measuring Henry's constants because the amount of gas adsorbed is determined by the large difference between the amount of gas dosed to the system and the amount of gas left in the system after adsorption.

Interpolation of adsorption isotherms with respect to temperature is based on the thermodynamic equation:[7]

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

where $\bar{h}$ is the differential enthalpy of adsorption, a negative quantity because adsorption is exothermic. The absolute value of $\bar{h}$ is called "isosteric heat". The partial differentiation is performed at constant n. In the rigorous equation, the pressure P is replaced by the fugacity of the gas. The differential enthalpy may be expressed as a polynomial:

$$\bar{h}(n) = D_0 + D_1 n + D_2 n^2 + D_3 n^3 + \cdots \tag{3}$$

The constants D_i are assumed to be independent of temperature. For wide variations in temperature over several hundred degrees Kelvin, this approximation can be corrected by introducing heat capacities. The integrated form of Equation (2) is

$$\ln\left[\frac{P}{P^*}\right] = \frac{\bar{h}(n)}{R}\left[\frac{1}{T} - \frac{1}{T^*}\right] \quad \text{(constant } n\text{)} \tag{4}$$

which provides the temperature dependence $P(T)$ given a reference point $P^*(T^*)$ measured at the same value of n. Combination of Equations (1) and (4) yield an adsorption equation-of-state, which includes the temperature variable:

$$P(n,T) = \frac{n}{K}\left[\frac{m}{m-n}\right] \times \exp\left[\frac{\bar{h}(n)}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \times \exp[C_1 n + C_2 n^2 + C_3 n^3 + \cdots] \tag{5}$$

where the constants K, m, and the C_i refer to the reference isotherm at T^*. The constants of Equation (5) for the adsorption isotherms in Figure 1 are: $T^* = 298.15$ K, $K=1.9155$

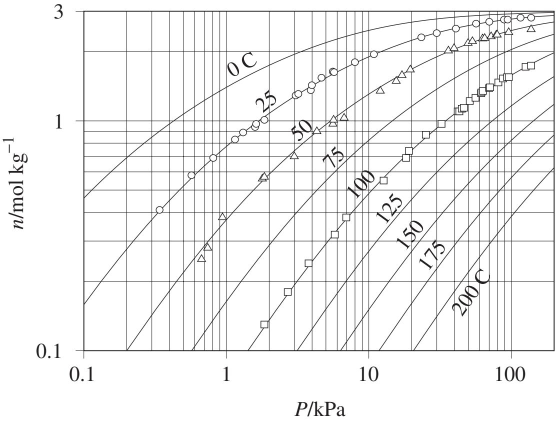

Figure 2 *Adsorption isotherms of C_2H_4 in NaX (zeolite structure FAU), where n is the amount adsorbed and P is the pressure. Points indicate experimental data.[6] Solid lines calculated from Equation (5)*

mol kg^{-1} kPa^{-1}, m=2.9997 mol kg^{-1}, C_1=0.841 kg mol^{-1}, C_2=−0.06311 kg^2 mol^{-2}, C_3=−0.009415 kg^3 mol^{-3}, D_0=−39.5 kJ mol^{-1}, and D_1=2.25 kJ kg mol^{-2}. The experimental data are compared with Eq. (5) in Figure 2, which includes interpolated and extrapolated isotherms. Logarithmic plots are useful for examining the accuracy of the equation-of-state at low pressure. The calculation of enthalpy, free energy, and entropy from these constants is explained in the next section.

Usually, the differential enthalpy is determined from Equation (2) using two or more adsorption isotherms. Alternatively, the differential enthalpy can be measured directly using a calorimeter.[8] In either case, a reference isotherm should be measured for the lowest temperature at which an accurate value of the Henry constant can be extracted. In the example shown in Figure 1, the reference isotherm is at 25 °C. For a particular gas and solid, the combination of a reference isotherm with the differential enthalpy provides complete thermodynamic information about the system.

