Rigorous Thermodynamic Treatment of Gas Adsorption

Multicomponent adsorption equilibria are predicted from theories based on experimental data for single-gas adsorption isotherms. Theories of multicomponent adsorption differ in the details of their results but should agree in special cases such as low surface coverage and ideal solution behavior. This paper is a summary of rules, limits, and consistency requirements that apply to adsorption of single gases and their mixtures. These rules and limits provide a basis for comparing theories with each other and with experimental data.

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Introduction

Equilibrium data for gas adsorption resemble vapor-liquid equilibria (VLE). Figure 1 shows the mole fraction y in the gas phase plotted v. the mole fraction x in the adsorbed phase at constant pressure and temperature. VLE experiments generate similar diagrams in which x is the mole fraction in the liquid phase and either pressure or temperature (but not both) is constant. The essential difference between VLE and gas adsorption is that the presence of the solid adsorbent introduces an additional degree of freedom. The solid imposes a potential field upon the adsorbed (surface) phase, which behaves like a two-dimensional gas at low density and like a bulk liquid at high density. The effect of spreading pressure upon the density of the surface phase must be accounted for in a rigorous treatment of physical adsorption.

Partly because of heterogeneities in the structure of the surface and partly because of the small-system effect (micropores contain only a few dozen adsorbate molecules), phase splitting in the adsorbed phase is not observed in high-area adsorbents and is not considered in this paper.

The specific amount adsorbed, n_i, is measured as a function of temperature T, pressure P, and gas-phase mole fraction y_i. Theories of adsorption provide explicit or implicit equations for the relations between these variables. Various rules derived from the laws of thermodynamics and statistical mechanics are valuable for evaluating the reliability of experimental data and for testing theories. The objective of this work is to summarize these rules and to illustrate their usefulness.

Adsorption of Pure Gases

Low-pressure limit of isotherm

The limiting slope of an adsorption isotherm at low pressure is:

$$\lim_{P \to 0} \frac{dn}{dP} = \lim_{P \to 0} \frac{n}{P} = \frac{B_{1S}}{RT} \tag{1}$$

where B_{1S} is the adsorption second virial coefficient that characterizes the interaction between one molecule and the surface. Since B_{1S} is positive and finite, the limiting slope must also be finite. Experimental data conform to this low-coverage limit but some adsorption equations do not, for example, the Freundlich equation:

$$n = KP^t \tag{2}$$

has an infinite slope at the origin:

$$\lim_{P \to 0} \frac{dn}{dP} = \lim_{P \to 0} \frac{Kt}{P^{1-t}} = \infty \tag{3}$$

since t is less than unity in the model. The Freundlich equation has a singularity unless $t = 1$. The Sips (1948) equation:

