Corresponding States. III. Henry's Constants for Nonpolar Binary Mixtures

A Henry's constant correlation is developed from a macroscopic corresponding states theory for fluid mixtures. The method requires three interaction parameters which are correlated for mixtures of a paraffin with nitrogen, carbon dioxide, hydrogen sulfide, or another paraffin. Henry's constants can be calculated by this method to within experimental accuracy (about ± 5%) for the mixtures tested.

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SCOPE

Phase equilibrium calculation for mixtures of industrial interest often require the use of Henry's constants, and there is growing interest in methods for correlating these parameters. The prediction of Henry's constants also provides a valuable and very demanding test of the accuracy for a theory of solutions. A number of statistical mechanical procedures for calculating Henry's constants are available in the literature. Unfortunately such methods involve approximations which place serious restrictions on their applicability to mixtures and conditions of engineering interest. Preston and Prausnitz (1971) have developed one of the most widely applicable methods in which they successfully circumvented some of the less accurate statistical mechanical approximations.

A macroscopic corresponding states theory for mixtures (Gunn, 1972) is employed in this work to develop a Henry's constant correlation. Generalized functions required for these calculations are tabulated. The three interaction parameters required are correlated for binary mixtures involving a paraffin and nitrogen, carbon dioxide, hydrogen sulfide, or another paraffin.

A procedure is also recommended for the reduction of vapor-liquid equilibrium data to obtain Henry's constants.

CONCLUSIONS AND SIGNIFICANCE

A primary consideration in developing a correlation for Henry's constants is to begin with accurate experimental values. This is not easily accomplished, however, because Henry's constants are defined at the limiting condition of zero solute concentration and experimental errors tend to be very large in the dilute region. The data reduction method adopted in this work performs very satisfactorily primarily because data are utilized at higher concentrations for which errors in experimentally measured compositions are fairly minimal.

The proposed relationship for calculating Henry's constants predicts the data to within experimental accuracy (about ± 5%) over the entire temperature range. A plot of the logarithm of the Henry's constant versus reciprocal temperature exhibits two major characteristics: A maximum in the curve near the solvent critical temperature and a straight line portion at low temperatures. Both characteristics are readily explained by the mathematical behavior of the derived equations.

For a particular binary mixture the proposed correlation for Henry's constants may be used to extrapolate to higher or lower temperatures provided some data are available to establish values for a characteristic temperature T_{cij} and a characteristic acentric factor ω_{ij}. The characteristic volume V_{cij} should be determined from volumetric data for liquid mixtures whenever possible.

Mixture enthalpy departures and gas phase compressibility factors are many times less sensitive to the parameters T_{cij}, ω_{ij}, and V_{cij} than Henry's constants; but values of these parameters calculated from Henry's constants do improve slightly the prediction of these other thermodynamic properties for many systems not containing nitrogen.

A number of methods for predicting phase equilibria require the use of Henry's constants (Prausnitz and Chueh, 1968; Prausnitz, 1969); therefore, there is considerable interest in procedures for correlating these parameters. In addition, the prediction of Henry's constants provides a valuable and severe test of solution theory for reasons which are discussed next.

Two equations rigorously define Henry's law:

$$f_{ig} = H_{ij} x_i \tag{1}$$

$$H_{ij} = \lim_{x_i \to 0} \frac{f_{il}}{x_i} \tag{2}$$

When the pressure of a gas-liquid system is low, the fugacity of component i in the gaseous phase can be replaced to a good approximation by the partial pressure of component i.

$$P_i = H_{ij} x_i \tag{3}$$

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This approximate equation is often referred to as Henry's law because a form very similar to Equation (3) was originally proposed (Henry, 1803) long before the fugacity function came into use. This work, however, concerns only the rigorous form of the law defined by Equations (1) and (2).

If component i is below its critical temperature, the Henry's constant can be related to the infinite dilution activity coefficient.

$$H_{ij} = \gamma^{\infty}{}_{il} f^{0}{}_{il} \quad (4)$$

All mixtures considered here exhibit positive deviations from ideal solution behavior. In such cases the activity coefficient of component i, which measures liquid phase nonideality, increases rapidly with decreasing concentration of i and attains its maximum value at infinite dilution. Because the Henry's constant is a measure of the maximum departure of a component from ideal solution behavior, these constants are difficult to predict accurately and pose a severe test for a theory of liquid mixtures.

Recently a number of investigators have developed statistical mechanical methods for calculating Henry's constants (Neff and McQuarrie, 1973; Tiepel and Gubbins, 1972; Pierotti, 1963), and additional earlier work is cited by these authors. The best statistical mechanical methods have been shown to be quite successful in limited applications. Nevertheless, each of these methods contains a number of approximations such as the use of the Lennard-Jones potential and Lennard-Jones parameters, Percus-Yevick theory, and first-order perturbation methods. It is doubtful that these approximations provide the very demanding precision necessary for the quantitative prediction of Henry's constants over a wide range of temperatures and for a variety of nonspherical molecules.

Nakahara and Hirata (1969) have developed a solution model with some success for predicting Henry's constants in hydrogen-hydrocarbon mixtures. Miller and Prausnitz (1969), Funk and Prausnitz (1971), and Preston and Prausnitz (1971) have developed additional theoretical methods. Preston and Prausnitz in particular present one of the most accurate and most widely applicable methods available. Although their procedure is derived from statistical mechanics, some of the less accurate statistical mechanical approximations have been circumvented by casting the final equation into a framework which permits the use of an empirical but very accurate macroscopic equation of state. The objective of this paper is to use a macroscopic corresponding states theory for fluid mixtures (Gunn, 1972) for the development of a new method for calculating Henry's constants.

DETERMINATION OF HENRY'S CONSTANTS

Vapor-liquid equilibrium data provide a major source for experimental Henry's constants. Reduction of VLE data to obtain these constants is accomplished with the following equation:

$$\ln \frac{f_{ig}}{x_i} - \frac{\bar{v}_i^{\infty} (P - P_j^s)}{RT} = A\bar{v}_i^{\infty} (\phi_j^2 - 1) + \ln H^s{}_{ij} \quad (5)$$

where

$$\phi_j = \frac{x_j v_j}{x_i \bar{v}_i^{\infty} + x_j v_j} \quad (6)$$

At a given temperature a plot of the left-hand side of Equation (5) against the volume fraction term $\phi_j^2 - 1$ produces a straight line with an intercept equal to the logarithm of the Henry's constant at the saturation pressure of pure solvent j. Equation (5) is similar to one proposed by Krichevsky and Ilinskaya (1945) (see also Prausnitz, 1969) except that the van Laar rather than the Margules equation has been used here to represent liquid phase nonideality.