3 Thermodynamic Functions

The grand potential plays a central role in adsorption thermodynamics. The grand potential is defined by

$$\Omega = F - \sum_i n_i \mu_i = -PV \tag{6}$$

where F is the Helmholtz free energy. The independent variables of the grand potential are temperature, volume, and chemical potential. These variables are precisely the ones needed to describe the amount adsorbed from a bulk gas at specified values of temperature and chemical potential in a solid adsorbent of fixed volume. For the same reason, molecule simulations of adsorption are conveniently performed in the grand canonical ensemble for which $\Omega = -kT \ln \Xi$, where Ξ is the grand canonical partition function.[9]

For adsorption of a pure gas, the grand potential is obtained from an isothermal integration:[4]

$$\Omega = -RT\int_0^P \frac{n}{P}\,\mathrm{d}P = -RT\int_0^n \left[\frac{\partial \ln P}{\partial \ln n}\right]_T \mathrm{d}n \tag{7}$$

Ω is expressed in J kg^{-1} of solid adsorbent. Physically, the grand potential is the free energy change associated with isothermal immersion of fresh adsorbent in the bulk fluid. The absolute value of the grand potential is the minimum isothermal work necessary to clean the adsorbent. Since adsorption occurs spontaneously, the cleaning or regeneration of the adsorbent after it equilibrates with the feed stream is the main operating cost of an adsorptive separation process.

Any extensive thermodynamic property of the system (free energy, enthalpy, entropy, or heat capacity) may be written as the sum of three terms for:

1. the value of the property for the adsorbate molecules at the state of the equilibrated bulk gas mixture at $\{T, P, y_i\}$;
2. the value of the property for the clean solid adsorbent *in vacuo* at T; and
3. the change in the property associated with immersion of the clean adsorbent in the bulk gas at constant $\{T, P, y_i\}$.

The thermodynamic functions for items 1 and 2 are calculated using the standard equations for bulk gases and solids, respectively,[10] so that the focus for adsorption thermodynamics is on item 3. It follows from Equations (5) and (7) that the grand potential (free energy of immersion) for each pure component is

$$\begin{aligned}\Omega(n,T) = -RT\Big\{&-m\ln\left(1-\frac{n}{m}\right) + \left(\frac{1}{2}C_1n^2 + \frac{2}{3}C_2n^3 + \frac{3}{4}C_3n^4 + \cdots\right)\\ &+ \frac{1}{R}\left[\frac{1}{T} - \frac{1}{T^*}\right]\left(\frac{1}{2}D_1n^2 + \frac{2}{3}D_2n^3 + \frac{3}{4}D_3n^4 + \cdots\right)\Big\}\end{aligned} \tag{8}$$

The constants m and C_i refer to the values for the reference isotherm at T^*; the constants D_i refer to the polynomial for the differential enthalpy in Equation (3). Note that the free energy is independent of the limiting value of the enthalpy at zero pressure, D_o in Equation (3).

The enthalpy of immersion (H) is the integral of the differential enthalpy ($\bar{h}$):

$$H = \int_0^n \bar{h}\,\mathrm{d}n \tag{9}$$

The enthalpy of immersion, like Ω, has units of J kg^{-1}. From Equations (3) and (9):

$$H(n) = D_0n + \frac{1}{2}D_1n^2 + \frac{1}{3}D_2n^3 + \frac{1}{4}D_3n^4 + \cdots \tag{10}$$

It is convenient to report the enthalpy of immersion as an integral molar enthalpy (J mol^{-1}) using $h=H/n$:

$$h(n) = D_0 + \frac{1}{2}D_1n + \frac{1}{3}D_2n^2 + \frac{1}{4}D_3n^3 + \cdots \tag{11}$$