$$n = \frac{n_m KP^t}{1 + KP^t} \tag{4}$$

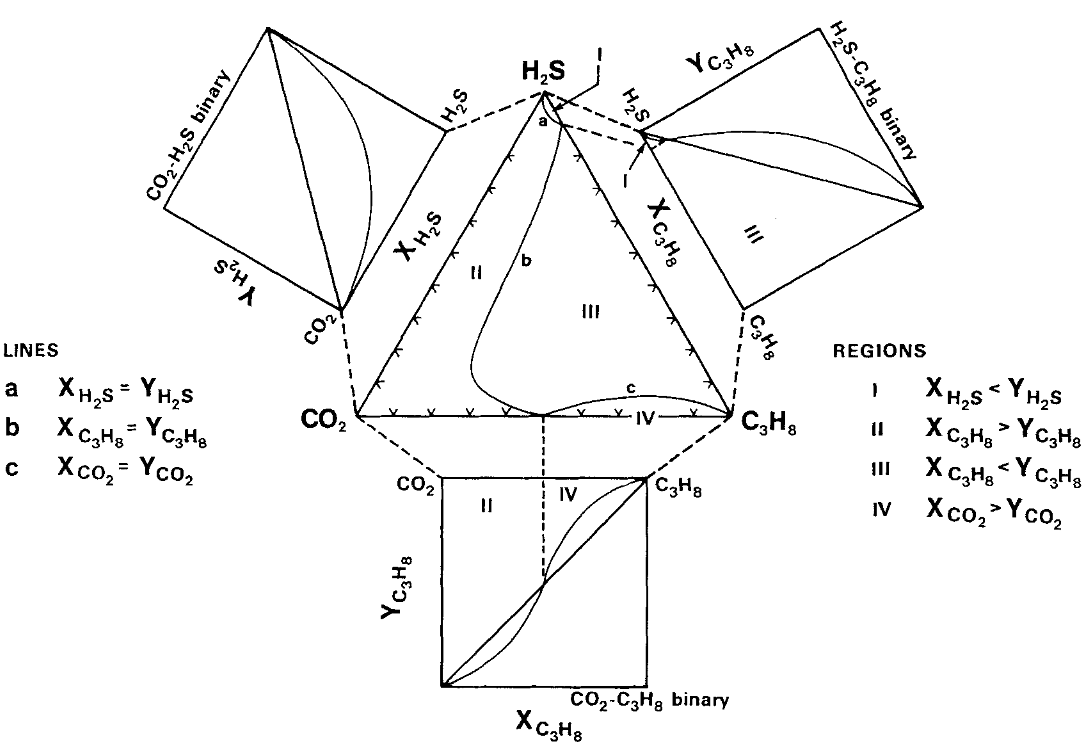

Figure 1. Continuity of ternary and binary data for adsorption of mixtures of $CO_2 + C_3H_8 + H_2S$ at 30°C and 13 kPa.

also has an infinite slope at the origin:

$$\lim_{P\to 0}\frac{dn}{dP}=\lim_{P\to 0}\frac{n_mKt}{P^{1-t}(1+KP^t)^2}=\infty \tag{5}$$

since $t < 1$. Because their adsorption second virial coefficients are undefined, the Freundlich and Sips equations cannot be used to extrapolate experimental data to low pressure or to calculating spreading pressure (see following section). However, both equations are widely used for fitting experimental data over a limited range (one or two decades) of pressure.

The Dubinin-Radushkevich (DR) equation (Yang, 1987)

$$n = n_m\exp\{-D[\ln(P^s/P)]^2\} \tag{6}$$

has a slope at the origin that is finite but incorrect (zero):

$$\lim_{P\to 0}\frac{dn}{dP} = \lim_{P\to 0}\frac{2Dn_m\ln(P^s/P)\exp\{-D[\ln(P^s/P)]^2\}}{P}=0 \tag{7}$$

The DR equation is widely used to fit experimental adsorption isotherms over a wide range of pressure, but it cannot be extrapolated to very low pressure and it does not permit the calculation of adsorption second virial coefficients.

Some equations have singularities in their higher order derivatives. For example, for the Toth (1971) equation:

$$n=\frac{n_mP}{(b+P^t)^{1/t}} \tag{8}$$

the limit of the second derivative at the origin is:

$$\lim_{P\to 0}\frac{d^2n}{dP^2}=\lim_{P\to 0}\frac{-n_mb(1+t)}{P^{1-t}(b+P^t)^{(2t+1)/t}}=-\infty \tag{9}$$

since $t < 1$. Because of the singularity in the second derivative, adsorption second virial coefficients calculated from the Toth equation by Eq. 1 are somewhat too large. Nevertheless, the Toth equation fits experimental data at moderate and high surface coverage as well as other three-parameter equations for adsorption in micropores.