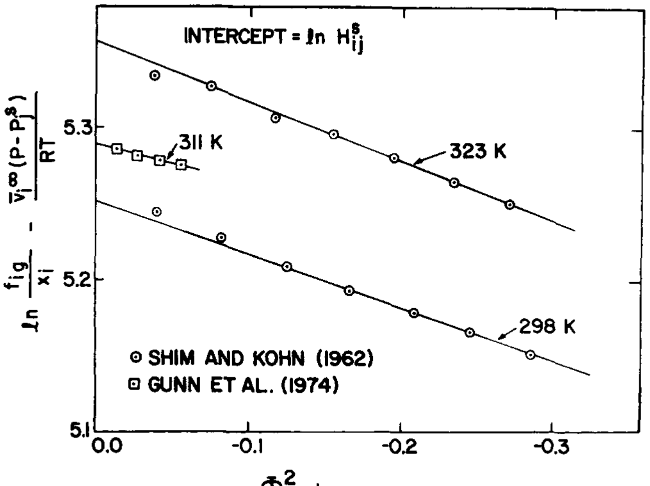

Fig. 1. Plot of experimental data for the determination of Henry's constants: methane-*n*-hexane system.

In Equation (5) the fugacity of component i in the gas phase is calculated from the virial equation. The partial molar volumes can be calculated from experimental volumetric data or may be obtained from a correlation such as the one proposed by Prausnitz and Chueh (1968).

Figure 1 shows a plot of the type described. The plotted data tend to become scattered close to the intercept. This reflects the large percentage error in the mole fraction x_i as x_i approaches zero. Because Henry's constants are defined at infinite dilution, they are difficult to determine accurately and are often in error by ± 5% or more.

Equation (5) cannot be used for mixtures for which a second-order van Laar equation is inadequate to represent solution nonideality. In such cases the failure of the van Laar equation is apparent because a plot of the type shown in Figure 1 produces a curve rather than a straight line. None of the mixtures studied in this work exhibited such behavior. A few isolated isotherms did show curved lines, but in all cases other isotherms for the same systems showed the curvature to be purely erratic.

A successful Henry's constant correlation requires accurate experimental data. The data reduction method proposed here is very satisfactory primarily because it utilizes in part data at fairly high solute concentrations for which errors in composition measurements are at a minimum. All Henry's constants used in this work have been calculated by the procedures outlined. A list of experimental data references is available from the authors.

PRINCIPLE OF CORRESPONDING STATES

A configurational thermodynamic property, for example, the compressibility factor z, can be calculated accurately for a nonpolar pure fluid if the critical temperature and pressure and the acentric factor are known for that fluid. For this purpose, use is made of the following relationship:

$$\psi = \psi^{(0)}\left(\frac{T}{T_c}, \frac{P}{P_c}\right) + \omega\psi^{(1)}\left(\frac{T}{T_c}, \frac{P}{P_c}\right) \quad (7)$$

Equation (7) is a three-parameter corresponding states correlation where $\psi^{(0)}$ and $\psi^{(1)}$ are generalized functions of reduced temperature and pressure only and are valid for nonpolar fluids with acentric factors of 0.5 or less. The respective generalized functions for calculating compressibility factors, fugacity coefficients, and enthalpy and entropy departures have been tabulated by Pitzer et al. (1955, 1958).

In this work the authors extend this general approach to the calculation of Henry's constants in binary mixtures. This is possible because the corresponding states framework applies to mixtures as well as to pure components. For example for a mixture Equation (7) becomes

$$\psi_m = \psi^{(0)}\left(\frac{T}{T_{sp}}, \frac{P}{P_{sp}}\right) + \omega_m \psi^{(1)}\left(\frac{T}{T_{sp}}, \frac{P}{P_{sp}}\right) \tag{8}$$

In Equation (8) $\psi^{(0)}$ and $\psi^{(1)}$ are the same generalized functions used to predict the properties of pure substances. In order to use Equation (8), however, the mixture scaling parameters T_{sp}, P_{sp}, and ω_m must be determined in some fashion. This problem is considered next.

A macroscopic corresponding states theory for fluid mixtures (Gunn, 1972) has been developed on the basis of two assumptions: (1) The existence of a three parameter generalized equation of state for pure substances, and (2) the existence of a valid mixing rule. When these assumptions are applicable, expressions can be derived for the parameters V_{sp}, T_{sp}, ω_m, and P_{sp}. These are designated here as scaling parameters although they are often called *pseudocritical constants*. The latter name has led to much confusion because it is often assumed that these constants are directly related to mixture critical behavior. This is definitely not the case; they are simply mathematical scaling parameters which permit a generalized equation of state or generalized tables of thermodynamic properties developed for pure components to be used for mixtures as well. In addition, the acentric factor is not a critical property even for pure components.

From a practical standpoint it is possible to derive a large if not an infinite number of relationships for the scaling parameters. Each different generalized equation of state and each different mixing rule leads to a different set of constants. For example, there are theoretical but different mixing rules for second virial coefficients, for third virial coefficients, and for each of the higher virial coefficients. There are also a number of different empirical mixing rules for liquid mixtures which have been used more or less successfully.

From all of the possible derived relationships for the scaling parameters those selected should be both simple and accurate. In addition, they should be essentially independent of temperature and density. In general, the scaling parameters are weak functions of both density and temperature. The expressions for T_{sp}, V_{sp}, and ω_m used in this work are listed below. They have been selected for the reasons listed and have been used previously with considerable success (Yamada, 1973). For a binary mixture

$$V_{sp} = x_i^2 V_{ci} + 2x_i x_j V_{cij} + x_j^2 V_{cj} \tag{9}$$

$$\omega_m = \frac{x_i^2 V_{ci}\omega_i + 2x_1 x_2 V_{cij}\omega_{ij} + x_j^2 V_{cj}\omega_j}{V_{sp}} \tag{10}$$

$$T_{sp} = \left[\frac{x_i^2 V_{ci} T^2_{ci} + 2x_i x_j V_{cij} T^2_{cij} + x_j^2 V_{cj} T^2_{cj}}{V_{sp}}\right]^{1/2} \tag{11}$$

Once equations are available which determine the composition dependence of the scaling parameters, it is possible to calculate not only mixture thermodynamic properties but also component and partial molar properties as well. For example, an expression for Henry's constants is obtainable from an equation derived previously for the prediction of fugacity coefficients (Gunn, 1972). For a binary mixture this equation reduces to the following expression:

$$\ln \frac{f_i}{x_i P} = \ln \frac{f_m}{P} - x_j \left[\frac{u_m^* - u_m}{RT} \left(\frac{1}{T_{sp}} \frac{dT_{sp}}{dx_i} \right) + (1 - z_m) \left(\frac{1}{V_{sp}} \frac{dV_{sp}}{dx_i} \right) + \ln (g/v)_m{}^{(1)} \left(\frac{d\omega_m}{dx_i} \right) \right] \tag{12}$$

