Phase Equilibria for Strongly Nonideal Liquid Mixtures at Low Temperatures

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Investigation of the nonideal behavior of mixtures of simple molecules is an important step toward improved understanding of the theory of solutions. This work describes an equilibrium apparatus suitable for the measurement of vapor-liquid and vapor-liquid-liquid equilibria of simple fluid mixtures at cryogenic temperatures. Vapor-liquid data are reported for the argon-ethane and nitrogen-carbon tetrafluoride systems. Contrary to expectations, limited liquid-phase miscibility was not observed for either of these mixtures. These results and those for other nonideal mixtures of simple molecules are compared with predictions of upper critical solution temperatures by the theory of regular solutions. Usefulness of this theory is impaired by its neglect of the order-disorder phenomenon and, more seriously, by the geometric-mean assumption for the intermolecular forces between dissimilar molecules.

The thermodynamic properties of mixtures of condensed gases are of interest for two primary reasons. First, such properties are of direct use in the solution of engineering problems in the cryogenic and space industries. Second, the properties of such mixtures serve to test and extend current molecular theories of liquid mixtures. Condensed gases such as argon, methane, nitrogen, etc., form relatively simple liquid mixtures which are more susceptible of theoretical treatment than mixtures of more common liquids; the intermolecular forces operating between small, nonpolar molecules are, relatively speaking, easier to understand, and as a result one may give a theoretical, molecular interpretation to observed macroscopic phenomena for mixtures of simple liquids. This work considers the thermodynamic properties of strongly nonideal liquid mixtures of condensed gases and reports experimental data for two such mixtures. A recent theoretical study of mixtures of simple liquids is given elsewhere (*9*).

While the properties of condensed gases are more easily treated by theory than are those of common liquids, the experimental determination of these properties is necessarily more difficult, since simple gases can be condensed only at low temperatures. In spite of the additional difficulties of working at low temperatures, a great many experimental studies have been carried out on mixtures of simple molecules. These are reviewed elsewhere (*18, 19, 22*). However, most previous work has been carried out on relatively ideal systems, such as oxygen-nitrogen, nitrogen-carbon monoxide, and argon-nitrogen, where the excess properties are small, and thus the molecular effects of mixing are small. This work is concerned with mixtures of simple molecules which are more nonideal.

One manifestation of strong nonideality is phase splitting or partial immiscibility of liquids. Accordingly, an apparatus has been designed and constructed to study both vapor-liquid and liquid-liquid phase equilibria of simple mixtures, and two such mixtures have been investigated.

Some studies have been carried out previously on a number of simple, yet strongly nonideal systems. Thorp and Scott (*27*) measured the vapor pressures of methane–carbon tetrafluoride and krypton–carbon tetrafluoride mixtures somewhat above 100°K.; neither system was observed to split. Croll and Scott (*3*) later investigated methane–carbon tetrafluoride at lower temperatures and found partial immiscibility below 94.5°K. McKinley and Wang (*16*) studied the mutual solubility of oxygen and ethane, reporting an upper critical solution temperature around 108°K. Unfortunately, neither of the latter two papers reports vapor-liquid equilibrium data. Also, Scott (*23*) reports the consolute temperature only (150°K.) for the ethane–carbon tetrafluoride system.

Other very nonideal mixtures have been investigated at low temperatures but are not particularly suited to theoretical interpretation. Nitrogen and ethane have been found to be quite immiscible up to the vapor-liquid critical point of the nitrogen phase (*10*). Several mixtures with ozone have been studied: oxygen (*2*), carbon tetrafluoride (*25*), nitrogen (*24*), and carbon monoxide (*24*). However, it appears that ozone is far from a simple molecule.

A very approximate interpretation of critical solution phenomena for simple fluids may be carried out in terms of Hildebrand's regular solution theory (*13*). It gives as the upper critical solution temperature (U.C.S.T.) the expression

$$\text{U.C.S.T.} = \frac{2x_1 x_2 v_1^2 v_2^2 [\delta_1 - \delta_2]^2}{R(x_1v_1 + x_2v_2)^3} \tag{1}$$

where the composition is given by

$$x_{1\ \text{U.C.S.T.}} = \frac{(v_1^2 + v_2^2 - v_1v_2)^{1/2} - v_1}{v_2 - v_1} \tag{2}$$

Solubility parameters δ may be calculated from known properties of the pure components (see Table 1). The U.C.S.T.'s for several of the mixtures mentioned have been calculated from regular solution theory, and these are compared with experiment in Table 2.

Although a few values are qualitatively correct, it is apparent that regular solution theory fails to predict consolute points with any dependability. The failure of regular solution theory in these cases comes primarily from the invalidity of the assumption that the energy between unlike species may be characterized by the geometric-mean mixing rule. Recently Hildebrand (*12*) has pointed out the necessity for recognizing the differences in interactions between different classes of molecules, such as paraffins, olefins, aromatics, halocarbons, etc., and has stressed the need for a more sophisticated theory of intermolecular forces than that currently available.