Spreading pressure

Prediction of multicomponent adsorption equilibria is based upon accurate values of spreading pressure for adsorption of single gases, obtained by integration as follows:

$$\frac{\Pi A}{RT}=\int_0^P\frac{n}{P}\,dP \tag{10}$$

Figure 2 shows the limiting behavior of n/P for the adsorption equations of Freundlich, Toth, and Dubinin-Radushkevich (DR). The limit of ∞ for the Freundlich equation makes it unsuitable for calculating spreading pressure under any conditions. The other two equations have finite limits of n/P at $P = 0$. The limit of the Toth equation is too large because the slope of the n/P curve goes to $-\infty$ at the origin, and the limit of the DR equation is too small (zero) because the slope of the n/P curve goes to $+\infty$ at the origin. However, the error in the integral of Eq. 10 introduced by the incorrect limits of the Toth and DR equations is in fact small unless the pressure is very low. The

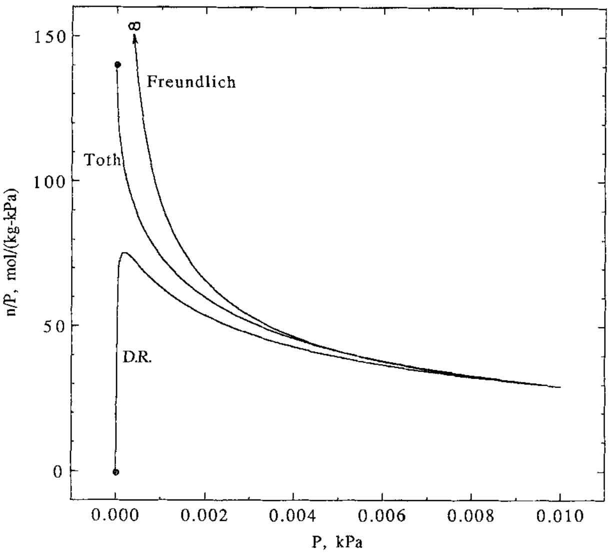

Figure 2. Limiting behavior of integrand n/P in Eq. 10 at low pressure for three isotherm equations.

maximum in Figure 2 for the DR equation is $(n/P)_{max} = (n_m/P^s)e^{1/(4D)}$ (Richter et al., 1988). The error in spreading pressure introduced by the false maximum is:

$$\Delta(\Pi A/RT) \approx n_m e^{-1/(4D)} \tag{11}$$

This error is usually less than the experimental error in $\Pi A/RT$. Also, the point $P = P^s e^{-1/(2D)}$ at which n/P attains its maximum value and begins to deviate significantly from experiment is usually a very low pressure.

Heat of adsorption

The energetics of adsorption are given by Clapeyron-type equations. For example, the isosteric heat of adsorption, q_{st}, is:

$$q_{st} = -R\left[\frac{\partial \ln P}{\partial(1/T)}\right]_n \tag{12}$$

The isosteric heat can be determined from experimental isotherms measured at several temperatures, or from isotherm equations if the model prescribes the temperature functionality of its parameters. Isosteric heat is a function of surface coverage and temperature. Temperature dependency is often neglected since the sensible heat of the adsorbed phase is small compared to the much higher energy necessary to remove a molecule from the surface. The requirement that the isosteric heat be finite imposes restrictions on the temperature coefficients of parameters in isotherm equations (Talu and Kabel, 1987). For example, for the Langmuir equation:

$$P = \frac{1}{K}\left[\frac{n}{n_m - n}\right] \tag{13}$$

where

$$K = K_0 \exp(\epsilon/RT) \tag{14}$$

Eq. 12 gives:

$$\frac{q_{st}}{RT} = \frac{\epsilon}{RT} - \frac{1}{1-\theta}\left[\frac{d \ln n_m}{d \ln T}\right] \tag{15}$$

where ϵ is the energy of desorption (a positive quantity) and $\theta = n/n_m$. When experimental adsorption isotherms are fitted by monolayer equations, it is found that n_m decreases with temperature: $d \ln n_m/d \ln T$ is of the order of -1. Equation 15 predicts that q_{st} is infinite at monolayer coverage. The explanation of the singularity is that the Langmuir model is derived for constant n_m and is therefore inconsistent with a finite value of dn_m/dT. If the Langmuir equation (with $dn_m/dT \neq 0$) fits experimental data for two or more adsorption isotherms in the region $0 < n < n_{max}$, then Eq. 15 gives the correct heat of adsorption for that region but is incorrect if extrapolated beyond n_{max}. This problem is not limited to the Langmuir equation; all monolayer theories of adsorption have a singularity in the isosteric heat at saturation capacity.