The function $\ln (g/v)$ is related to the configuration potential (Gunn, 1972) and may be calculated from the following relationships:

$$\ln (g/v) = \ln (g/v)^{(0)} + \omega \ln (g/v)^{(1)} \tag{13}$$

$$\ln (g/v)^{(0)} = \int_\infty^v \frac{z^{(0)} - 1}{V} dV \tag{14}$$

$$\ln (g/v)^{(1)} = \int_\infty^v \frac{z^{(1)}}{V} dV \tag{15}$$

In Equation (15) $z^{(1)}$ is defined

$$z^{(1)} = \left(\frac{\partial z}{\partial \omega}\right)_{T_R, V_R} \tag{16}$$

$z^{(1)}$ is not the same function which has been tabulated by Pitzer et al. (1955). The latter function is defined as a partial derivative with reduced pressure rather than reduced volume held constant.

$$z_p{}^{(1)} = \left(\frac{\partial z}{\partial \omega}\right)_{T_R, P_R} \tag{17}$$

In Equation (2) Henry's constants are defined at the limiting condition of x_i approaching zero; and a relationship for calculating these constants is obtained if this limit is imposed on Equation (12).

$$\ln \frac{H^s{}_{ij}}{f_j^s} = -\frac{u_j^* - u_j^s}{RT} \left[\lim_{x_i \to 0} \frac{1}{T_{sp}} \frac{dT_{sp}}{dx_i} \right] - (1 - z_j^s) \left[\lim_{x_i \to 0} \frac{1}{V_{sp}} \frac{dV_{sp}}{dx_i} \right] - \ln (g/v)_j{}^{(1)s} \left[\lim_{x_i \to 0} \frac{d\omega_m}{dx_i} \right] \tag{18}$$

In Equation (18) component i represents the solute and component j the solvent. Mixture properties in this equation become identical to the pure solvent properties at saturation conditions in the limit of x_i approaching zero.

The final form for the Henry's constant relationship is obtained by substitution of Equations (9), (10), and (11) into Equation (18).

$$\ln \frac{H^s{}_{ij}}{f_j^s} = + \frac{u_j^* - u_j^s}{RT} \left[\frac{V_{cij}}{V_{cj}} \left(1 - \frac{T^2_{cij}}{T^2_{cj}} \right) \right] + (1 - z_j^s) \left[2 \left(1 - \frac{V_{cij}}{V_{cj}} \right) \right] + \ln (g/v)_j{}^{(1)s} \left[2 \frac{V_{cij}}{V_{cj}} (\omega_j - \omega_{ij}) \right] \tag{19}$$

Equations (18) and (19) show that Henry's constants can be calculated from a knowledge of the thermodynamic properties of the pure solvent at its saturation pressure and from the limiting derivatives of the scaling parameters. These derivatives in turn require numerical values for three interaction parameters. These constants are discussed further in the next section.

Table 1. Generalized Functions for Saturated Liquids Used in Equation (19)

TR	$\left(\frac{u^* - u}{RT}\right)^{(0)}$	$\left(\frac{u^* - u}{RT}\right)^{(1)}$	$z^{(0)}$	$z^{(1)}$	$z^{(2)}$	$\ln(g/v)^{(1)}$	$\ln(f/Pc)^{(0)}$	$\ln(f/Pc)^{(1)}$
0.30	18.1444	43.3323	0.0000	0.0000	0.0000	22.1001	−12.7931	−21.2064
0.32	16.8359	39.1508	0.0000	0.0000	0.0000	19.4396	−11.5996	−19.1267
0.34	15.6788	35.5215	0.0000	0.0000	0.0000	17.1769	−10.5540	−16.7791
0.36	14.6478	32.3509	0.0000	0.0000	0.0000	15.2378	−9.6304	−14.8214
0.38	13.7230	29.5641	0.0000	0.0000	0.0000	13.5644	−8.8095	−13.1555
0.40	12.8883	27.1021	0.0001	−0.0006	0.0009	12.1114	−8.0758	−11.7009
0.42	12.1308	24.9167	0.0001	−0.0006	0.0009	10.8427	−7.4168	−10.4329
0.44	11.4401	22.9675	0.0002	−0.0012	0.0018	9.7290	−6.8220	−9.3204
0.46	10.8073	21.2224	0.0004	−0.0019	0.0023	8.7470	−6.2830	−8.3393
0.48	10.2252	19.6538	0.0007	−0.0038	0.0049	7.8772	−5.7928	−7.4703
0.50	9.6876	18.2391	0.0010	−0.0051	0.0063	7.1038	−5.3452	−6.6987
0.52	9.1893	16.9887	0.0015	−0.0067	0.0076	6.4136	−4.9354	−6.0102
0.54	8.7259	15.7959	0.0022	−0.0099	0.0116	5.7954	−4.5590	−5.3943
0.56	8.2936	14.7364	0.0030	−0.0125	0.0140	5.2402	−4.2124	−4.8416
0.58	7.8890	13.7681	0.0041	−0.0160	0.0171	4.7399	−3.8924	−4.3442
0.60	7.5092	12.8805	0.0054	−0.0196	0.0199	4.2881	−3.5962	−3.8960
0.62	7.1518	12.0636	0.0071	−0.0250	0.0257	3.8789	−3.3215	−3.4907
0.64	6.8144	11.3099	0.0091	−0.0293	0.0279	3.5077	−3.0662	−3.1236
0.66	6.4951	10.6118	0.0114	−0.0342	0.0312	3.1702	−2.8285	−2.7902
0.68	6.1921	9.9630	0.0142	−0.0397	0.0347	2.8627	−2.6066	−2.4880
0.70	5.9038	9.3577	0.0175	−0.0453	0.0375	2.5824	−2.3994	−2.2119
0.72	5.6286	8.7914	0.0213	−0.0512	0.0402	2.3264	−2.2053	−1.9611
0.74	5.3653	8.2589	0.0257	−0.0575	0.0430	2.0924	−2.0233	−1.7325
0.76	5.1126	7.7564	0.0307	−0.0634	0.0448	1.8783	−1.8524	−1.5238
0.78	4.8692	7.2806	0.0365	−0.0697	0.0466	1.6825	−1.6918	−1.3327
0.80	4.6342	6.8270	0.0430	−0.0753	0.0471	1.5033	−1.5404	−1.1591
0.82	4.4063	6.3934	0.0505	−0.0813	0.0475	1.3394	−1.3977	−1.0002
0.84	4.1844	5.9764	0.0590	−0.0870	0.0476	1.1896	−1.2630	−0.8549
0.86	3.9672	5.5736	0.0686	−0.0917	0.0462	1.0528	−1.1356	−0.7226
0.88	3.7531	5.1826	0.0797	−0.0964	0.0444	0.9281	−1.0150	−0.6018
0.90	3.5401	4.8006	0.0924	−0.1002	0.0422	0.8146	−0.9008	−0.4912
0.92	3.3252	4.4240	0.1072	−0.1024	0.0377	0.7115	−0.7924	−0.3906
0.94	3.1028	4.0488	0.1248	−0.1038	0.0331	0.6183	−0.6896	−0.2983
0.96	2.8608	3.6665	0.1465	−0.1034	0.0273	0.5340	−0.5920	−0.2139
0.98	2.6680	3.2500	0.1762	−0.1010	0.0182	0.4575	−0.5005	−0.1322
1.00	2.4520	2.8800	0.2918	−0.0967	0.0	0.3950	−0.4030	−0.0691