Given the free energy of immersion (Ω) and the enthalpy of immersion (*H*), the entropy of immersion is

$$S = \frac{H-\Omega}{T} \tag{12}$$

4 Mixtures

The grand potential provides the standard state for the formation of 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[7] to establish the amounts adsorbed (n_1^o, n_2^o) at the standard state:

$$Py_1 = P_1^o(n_1^o, T)x_1 \tag{13}$$

$$Py_2 = P_2^o(n_2^o, T)x_2 \tag{14}$$

$$\Omega_1(n_1^o, T) = \Omega_2(n_2^o, T) \tag{15}$$

Thus, the partial pressures on the left-hand side of Equations (13) and (14) are known and the three unknowns are n_1^o, n_2^o, and x_1, where $x_2=1-x_1$. For mixtures containing more than two components, each additional component adds two equations and two unknowns (n_i^o and x_i). In the rigorous form of Equations (5), (7), and (13)–(15), the pressure or partial pressure is replaced by the fugacity.

Given the adsorbed-phase composition x_1 from the solution of Equations (13)–(15), the selectivity of the adsorbent for component *i* relative to component *j* is

$$S_{i,j} = \frac{x_i/y_i}{x_j/y_j} \tag{16}$$

The larger the selectivity, the easier the separation of component *i* from component *j* by adsorption. Zeolites with a selectivity as high as 10 for nitrogen relative to oxygen are used in pressure-swing adsorption processes[11] to produce oxygen from air. The specific amount of each component adsorbed for an ideal solution is given by

$$n_i = n_t x_i \tag{17}$$

where the total specific amount adsorbed from a mixture of gases is

$$\frac{1}{n_t} = \sum_i \frac{x_i}{n_i^o} \tag{18}$$

In summary, the procedure for predicting the thermodynamic properties of an adsorbed mixture begins with the determination of the thermodynamic properties of each individual component as expressed by its equation of state, Equation (5). After fixing the independent variables $\{T, P, y_i\}$ for a system containing N_c components, the set of $(2N_c-1)$ Equations (13)–(15) is solved for the adsorbed-phase mole fractions x_i and standard-state amounts adsorbed (n_i^o), with the constraint that $\sum_i x_i = 1$.

Knowledge of the standard states and the adsorbed-phase composition allows the calculation of the selectivity by Equations (16) and the amount of each species adsorbed by Equations (17) and (18). Finally, the entropy and enthalpy of immersion are given by the equations:

$$H = \sum_i n_i H_i^{\mathrm{o}}(n_i^{\mathrm{o}}) \tag{19}$$

$$S = \sum_i n_i S_i^{\mathrm{o}}(n_i^{\mathrm{o}}) \tag{20}$$

H_i^{o} and S_i^{o} are evaluated at the standard-state amount adsorbed (n_i^{o}). It may seem at first glance that an entropy of mixing term is missing from Eq. (20), but S refers to the entropy of immersion of the solid in the gas mixture. 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 $\{T, P, y_i\}$. The integral enthalpy H of the mixture divided by the total amount adsorbed is the integral molar enthalpy h, as in Equation (11) for adsorption of a single component.

5 Example

The application of Equations (13)–(20) is illustrated for binary mixtures of ethylene (1) and ethane (2) adsorbed on NaX zeolite (faujasite). The constants for the single-gas adsorption equations of state[5] are given in Tables 1 and 2. The selectivity of NaX for ethylene relative to ethane ($S_{1,2}$) is a function of temperature, pressure, and the composition of the gas. The selectivity at constant temperature (20 °C) is shown in Figure 3. The selectivity at the limit of zero pressure is the ratio of Henry's constants ($K_1/K_2=33.7$). At constant mole fraction of ethylene in the gas, the selectivity decreases rapidly with increasing pressure. At constant pressure, the selectivity decreases with increasing mole fraction of ethylene in the gas. The selectivity at constant pressure and gas composition decreases with temperature, as shown in Figure 4. Decrease of the selectivity with temperature, pressure, and the mole fraction of the preferentially adsorbed species is typical behavior for binary adsorption.