Multicomponent Adsorption

Continuity of ternary and binary data

Either experimental data for adsorption of mixtures, or theories for multicomponent adsorption, must reduce to the next lower order (ternary to binary, binary to single component) as the mole fraction of one component approaches zero. This reduction is exemplified by the data of Talu and Zwiebel (1986) for CO_2, H_2S, and C_3H_8 adsorbed on H-mordenite. Figure 1 shows loci of azeotropes in the ternary phase diagram; on each locus $x = y$ for one component. Consistency requires the ternary locus to intersect the binary side of the triangle at the azeotropic composition, as illustrated in Figure 1. For C_3H_8, $x = y$ on locus *b*, $x < y$ in regions III and IV, and $x > y$ in regions I and II. For CO_2, $x = y$ on locus *c*, $x < y$ in regions I, II, and III, and $x > y$ in region IV. For H_2S, $x = y$ on locus *a*, $x < y$ in region I, and $x > y$ in regions II, III, and IV.

For mixtures that exhibit nonideal behavior in the adsorbed phase, the usual procedure is to predict ternary equilibria using data for the constituent binaries. Ternary data should first be checked for consistency with the binary data. The selectivity of adsorbate *A* relative to adsorbate *B* should be examined for continuity along a ternary locus that intersects the *A*-*B* binary data. Figure 1 is a special case for a selectivity of unity.

Continuity of binary and single gas isotherms

In the limit as the composition of the gas phase approaches unity, the total amount adsorbed from a gas mixture is equal to the amount adsorbed from the pure gas:

$$\lim_{y_i \to 1} n = n_i^0 \text{ (constant } P, T) \tag{16}$$

Equation 16 is often overlooked. It is a sensitive test for mixed-gas adsorption experiments performed by recirculating the gas through a bed of adsorbent until equilibrium is reached. The bed is isolated and the total amount adsorbed is determined by degassing the adsorbate mixture into a calibrated space, followed by analysis to determine its composition. The pure-gas isotherms could be obtained the same way, but it is more convenient to determine them volumetrically or gravimetrically in a static apparatus. Since the two measurements are independent, Eq. 16 is a test of the absolute accuracy of the amount adsorbed.

To calculate mixed-gas adsorption, experimental single-gas isotherms are first fitted with an equation containing several parameters. These parameters are used within the framework of a theory to predict multicomponent adsorption. Figure 3 is an example for which the mixture theory (solid line) disagrees with experiment because the theory fails to fit the data for adsorption of single gases at $y_1 = 0$ and $y_1 = 1$. Plots like Figure 3 are useful for establishing continuity of experimental data and for identifying errors in the fit of single-gas isotherms.

Vapor-liquid equilibrium calculations are sensitive to small errors in the vapor pressure of the pure liquids. In adsorption, the vapor pressure of an adsorbate is a function of coverage as well as temperature. In the region where the adsorption isotherm reaches a plateau, a small error in the amount adsorbed from the pure gas generates a large error in adsorbate vapor pressure. Therefore the accuracy of adsorption equilibrium calculations depends strongly on continuity of binary and single gas adsorption isotherms.

Intersection rule for x-y *diagrams*

At fixed pressure and temperature, the *x-y* curves of experimental data and theory should either coincide or cross each other; if they do not, either the theory or the data are thermodynamically inconsistent. In Figure 4, the prediction of ideal adsorbed solution (IAS) theory (Myers and Prausnitz, 1965) is thermodynamically consistent but does not agree with the experimental data except at $y_1 = 0.22$ where the two curves intersect. However, since the curves intersect, the data and the theory are mutually consistent. Therefore the deviations for ideality can be explained by adsorbed-phase activity coefficients.