The thermodynamic properties required in Equation (19) have not been measured experimentally for many solvents. Experimental measurements at low reduced temperatures are especially scarce, and even when some data exist it is usually inconvenient to calculate from this information the derived properties such as the internal energy departure. For this reason generalized correlations have been developed for the needed saturated liquid properties from the available experimental data for pure substances. These generalized functions are listed at even values of the reduced temperature in Table 1. The saturated liquid properties required by Equation (19) are functions of the reduced temperature only. ln f_j^s and $\frac{u_j^* - u_j^s}{RT}$ are also linear functions of the acentric factor as indicated by Equation (7).

A quadratic function with respect to the acentric factor approximates the saturated liquid compressibility factor z^s. This latter property is not a linear function because the definition for z^s includes the nonlinear product $P^s v^s$. Saturated liquid volumes are linear functions of the acentric factor; but at low reduced temperatures if log P^s is a linear function in ω, then P^s itself must be very nonlinear.

The critical constants and the acentric factors used in this work are recorded in Table 2. The column in this table which is titled V_{sc} (the scaling volume) is explained further in the next section of this paper.

Table 2. Pure Component Critical Constants and Acentric Factors

Compound	T_c K	P_c atm	V_{sc} cc/g-mol	ω
Nitrogen	126.20	33.499	89.64	0.040
Carbon dioxide	304.19	72.850	93.55	0.225
Hydrogen sulfide	373.60	88.902	97.58	0.100
Methane	190.55	45.441	99.53	0.013
Ethane	305.43	48.163	145.42	0.099
Propane	369.82	41.943	199.79	0.153
iso-Butane	408.13	36.003	256.72	0.185
n-Butane	425.16	37.473	254.07	0.202
iso-Pentane	460.39	33.370	308.17	0.229
n-Pentane	469.67	33.247	310.97	0.253
n-Hexane	507.33	29.729	368.48	0.294
n-Heptane	540.17	27.000	429.28	0.350
n-Octane	568.76	24.537	490.30	0.390
n-Nonane	594.56	22.795	552.97	0.446
n-Decane	617.44	20.720	617.43	0.490

INTERACTION PARAMETERS

As indicated by Equation (7) the configurational thermodynamic properties of nonpolar fluids can be correlated with three characteristic constants ω, T_c, and V_c (or P_c). Similarly, correlations for these same properties may be based on molecular parameters, for example, the

TABLE 3. COMPARISON OF CALCULATED AND EXPERIMENTAL HENRY'S CONSTANTS FOR THE METHANE-n-HEPTANE SYSTEM

Temperature, K	Henry's constant, N/m² × 10^{-5}* Experimental	Calculated Equation (19)
183.16	60.4	60.4
188.72	64.9	66.8
194.27	73.3	72.2
199.83	81.0	79.7
210.94	93.5	93.1
222.05	107.1	107.1
233.16	120.8	120.8
244.27	134.4	134.5
255.38	147.8	147.9
266.49	160.9	160.8
277.60	175.9	173.2
310.94	206.9	206.2
344.22	231	231.3
377.60	248.7	247.4
410.94	256	253.6
444.27	243	242.2
477.60	247	234.5
510.94	208	206.2

Data References: Reamer et al. (1956) and Kohn (1961).

* 1 atm. = 1.01325 × 10^5 N/m².

three parameters of the Kihara intermolecular potential function. As a rule for the latter type of correlation some loss of predictive accuracy results because values for the molecular parameters are usually much more uncertain than the corresponding values of the critical constants. Nevertheless, for the same compound and at equivalent conditions, correlations of the two types must predict essentially the same values for the thermodynamic properties. This requirement can be satisfied only if there exists a fixed mathematical relationship between the macroscopic and molecular parameters. This conclusion has been discussed previously by Reid and Leland (1965), and Tee et al. (1966) and Eisenman and Stiel (1971) have proposed and investigated in some detail simple mathematical relationships relating critical constants to the molecular parameters for the Lennard-Jones and Kihara potential functions. Because a mathematical correspondence exists between the two types of parameters, the following qualitative discussion of interaction parameters applies equally to the macroscopic formulation and to the microscopic formulation of the corresponding states principle.

According to a three-parameter principle of corresponding states, the constants V_{ci}, T_{ci}, and ω_i characterize fully the effect on the thermodynamic properties of the energy of interaction between the molecules of a pure substance. Similarly, the parameters V_{cij}, T_{cij}, and ω_{ij}, or the equivalent molecular parameters characterize the effect of the interaction between unlike molecules of types i and j. Because even the simpler molecules are complex bodies, it has been possible only to a rough approximation to calculate the characteristic parameters V_{cij}, T_{cij}, and ω_{ij} from data for pure compounds. For improved accuracy such parameters must be determined from experimental data for mixtures.

Early investigators (Prausnitz and Gunn, 1958; Chueh and Prausnitz, 1967; Brewer, 1967) correlated cross second virial coefficients by using simple approximations involving only pure component properties for two parameters, and by adjusting the characteristic temperature T_{cij} to fit the experimental results. The accuracy of most measured cross virial coefficients is so low that it is generally impossible to obtain a unique set of characteristic parameters if more than one of these is adjusted to the data.

Recently, however, accurate measurements have become available for noble gas mixtures over a wide temperature range. In this case Robinson (1973) found it necessary to adjust two characteristic parameters in order to correlate the experimental results. Massengill and Miller (1973) have reached similar conclusions in working with precisely measured liquid mixture properties.