Table 1 *Constants of Eq. (1) for reference adsorption isotherms of gases in NaX zeolite[5] at 293.15 K. Virial coefficients C_i in units of kg^i mol^{-i}*

Gas	*K (mol kg^{-1} kPa^{-1})*	*m (mol kg^{-1})*	C_1	C_2	C_3	C_4
C_2H_4	5.2039	4.5341	0.385	0.0075	0.0012	0.0012
C_2H_6	0.1545	3.8937	−0.267	−0.0499	0.0192	0.0

Table 2 *Constants of Eq. (3) for differential enthalpy (isosteric heat) of adsorption of gases in NaX zeolite[5] at 298.15 K. Virial coefficients D_i in units of kJ kg^i mol$^{-(i+1)}$*

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_6	−26.893	−1.1719	0.0328	−0.1195	0.0

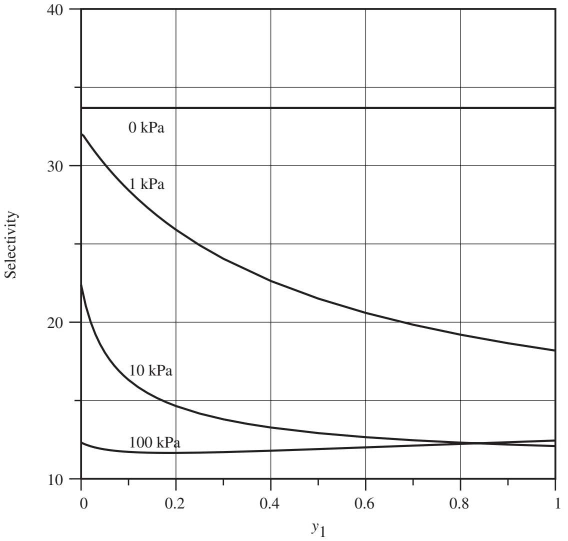

Figure 3 *Selectivity $(x_1y_2)/(x_2y_1)$ for adsorption of ethylene (1) relative to ethane (2) in NaX (zeolite structure FAU) at 20°C, plotted against y_1, the mole fraction of C_2H_4 in the gas. Isobars calculated from Equations (13)–(16) using the constants for pure gases in Table 1*

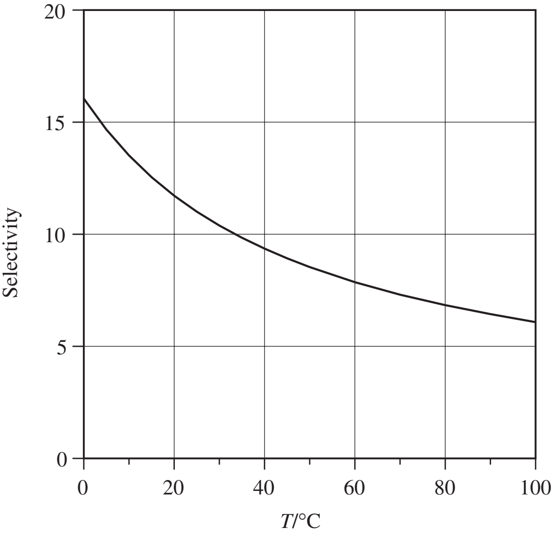

Figure 4 *Selectivity $(x_1y_2)/(x_2y_1)$ for adsorption of ethylene (1) relative to ethane (2) in NaX (zeolite structure FAU) at 100 kPa and $y_1=0.1$, plotted against the temperature. Calculated from Equations (13)–(16) using the constants for pure gases in Tables 1 and 2*

The selectivities in Figures 3 and 4 were calculated from the single-gas isotherms using Equations (13) and (14), which are written for ideal adsorbed solutions (IAS) with activity coefficients $\gamma_i=1$. These equations are rigorous at the limit of low pressure. At high pressure, mixtures adsorbed in nanopores display negative