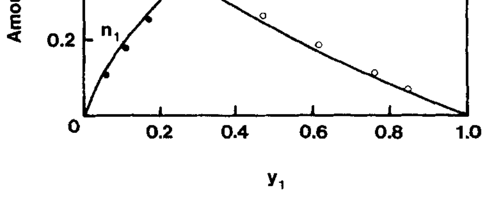

Figure 3. Individual isotherms for adsorption from binary gas mixtures compared with theory at constant *T* and *P*.

○ ● Experimental mixture points are consistent with single-gas data. ——— Theory for mixture is based on incorrect standard states for adsorption of single gases

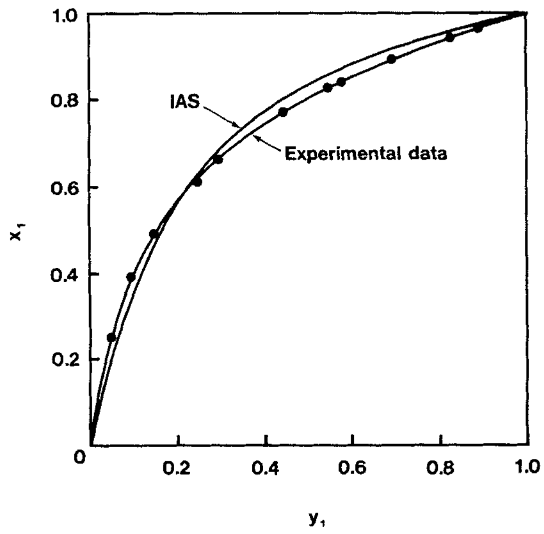

Figure 4. Isothermal, isobaric *x-y* diagram.

Experimental data intersect IAS curve

Proof that isobaric, isothermal *x-y* adsorption equilibrium curves of binary gas mixtures must intersect at least once within the region $0 < x_1 < 1$ follows from the Gibbs adsorption isotherm. The family of thermodynamically consistent curves is characterized by the excess Gibbs free energy in the adsorbed phase Δg^e. At constant spreading pressure, Π, the Gibbs adsorption isotherm reduces to:

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0 \tag{17}$$

which is called the restricted form of the Gibbs-Duhem equation when applied to VLE. Under these conditions (constant Π) the data must satisfy an integral consistency test:

$$\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0 \tag{18}$$

Therefore $\gamma_1 = \gamma_2$ at least once in the region $0 < x_1 < 1$ (twice if Δg^e is the S-shaped curve, which is rare). Let the selectivity, $s_{1,2}$, of the adsorbent for component 1 relative to component 2 be defined by:

$$s_{1,2} = \frac{x_1/y_1}{x_2/y_2} \tag{19}$$

If follows from the fugacity equations that:

$$s_{1,2} = \frac{P_2^\circ \gamma_2}{P_1^\circ \gamma_1} \tag{20}$$

The standard-state pressures P_i° are functions only of Π. For an ideal adsorbed solution (IAS), $\gamma_1 = \gamma_2 = 1$. For a nonideal mixture, there is at least one point where $\gamma_1 = \gamma_2$. At this point, $s_{1,2}$ has the same value for the ideal and nonideal mixtures so the *x-y* curves intersect. Pressure P increases monotonically with spreading pressure Π; since *x-y* curves at constant Π intersect, *x-y* curves at constant P must also intersect.