Henry's constants, on the other hand, are exceptionally sensitive to values for all three characteristic constants V_{cij}, T_{cij}, and ω_{ij}. For example, if an interaction parameter k_{ij} is defined by the following equation:

$$T_{cij} = (1 - k_{ij})(T_{ci}T_{cj})^{1/2} \tag{20}$$

then it is found that a variation of k_{ij} of about ± 0.02 leads to variations on the order of ± 20% for Henry's constants calculated from Equation (19). Miller and Prausnitz (1969) reported similar findings.

In principle it is possible to determine each of the required interaction parameters from a thermodynamic property which is especially sensitive to the specific constant. For example, ω_{ij} might be determined from liquid mixture enthalpy departures which are affected quite strongly by this parameter. k_{ij} might be determined from cross virial coefficients, and V_{cij} from densities of liquid mixtures. For the types of mixtures considered in this study, however, virial coefficients and enthalpy departures of the required accuracy are almost never available. For this reason the characteristic parameters V_{cij}, T_{cij}, and ω_{ij} have been calculated from liquid volumes for mixtures and from Henry's constants. In most cases these characteristic parameters may be used to calculate other thermodynamic properties as well.

The interaction parameters needed for calculating Henry's constants for a variety of binary mixtures are correlated in Figures 2, 3, and 4. The interaction parameters plotted in these figures are k_{ij} defined by Equation (20) and l_{ij} and $\Delta\omega_{ij}$ defined by the following relationships:

$$V_{cij} = (1 + l_{ij})\left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3 \tag{21}$$

$$\Delta\omega_{ij} = \omega_{ij} - \frac{\omega_i + \omega_j}{2} \tag{22}$$

Values of k_{ij}, l_{ij}, and $\Delta\omega_{ij}$ are given in Table 4. Graphs of

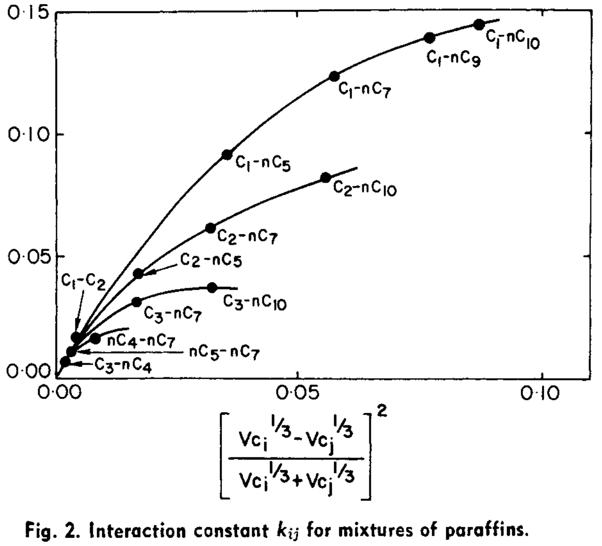

Fig. 2. Interaction constant k_{ij} for mixtures of paraffins.

TABLE 4. COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL HENRY'S CONSTANTS

Solute	Solvent	Temp. range, K	k_{ij}	$\Delta\omega_{ij}$	l_{ij}	Average % dev. Equation (19)	Average % dev. Preston-Prausnitz 1971
Methane	Ethane	186-278	0.0165	−0.0030	0.0105	2.0	3.0
Methane	Butane	194-411	0.0685	−0.0200	0.0530	6.9	2.0
Methane	Pentane	311-444	0.0910	−0.0330	0.0720	2.0	2.0
Methane	Hexane	311-411	0.1085	−0.0440	0.0860	3.5	4.0
Methane	Heptane	183-511	0.1229	−0.0591	0.1006	0.8	23.0
Methane	Octane	223-423	0.1320	−0.0770	0.1080	5.7	N.D.
Methane	Nonane	223-423	0.1383	−0.0946	0.1125	3.4	N.D.
Methane	Decane	248-511	0.1430	−0.1149	0.1170	2.3	N.D.
Ethane	Propane	311-355	0.0098	−0.0025	0.0075	2.4	7.0
Ethane	Butane	339-394	0.0275	−0.0070	0.0210	1.3	4.0
Ethane	Pentane	311-444	0.0426	−0.0145	0.0360	0.9	7.0
Ethane	Heptane	311-511	0.0610	−0.0280	0.0665	0.6	6.0
Ethane	Decane	311-511	0.0814	−0.0575	0.0982	1.7	N.D.
Propane	Butane	363-393	0.0070	−0.0007	0.0055	1.2	1.0
Propane	Pentane	361-423	0.0177	−0.0045	0.013	2.3	1.0
Propane	Hexane	373-453	0.0250	−0.0080	0.0230	0.7	N.D.
Propane	Heptane	363-453	0.0311	−0.0125	0.0365	0.6	N.D.
Propane	Decane	378-511	0.0365	−0.0310	0.0710	1.6	N.D.
Butane	Heptane	410-514	0.0163	−0.0062	0.0180	2.1	2.0
Pentane	Heptane	453-499	0.0120	−0.0020	0.0070	1.8	N.D.
Nitrogen	Methane	122-172	0.0684	−0.0031	0.0010	1.6	3.0
Nitrogen	Ethane	122-289	0.1850	−0.0073	0.0160	1.9	49.0
Nitrogen	Propane	248-353	0.2910	−0.0216	0.0395	2.4	N.D.
Nitrogen	Butane	311-411	0.3260	−0.0500	0.0625	1.0	4.0
Nitrogen	Hexane	344-444	0.3250	−0.1311	0.0955	2.7	3.0
Methane	Carbon dioxide	209-272	0.0470	−0.0246	−0.0480	1.6	1.0
Carbon dioxide	Propane	294-344	0.1379	−0.0650	0.0607	2.8	2.0
Carbon dioxide	Butane	311-378	0.1658	−0.0808	0.0718	2.8	1.0
Carbon dioxide	Decane	311-511	0.2455	−0.1935	0.1260	0.5	N.D.
Ethane	Hydrogen sulfide	292-319	0.0858	+0.0106	0.0109	0.9	5.0
Hydrogen sulfide	Pentane	378-411	0.1300	−0.0325	0.073	2.4	73.0
Hydrogen sulfide	Decane	378-444	0.1690	−0.1310	0.1170	0.3	N.D.

N.D. = No data.