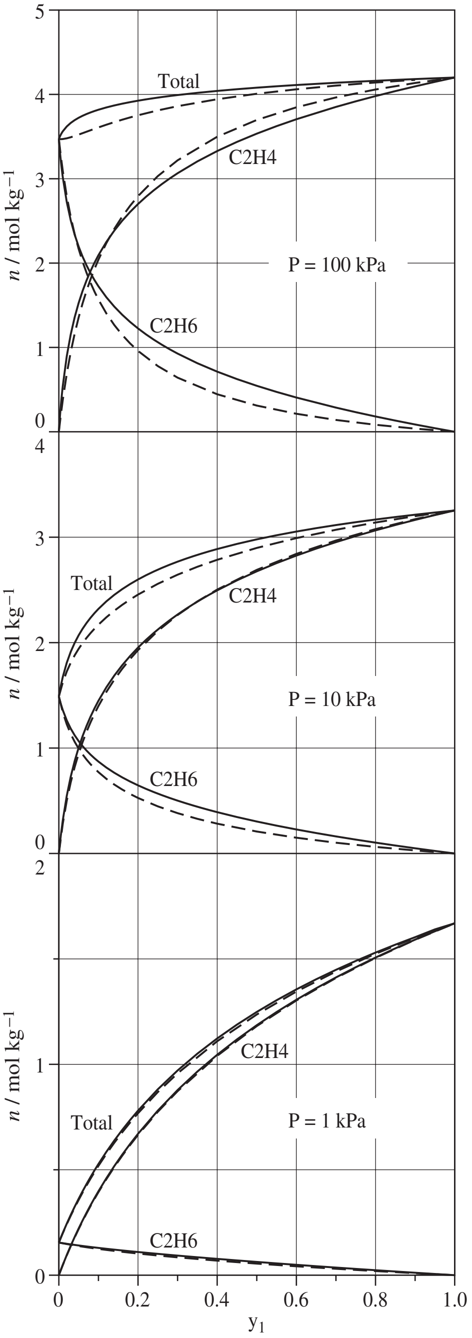

Figure 5 *Individual and total isotherms at 20 °C for isobaric adsorption of mixtures of ethylene (1) and ethane (2) in NaX (zeolite structure FAU), where n is the amount adsorbed and* y_1 *is the mole fraction of ethylene in the gas. Dashed lines calculated from Equations (13)–(15), (17) and (18) using the constants for pure gases in Table 1. Solid lines indicate experimental data*[5]

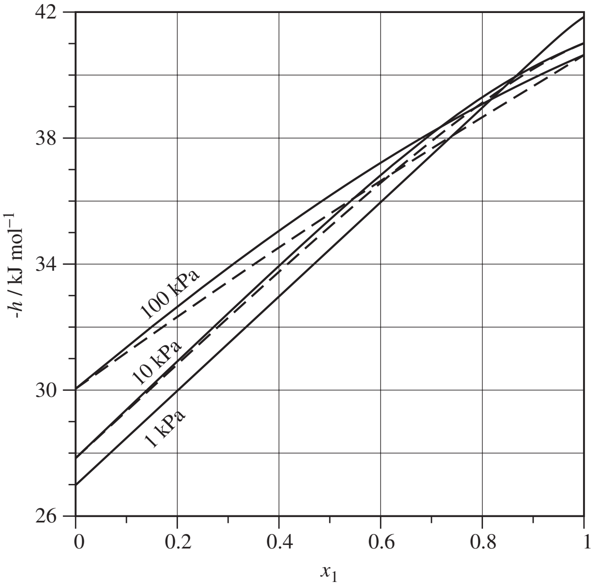

Figure 6 *Enthalpy for isobaric adsorption of mixtures of ethylene (1) and ethane (2) in NaX, where h is the integral enthalpy and x_1 is the mole fraction of ethylene in the nanopores. Dashed lines calculated from Equations (13)–(15) and (19) using constants for the pure gases in Tables 1 and 2. Solid lines indicate experimental data.[5] At 1 kPa, the dashed and solid line coincide*