The intersection rule is useful for checking theories. Figure 5 shows a comparison of IAS and HIAS (heterogeneous ideal adsorbed solution) theories for the adsorption of CO_2 and C_3H_8 on H-mordenite. The crossing of the *x-y* curves at $x_1 = 0.55$ indicates that IAS and HIAS theories (Valenzuela et al., 1988) are mutually consistent. Both theories are also consistent with the experimental data (Talu and Zwiebel, 1986), and can be made

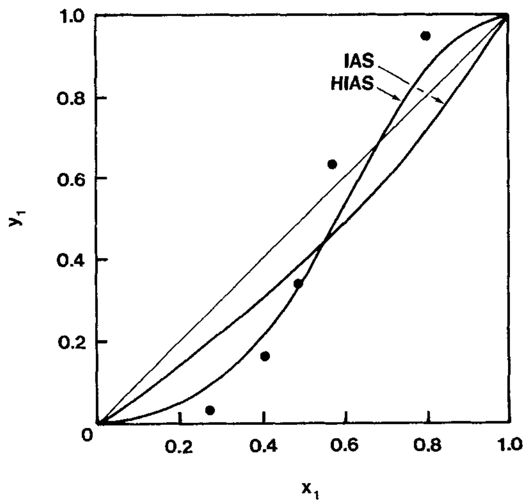

Figure 5. Mole fraction in gas phase y vs. mole fraction in adsorbed phase x for mixtures of CO_2 and C_3H_8 on H-mordenite at 30°C and 41 kPa.

● Experimental points of Talu and Zwiebel (1986)

to agree quantitatively by introducing activity coefficients. If a theoretical x-y curve does not intersect the experimental curve, then the discrepancy cannot be explained by surface-phase activity coefficients. In such a case, the experimental mixture data would be thermodynamically inconsistent with the single-gas adsorption isotherms.

Low-pressure limits

At the limit of zero pressure, adsorbate-adsorbate interactions on the surface of the adsorbent are negligible and the specific amount adsorbed of any species is given by Henry's law:

$$n_i = \frac{B_{is} P y_i}{RT} \tag{21}$$

where B_{is} is the adsorption second virial coefficient for the interaction between the ith species and the surface, obtainable from the pure-gas isotherm by Eq. 1. It follows from Eqs. 19 and 21 that:

$$\lim_{P \to 0} s_{i,j} = \frac{B_{is}}{B_{js}} \tag{22}$$

Since the limiting value of selectivity is independent of composition, selectivities measured at different gas-phase compositions must all extrapolate to the same limit (Henry's law). The multisite occupancy model (Nitta et al., 1984) and the statistical mechanical theory of Ruthven et al. (1973) satisfy Henry's law, but the vacancy solution model (Suwanayuen and Danner, 1980; Cochran et al., 1985) does not (Talu and Myers, 1988).

Adsorbed-phase activity coefficients

IAS theory can be extended to nonideal systems by introducing surface-phase activity coefficients as originally suggested by Myers and Prausnitz (1965). Let $\mathcal{G}(x_1)$ be any expression for excess Gibbs free energy such as the Wilson, UNIQUAC, or NRTL equation. For example, for the Wilson equation, $\mathcal{G}(x_1) = -RT\,\Sigma_i\,[x_i \ln(\Sigma_j(x_j \Lambda_{ij}))]$. The corresponding expression for adsorption has the form (Myers, 1986):

$$\Delta g^e = (1 - e^{-C\psi})\,\mathcal{G} \tag{23}$$

where $\psi = (\Pi A/RT)$. A different model that accounts for variation in spreading pressure was proposed by Talu and Zwiebel (1986). At the limit of zero surface coverage, $\Pi = 0$ and the adsorbed phase is ideal ($\Delta g^e = 0$). The Wilson equation applies for Δg^e only at constant Π. Experimental data are sometimes obtained at constant P but never at constant Π. If the Wilson equation by itself is used to fit experimental x-y data at constant P, then the calculated total amount adsorbed, n_t, is incorrect because the variation of activity coefficients with spreading pressure $(\partial \ln \gamma_i / \partial \psi)$ is not accounted for:

$$\frac{1}{n_t} = \sum_i \frac{x_i}{n_i^\circ} + \sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial \psi} \right)_{T,x_i} \tag{24}$$

The significance of the correction for nonideality increases with surface coverage; neglect of the last term in Eq. 24 introduces errors as large as 30% in n_t (Talu and Zwiebel, 1986).