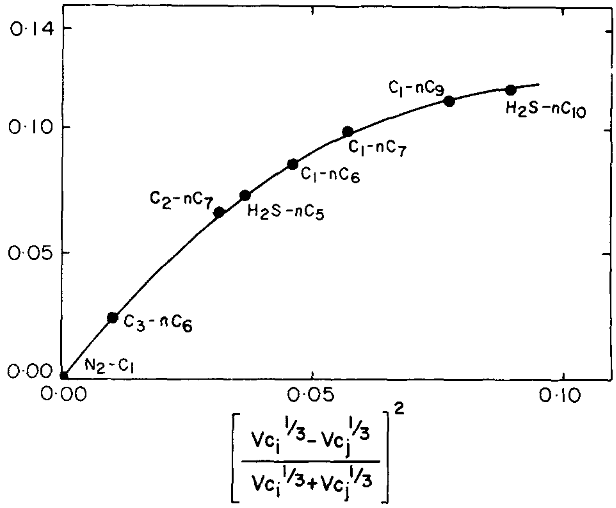

Fig. 3. Interaction constant l_{ij} for several mixtures studied.

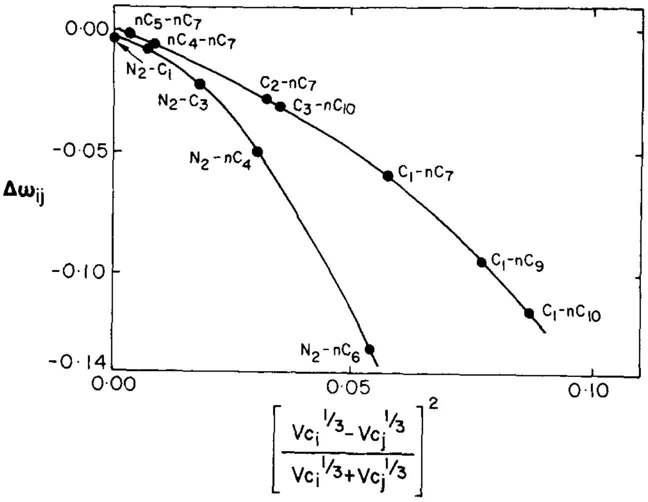

Fig. 4. Interaction constant $\Delta\omega_{ij}$ for two types of systems.

these data similar to Figures 2, 3, and 4 permit accurate estimates to be made of the respective interaction parameters for paraffin-paraffin, carbon dioxide-paraffin, nitrogen-paraffin, and hydrogen sulfide-paraffin binary mixtures even when experimental data are lacking.

The Henry's constant relationship, Equation (19), also requires very accurate values for the critical constants of pure components. At least for the compounds included in this work the critical temperatures and the acentric factors are believed to be known with sufficient accuracy. Precise values for the critical volume are also essential. Unfortunately critical volumes are difficult to measure and are subject to larger experimental errors. These errors occasionally exceed 5% even for the most common substances. To circumvent this problem it is recommended that scaling volumes (V_{sc}) be used everywhere in place of experimental critical volumes. The scaling volume, an approximation of the true critical volume, is calculated from liquid density at a reduced temperature of 0.6 at which accurate measurements are readily accomplished. V_{sc} is defined

$$V_{sc} = \frac{V_{0.6}}{0.3862 - 0.0866\omega} \tag{23}$$

The scaling volume has been used very successfully for a variety of corresponding states applications (Yamada, 1973; Gunn and Yamada, 1971), and a more detailed discussion of this parameter is given in the latter reference. Values of V_{sc} used in this work are listed in Table 2.

RESULTS OF CALCULATIONS

In this work the interaction parameter l_{ij} is calculated from volumetric data for liquid mixtures whenever possible. The remaining two interaction parameters are obtained by a least squares fit of the experimental Henry's constants. With this procedure Equation (19) correlates Henry's constants within experimental accuracy which is usually on the order of ± 5%. Table 3 compares calculated and experimental Henry's constants for the methane-*n*-heptane system. This particular system is unusual because accurate data are available for it over a very wide temperature range, 180 to 510 K. The maximum deviation shown in Table 3 is 5%, and the average deviation is 0.8%. For this same system and for the same temperature range, Preston and Prausnitz (1971) report an average deviation of 23% for their method.

Table 4 summarizes calculated results for a number of other binary mixtures. For comparative purposes Table 4 also includes calculated results reported by Preston and Prausnitz (1971). The Preston-Prausnitz correlation for Henry's constants is believed to be the only other method currently available which is comparable to the one proposed here in simplicity, scope, and accuracy.

Figure 5 shows a plot of the logarithm of calculated and experimental Henry's constants versus reciprocal temperature for the nitrogen-ethane system. The figure demonstrates clearly the maximum which is characteristic of the Henry's constant curve. The theory presented here readily provides a mathematical explanation for this behavior. The slope of the Henry's constant curve is proportional to the heat of absorption of gaseous solute i at infinite dilution.

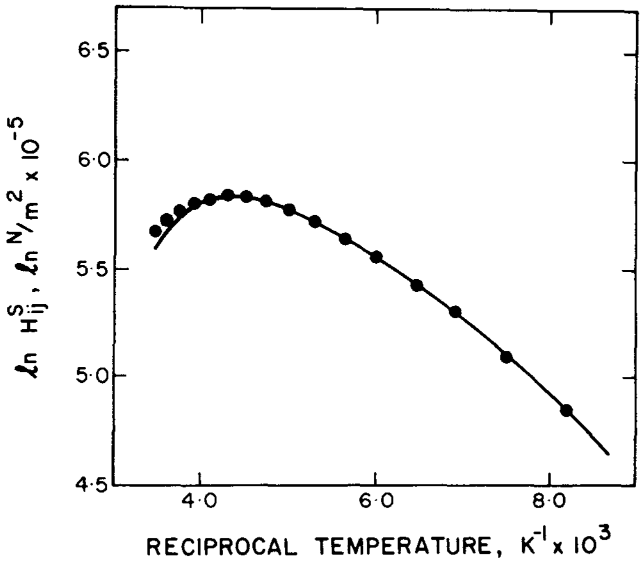

Fig. 5. Comparison of calculated [Equation (19)] and experimental Henry's constants for the nitrogen-ethane system. Solid line represents the calculated data.

$$\frac{d \ln H^s{}_{ij}}{d\left(\frac{1}{T}\right)} = -\frac{\bar{h}_i{}^a}{R} \tag{24}$$

The slope of the curve can also be derived from Equation (19).

$$\frac{d \ln H^s{}_{ij}}{d\left(\frac{1}{T}\right)} = \frac{d \ln f_j{}^s}{d\left(\frac{1}{T}\right)} + \left\{\frac{u_j{}^* - u_j{}^s}{R} + \frac{1}{RT}\frac{d(u_j{}^* - u_j{}^s)}{d\left(\frac{1}{T}\right)}\right\}\left[\frac{V_{cij}}{V_{cj}}\left(1 - \frac{T^2{}_{cij}}{T^2{}_{cj}}\right)\right] - \frac{dz_j{}^s}{d\left(\frac{1}{T}\right)}\left[2\left(1 - \frac{V_{cij}}{V_{cj}}\right)\right] + \frac{d \ln (g/v)_j{}^{(1)*}}{d\left(\frac{1}{T}\right)}\left[2\frac{V_{cij}}{V_{cj}}(\omega_j - \omega_{ij})\right] \tag{25}$$