deviations from Raoult's law (γ_i<1). These deviations are dominated by heterogeneity of the gas–solid energy and therefore cannot be estimated from the activity coefficients of the bulk fluids. The strongest deviations from ideality are observed for mixtures in zeolites such as NaX (faujasite), which has strong electric fields and electric field gradients in its nanopores that interact differently with quadrupolar (C_2H_4) and nonpolar molecules (C_2H_6). Mixtures adsorbed in materials with weak electric field gradients such as silicalite (MFI structure) or active carbon are more nearly ideal ($\gamma_i \approx 1$) than zeolites like NaX, which contain exchangeable nonframework cations.

Activity coefficients for nonideal mixtures have been reported.[5] The error associated with the use of IAS theory is shown in Figure 5. The solid lines are the experimental data and the dashed lines were calculated from Equations (13)–(18). The comparison of the IAS prediction with experimental data in Figure 5 raises the following question: is it possible to predict activity coefficients? Correlations of activity coefficients with single-gas adsorptive properties[5] suggest that such predictions are possible, and reliable methods may be discovered in the future.

The estimate of the integral enthalpy (h) by Equation (19) is shown by the dashed lines in Figure 6. The solid lines are the experimental data determined by calorimetry.[5] The error in the estimated enthalpy (dashed lines) increases with pressure but the largest error is 1.6%. The values at the two end points ($y_1 = 0$ and $y_1 = 1$) are the integral enthalpies for pure ethylene and ethane given by Equation (11).

6 Summary

Equation (5) is an equation-of-state for the adsorption of a pure gas as a function of temperature and pressure. The constants of this equation are the Henry constant, the saturation capacity, and the virial coefficients at a reference temperature. The temperature variable is incorporated in Equation (5) by the virial coefficients for the differential enthalpy. This equation-of-state for adsorption of single gases provides an accurate basis for predicting the thermodynamic properties and phase equilibria for adsorption from gaseous mixtures.

References

1. D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York, 1984, 7, 50, 56.
2. http://www.iza-structure.org/databases
3. D. Nicholson and N. G. Parsonage, *Computer Simulation of the Statistical Mechanics of Adsorption*, Academic Press, London, 1982
4. A. L. Myers, P. A. Monson, Adsorption in porous materials at high pressure: theory and experiment, *Langmuir*, 2002, **18**, 10261–10273.
5. F. R. Siperstein and A. L. Myers, Mixed-gas adsorption, *A.I.Ch.E.J.*, 2001, **47**, 1141–1159.
6. S. H. Hyun and R. P. Danner, *J. Chem. Eng. Data*, 1982, **27**, 196.
7. A. L. Myers, Thermodynamics of adsorption in porous materials, *A.I.Ch.E. J.*, 2002, **48**, 145–160.
8. J. A. Dunne, R. Mariwala, M. Rao, S. Sircar, R. J. Gorte and A. L. Myers, Calorimetric heats of adsorption and adsorption isotherms. 1. O_2, N_2, Ar, CO_2, CH_4, C_2H_6, and SF_6 on silicalite, *Langmuir*, 1996, **12**, 5888–5895.
9. D. A. McQuarrie, *Statistical Mechanics*, Harper & Row, New York, 1976, p. 51.
10. J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd edn, Chapter 3, Prentice-Hall, Upper Saddle River, New Jersey, 1999.
11. D. M. Ruthven, S. Farooq and K. S. Knaebel, *Pressure Swing Adsorption*, John Wiley & Sons, New York, 1993.

Manuscript Queries

Title: Chemical Thermodynamics for Industry

Chapter-21

Page	Query Number	Query
		No queries

Manuscript Queries

Title: **Chemical Thermodynamics for Industry**

Chapter-21

Page	Query Number	Query
		No queries