Imperfect gas phase

The fundamental equation of equilibrium for adsorption is:

$$P y_i \phi_i = P_i^\circ \phi_i^\circ \gamma_i x_i \tag{25}$$

ϕ_i is the fugacity coefficient of the ith component at the pressure, temperature, and composition of the gas mixture; ϕ_i° is the fugacity coefficient of pure i at its reference pressure P_i°. Here the focus is on gas-phase imperfections and it is assumed that the adsorbed phase is ideal ($\gamma_i = 1$). Therefore the total amount adsorbed, n_t, from a binary mixture is:

$$\frac{1}{n_t} = \sum_{i=1}^{2} \frac{x_i}{n_i^\circ} \tag{26}$$

where $x_1 + x_2 = 1$ and individual amounts adsorbed, n_i, are:

$$n_i = n_t x_i \tag{27}$$

The standard-state vapor pressures P_i° and amounts adsorbed n_i° are implicit functions of $\psi = \psi_1^\circ = \psi_2^\circ$, which is obtained from the single-gas adsorption isotherm by:

$$\psi_i^\circ = \int_0^{f_i^\circ} n_i^\circ \, d \ln f_i^\circ \tag{28}$$

Assuming that the fugacity coefficient $\phi_i = f_i/P$ can be represented by the virial equation of state terminated after the second virial coefficient:

$$\ln \phi_i = \frac{P}{RT} [B_{ii} + (1 - y_i)^2 \delta_{12}] \tag{29}$$

for a binary mixture. For pure adsorbate at its reference state:

$$\ln \phi_i^\circ = \frac{B_{ii} P_i^\circ}{RT} \tag{30}$$

where $\delta_{12} \equiv 2B_{12} - B_{11} - B_{22}$. It follows that:

$$\psi_i^\circ = \int_0^{P_i^\circ} \frac{n_i^\circ}{P}\, dP + \frac{B_{ii}}{RT} \int_0^{P_i^\circ} n_i^\circ\, dP \tag{31}$$

The second integral in Eq. 31 is the correction for gas-phase imperfections. For most adsorption equations, both integrals must be calculated numerically.

It is instructive to compare results obtained from the above equations with approximate results for a perfect gas ($B_{ii} = 0$). Consider the adsorption of a binary gas mixture of ethylene (1) and methane (2) on BPL activated carbon at $y_1 = 0.235$, $P = 1{,}430.6$ kPa, and $T = 301.4$ K. Second virial coefficients at 301.4 K are $B_{11} = -137.0$ cm³/mol, $B_{12} = -76.0$ cm³/mol, and $B_{22} = -42.2$ cm³/mol. Table 1 summarizes IAS calculations for an imperfect gas compared to approximate results obtained by assuming a perfect gas. Single-gas adsorption isotherms for this system were measured by Reich et al. (1980).

Errors in the calculated amount adsorbed introduced by assuming a perfect gas are only a few percent, even when fugacity coefficients deviate from unity by 7%. The selectivity from Eqs. 19 and 25 is:

$$s_{1,2} = \frac{P_2^\circ \phi_2^\circ \phi_1}{P_1^\circ \phi_1^\circ \phi_2} \tag{32}$$

There is a partial compensation of errors: the perfect-gas approximation for the weakly adsorbed species ($B_{22} = 0$) lowers the vapor-pressure ratio P_2°/P_1°, while the perfect-gas approximation for the strongly adsorbed species ($B_{11} = 0$) raises the value of P_2°/P_1°.

Experimental results (Reich, et al., 1980) for this point are $n_t = 4.527$ and $x_1 = 0.612$, which is in poor agreement with both calculations in Table 1. The discrepancy must be due to nonidealities in the adsorbed phase. When the pressure is high enough to require corrections for gas-phase imperfections, the surface coverage is also high and adsorbed phase nonidealities are dominant. In most cases, vapor-phase imperfections may be safely ignored unless the pressure is above 500 kPa and experimental error is less than a few percent.