Equation (25) may be simplified somewhat with the aid of the following identities which can be proven by standard thermodynamic methods.

$$\frac{d \ln f_j{}^s}{d\left(\frac{1}{T}\right)} = -\frac{h_j{}^v}{R}\left(\frac{z^s{}_{jg}}{z^s{}_{jg} - z^s{}_{jl}}\right) - \frac{h_j{}^* - h^s{}_{jg}}{R} \tag{26}$$

$$\frac{d \ln (g/v)_j{}^{(1)*}}{d\left(\frac{1}{T}\right)} = +\frac{(u_j{}^* - u_j{}^s)}{R} \tag{27}$$

Equations (26) and (27) are combined with Equation (25).

$$\frac{d \ln H^s{}_{ij}}{d\left(\frac{1}{T}\right)} = -\frac{h_j{}^v}{R}\left(\frac{z^s{}_{jg}}{z^s{}_{jg} - z^s{}_{jl}}\right) - \frac{h_j{}^* - h^s{}_{jg}}{R} + \left\{\frac{u_j{}^* - u_j{}^s}{R} + \frac{1}{RT}\frac{d(u_j{}^* - u_j{}^s)}{d\left(\frac{1}{T}\right)}\right\} \left[\frac{V_{cij}}{V_{cj}}\left(1 - \frac{T^2{}_{cij}}{T^2{}_{cj}}\right)\right] - \frac{dz_j{}^s}{d\left(\frac{1}{T}\right)}\left[2\left(1 - \frac{V_{cij}}{V_{cj}}\right)\right] + \frac{(u_j{}^* - u_j{}^s)^{(1)}}{R}\left[2\frac{V_{cij}}{V_{cj}}(\omega_j - \omega_{ij})\right] \tag{28}$$

At moderate temperatures the enthalpy terms in Equation (28) dominate; therefore, the slope of the Henry's constant curve is negative. Close to the critical temperature of the solvent, however, the enthalpy terms remain approximately constant, the derivative $d(u_j{}^* - u_j{}^s)/d(1/T)$ is positive and large and the derivative $-dz_j{}^s/d(1/T)$ is also positive and approaches infinity. Therefore, as the critical temperature of component j is approached, the Henry's constant curve passes through a maximum after which its slope becomes positive.

The straight line portion of the curve shown in Figure 6 at low temperatures is a second typical characteristic of Henry's constants. This type of behavior implies that the heat of absorption for the gaseous solute is nearly constant and independent of temperature. At temperatures far removed from the critical state for solvent j, the compressibility factor for liquid j is very small and the derivative $dz_j^s/d(1/T)$ is nearly zero. Similarly the derivative $d(u_j^* - u_j^s)/d(1/T)$ is approximately independent of temperature. The gas phase is nearly ideal so that the enthalpy departure term is small and z_g is about 1.0. Therefore, at low reduced temperatures for the solvent Equation (28) reduces to the following approximate relationship:

$$\frac{d \ln H^s{}_{ij}}{d\left(\frac{1}{T}\right)} = -\frac{h_j^v}{R} + \left\{ \frac{(u_j^* - u_j^s)}{R} + \frac{d(u_j^* - u_j^s)}{RT\, d\left(\frac{1}{T}\right)} \right\} \left[\frac{V_{cij}}{V_{cj}} \left(1 - \frac{T^2{}_{cij}}{T^2{}_{cj}}\right) \right] + \frac{(u_j^* - u_j^s)^{(1)}}{R} \left[2\frac{V_{cij}}{V_{cj}} (\omega_j - \omega_{ij}) \right] \quad (29)$$

In the applicable region for Equation (29) the internal energy departure is closely approximated by the internal energy of vaporization. At low reduced temperatures both the heat of vaporization and the internal energy of vaporization are very weak functions of temperature. Consequently Equation (29) predicts a nearly constant slope, and this produces the constant slope or straight line portion of the curve shown in Figure 5.

The equations just discussed also permit a physical interpretation of the Henry's constant curve. Comparison of Equation (24) with Equation (29) shows that the heat of adsorption for the solute is equal to the heat of vaporization of the solvent plus additional terms. At low reduced temperatures for the solvent these additional terms have a negative sign. Consequently, the heat of adsorption is positive and larger than the heat of vaporization. Standard thermodynamic relationships similar to the Clausius-Clapeyron equation require, therefore, that with increasing temperature the solute fugacity must increase more rapidly than that of the solvent, a fact which is also apparent from Equation (25). This in turn causes the equilibrium ratio of the solute to increase, that is, its solubility decreases, with higher temperatures. This fact is readily deduced from the following rigorous relationship:

$$K_i^\infty = \frac{H^s{}_{ij}}{\nu_{ig} P_j^s} \quad (30)$$

At still higher temperatures, however, a new tendency becomes important. The volume increases very rapidly for the liquid solvent as its critical temperature is approached. The smaller solute molecules now fit much more easily into the vacant holes between the molecules of the greatly expanded solvent, and the solubility of the light component begins to increase as the critical point is approached. In this region the volumetric (compressibility) term $dz_j^s/d(1/T)$ in Equation (25) becomes extremely large and changes the Henry's constant curve from a negative to a positive slope.

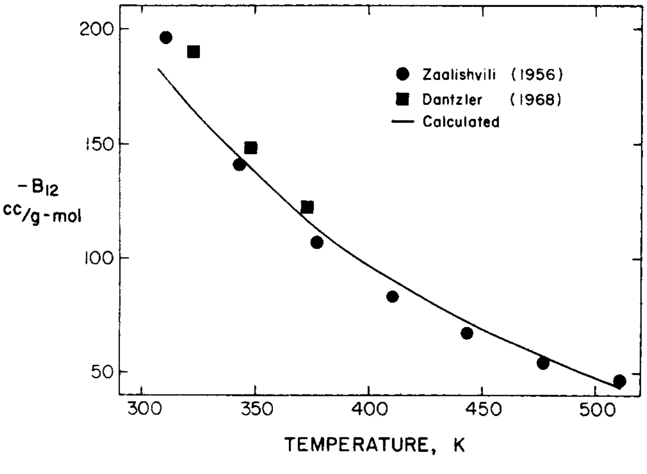

Fig. 6. Calculated and experimental cross second virial coefficients for the methane-n-pentane system.

OTHER THERMODYNAMIC PROPERTIES

Can the characteristic constants or interaction parameters obtained for Henry's constants be used to improve the prediction of other thermodynamic properties of mixtures? The general applicability of these parameters is an important requirement in the development of a unified corresponding states theory for fluid mixtures. With the exception of nitrogen mixtures, which are discussed briefly later, values of V_{cij} and ω_{ij} obtained in this work vary only a little from those calculated from empirical combining rules (Yamada, 1973). Similarly, values of k_{ij} do not differ greatly from those tabulated by Chueh and Prausnitz (1967). These small differences affect very significantly the calculation of Henry's constants, but they change only a little the prediction of enthalpy departures and gas phase compressibility factors. In addition, their effect is partly masked by uncertainties in the experimental data and by small inaccuracies in the generalized correlations used.

Figure 6 illustrates the significance of uncertainties in experimental data. In this figure two different sets of experimental cross second virial coefficients are plotted against temperature. In the region of overlap the two data sets deviate by 10 to 15 cc/g-mol. The line representing calculated virial coefficients is computed from a generalized equation (Gunn, 1971) and from characteristic parameters determined only from Henry's constants and liquid volumes. Average deviation between calculated and experimental cross virial coefficients is 8.5 cc/g-mol. Average deviation for the original correlation proposed by Prausnitz and Gunn (1958) is 9.5 cc/g-mol. This latter correlation contains one adjustable parameter T_{cij} which was fit to the experimental data.

Durnil (1973) has used a more sophisticated approach for predicting B_{ij}'s for this system by making use of the very accurate Klein-Hanley 11-6-8 potential function. Using a nonspherical hard core and an adjustable force constant, Durnil reports an average deviation between calculated and experimental cross virial coefficients which is 2.1 cc/g-mol larger than the corresponding value illustrated by the solid line in Figure 6. This comparison is based on the same number of data points used by Durnil who records results only for the B_{12}'s of Zaalishvili (1956).

Other virial coefficient correlations show larger deviations. For example the method of Huff and Reed (1963) with no adjustable parameters has an average deviation of 19 cc/g-mol. The spherical core Kihara potential produces an average deviation of 21 cc/g-mol even with an adjustable force constant.

Figure 6 also indicates that a significant level of experimental uncertainty exists in the B_{12}'s for the methane-n-

pentane system; therefore, it is not possible to determine conclusively if a difference exists between the value of k_{ij} calculated from virial coefficients and that calculated from Henry's constants. For similar reasons no definitive conclusion is reached on this question for other systems not containing nitrogen which have been investigated.

Values of k_{ij} for nitrogen containing systems in Table 4 deviate radically from k_{ij} values obtained from virial coefficients. Unlike the other types of mixtures studied, these systems exhibit decreasing solubility of nitrogen with decreasing temperature over very wide ranges of temperatures. This behavior produces the unusually large k_{ij} values in Table 4. Hydrogen, helium, and carbon monoxide as solute gases are expected to show similar characteristics.

Finally the uniqueness of parameters listed in Table 4 needs to be considered. Volumetric data for liquid mixtures and Henry's constants are available for a large number of paraffin mixtures. For this reason the interaction parameters for these types of mixtures are believed to be reasonably unique.

Volumetric mixture data are far more scarce for mixtures of paraffins with nitrogen, hydrogen sulfide, or carbon dioxide. Without liquid mixture densities it is very difficult to obtain a unique set of three interaction parameters for a given binary mixture. This uncertainty is increased by the fact that Henry's constants often span a rather narrow temperature range for these types of systems. For mixtures of paraffins with nonhydrocarbons, therefore, the interaction constants listed in Table 4 can only be considered tentative. For example, values for k_{ij} are probably no better than ± 20%. Nevertheless, these constants do correlate Henry's constants accurately in the temperature range specified in Table 4.

ACKNOWLEDGMENT

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NOTATION

A = van Laar constant
f = fugacity
$f^0{}_{il}$ = standard fugacity, fugacity of pure liquid component i at the same T and P as the mixture
(g/v) = nondimensionalized configuration potential
$\bar{h}^a$ = molar heat of adsorption
h^v = heat of vaporization
$h^* - h$ = enthalpy departure
k_{ij}, l_{ij}, $\Delta\omega_{ij}$ = interaction parameters defined by Equations (20), (21) and (22)
k_i^∞ = y_i/x_i = equilibrium constant for component i at infinite dilution
P = pressure
P_i = partial pressure of component i
P^s = vapor pressure
R = gas constant
T = temperature
$u^* - u$ = internal energy departure
$\bar{v}_i^\infty$ = partial molar volumes at infinite dilution
v = molar volume
V = volume, variable of integration
V_{sc} = scaling volume defined by Equation (23)
$V_{0.6}$ = volume of pure liquid at a reduced temperature of 0.6
x = mole fraction
z = Pv/RT, compressibility factor

Greek Letters

γ_i^∞ = activity coefficient at infinite dilution
ν_{ig} = fugacity coefficient at infinite dilution
ϕ = volume fraction
ψ = any configurational thermodynamic property
ω = acentric factor

Subscripts

c = critical property
g = gaseous state
l = liquid state
i = solute, component i
j = solvent, component j
m = mixture property
sp = scaling parameters defined by Equations (9), (10), and (11)

Superscripts

s = property at saturation conditions (vapor pressure)
(0) = generalized function for a simple fluid
(1) = deviation function
— = partial molal property
$*$ = ideal gas property at same T and P as real gas
0 = standard state property

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Fixed Bed Desorption Behavior of Gases with Nonlinear Equilibria:

Part II. Dilute, Multicomponent, Isothermal Systems

Generalized depletion curves for desorption (and corresponding breakthrough curves for adsorption) were calculated for systems characterized by the Langmuir-type multicomponent equilibrium equation and controlled by the film type rate model. In contrast with adsorption where the nonkey (or less strongly adsorbed) component curves display overshoots above feed concentration, in desorption the key component depletion curves exhibit the instabilities in the form of inflections and curvatures. As in the one component case, the differences in the depletion and breakthrough curves may be related to the rate phenomena. The undulations in the key component depletion curves may be characterized by derivatives of the rate data. The major significance of these instabilities is to elongate the depletion curves, which in turn requires the expenditure of added effort during regeneration. Process modifications are indicated, which could suppress the instabilities. The predicted trends were confirmed by experimental depletion curves.

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SCOPE

Most of the studies dealing with the design of sorption based separation processes have focused on the description of the adsorption step; and even these have been confined mostly to single component systems. From experience, however, the desorption is known to be the controlling step in the operation of the cyclic processes. Recently it was shown that in systems characterized by favorable isotherms ($d^2W/dC^2 < 0$) the depletion curves are considerably elongated in comparison to the corresponding breakthrough curves. Mechanistically the elongation may be