Table 1. Comparison of Perfect-gas Approximation with Calculation for Real Gas

Quantity*	Imperfect Gas	Perfect Gas	Error %
P_1^0	449.3	462.8	+3.0
P_2^0	4,024.2	3,999.6	−0.6
P_2^0/P_1^0	8.956	8.641	−3.5
n_1^0	4.0087	4.0394	+0.8
n_2^0	4.3385	4.3325	−0.1
ϕ_1	0.9332	1.0	+7.2
ϕ_2	0.9770	1.0	+2.4
ϕ_1^0	0.9757	1.0	+2.5
ϕ_2^0	0.9345	1.0	+7.0
x_1	0.7156	0.7264	+1.5
x_2	0.2844	0.2736	−3.8
n_1	2.9322	2.9894	+2.0
n_2	1.1650	1.1262	−3.3
n_t	4.0972	4.1156	+0.4
ψ	8.8392	9.0324	+2.2
$s_{1,2}$	8.193	8.641	+5.5

Adsorption of binary mixture of ethylene (1) and methane (2) on BPL activated carbon at 301.4 K, 1,430.6 kPa, $y_1 = 0.235$

*P in kPa; n, ψ in mol/kg.

Conclusions

Rules, limits and consistency tests for equilibrium adsorption of gases and their mixtures are:

1. Single-gas adsorption isotherms should reduce to Henry's law at the limit of zero pressure, Eq. 1.
2. In spite of incorrect limits of n/P at zero pressure, both the Toth and DR equations are accurate for calculating spreading pressure provided the pressure is sufficiently high.
3. Multicomponent isotherms should display continuity with single-gas isotherms, Eq. 16. Discontinuities generate inaccurate values of adsorbate vapor pressure that lower the quality of calculations of mixed-gas adsorption.
4. At fixed temperature and pressure, thermodynamically consistent x-y diagrams intersect each other at least once, Figure 4.
5. Isothermal selectivity curves for different vapor compositions should intersect at the limit of zero pressure.
6. Activity coefficients in the adsorbed phase are functions of spreading pressure as well as composition, Eq. 23.
7. Imperfections in the gas phase lead to corrections in fugacity that are small compared to the effect of nonidealities in the adsorbed phase.

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Notation

A = specific surface area, m²/g
B_{ii} = second virial coefficient, m³/mol
B_{1S} = adsorption second virial coefficient, Eq. 1, m³/kg
b = constant, Eq. 8
D = constant, Eq. 6
Δg^e = excess Gibbs free energy of adsorbed phase, J/mol
$\mathcal{G}$ = excess Gibbs free energy of liquid phase, Eq. 23, J/mol
K = constant, Eqs. 2, 4, 13
K_0 = constant, Eq. 14
n = specific amount adsorbed, mol/kg
n_m = specific amount adsorbed at saturation, mol/kg
n_t = total specific amount adsorbed, mol/kg
q_{st} = isosteric heat of adsorption, J/mol
P = pressure, Pa
P^s = vapor pressure of liquid, Pa
R = gas constant
$s_{i,j}$ = selectivity of adsorbate i relative to j
t = constant, Eqs. 2, 4, 8
x = mole fraction in adsorbed phase
y = mole fraction in gas phase
T = temperature, K

Greek letters

γ = activity coefficient in adsorbed phase
$\delta_{12} = 2B_{12} - B_{11} - B_{22}$, m³/mol
ϵ = energy of desorption, J/mol
θ = fractional surface coverage, Eq. 15
Π = spreading pressure, N/m
ϕ = gas phase fugacity coefficient
$\psi = (\Pi A/RT)$, mol/kg

Superscript

° = standard state or single-gas isotherm

Subsript

i = ith adsorbate

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