One modification of regular solution theory has not been applied: the order-disorder correction. The use of

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Table 1. Liquid Volumes and Solubility Parameters of Simple Molecules at 90°K.

Species	ΔU, cal./g. mole	v, cc./g. mole	δ, (cal./cc.)$^{1/2}$	Reference
N_2	1085	38.12	5.33	(*26*)
CO	1206	37.08	5.70	(*4*)
A	1361	29.00	6.83	(*4*)
O_2	1469	28.00	7.24	(*17*)
CH_4	1915	35.32	7.35	(*4*)
CF_4	3176	45.96	8.31	(*7*)
C_2H_6	4136	45.66	9.52	(*4*)
O_3	3300	30.55	10.4	(*24*)

Equation (1) to predict critical solubilities assumes random mixing; this assumption is known to be invalid near the consolute point (*11, 13, 20*). The effect of an order-disorder correction would be to lower the predicted consolute temperatures by about 10 to 20%. The order-disorder phenomenon in these and other simple mixtures is discussed elsewhere (*9*).

Two previously unstudied systems were chosen for investigation: argon-ethane and nitrogen-carbon tetrafluoride. On the basis of consolute points predicted from regular solution theory (69° and 94°K., respectively), these seemed to promise the best chance for investigation near or at the critical solution point. For both of the systems studied, no phase splitting was observed. The temperature range was limited on the low side by the freezing of the solution. However, it is apparent from the measured Gibbs energies that the upper critical solution temperature, if it can be said to exist, would occur within a few degrees of the lowest temperatures studied.

EXPERIMENTAL

The experimental apparatus consisted of a heavy-wall glass equilibrium cell in a vacuum cryostat. Equilibrium determinations were carried out by a dynamic technique in the temperature range of 70° to 120°K. and at pressures up to 20 atm. Provisions were made for sampling both liquid phases (if two were present) and the vapor phase, and samples were analyzed by gas chromatography. A somewhat similar apparatus has recently been described by Barrick and Herring (*1*).

The Cryostat

Operation at low temperatures was achieved by the use of a vacuum cryostat (see Figure 1). The equilibrium cell was placed inside one end of a copper bar, the other end of which was placed in a tank of boiling nitrogen. The temperature of the cell could then be controlled by means of an annular heater placed around the center of the bar. The entire assembly was suspended inside a stainless steel vacuum chamber for thermal insulation.

Table 2. Upper Critical Solution Temperatures for Some Mixtures of Condensed Gases

Mixture	U.C.S.T., °K. Predicted from regular solution theory	Experimental	Reference
N_2-C_2H_6	185	>133	(*10*)
O_2-C_2H_6	49	108	(*16*)
CF_4-CH_4	9.5	94	(*27*)
CF_4-C_2H_6	17	150	(*23*)
O_2-O_3	74	93	(*2*)
N_2-O_3	223	>82	(*24*)
CO-O_3	188	<77	(*24*)
CF_4-O_3	42	103	(*25*)

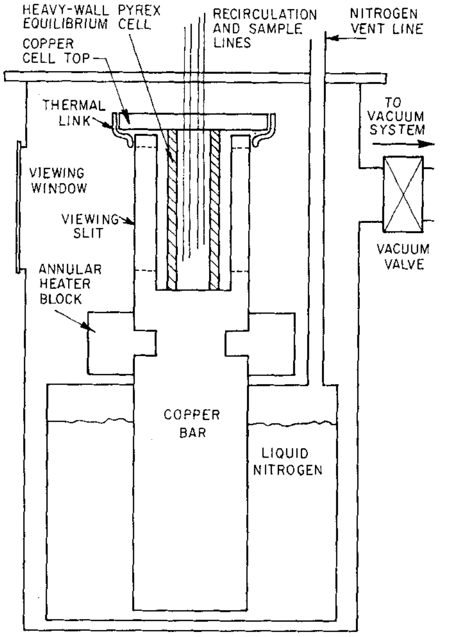

Fig. 1. Vacuum cryostat.

The bottom of the equilibrium cell was a copper block that fitted quite snugly into a recess in the bar. The copper top of the cell was thermally connected to the bar by heavy flexible copper thermal links. In this manner the cell could be maintained at essentially the temperature of the top of the bar, especially when the vapor was vigorously circulated. The temperature gradient in the cell was always less than 0.5°C. The heat leak to the bar was supplied by an annular heater collar fitting tightly around the center of the bar. In this collar were soldered eight cartridge heaters, adjustable from 0 to 140 w. each. The lower end of the bar, which was finned for better heat transfer, was immersed in a 15-liter liquid nitrogen tank. Normally the nitrogen was allowed to boil at atmospheric pressure (b.p. = 77.4°K.), but for operation of the equilibrium cell below about 80°K., the pressure above the liquid nitrogen was reduced to about 90 mm. Hg to boil the nitrogen at its triple point (63.2°K.). For the best temperature control, it was necessary to have at least a small heat input at all times. This requirement limited the lowest temperatures attainable to about 65° to 66°K. The upper temperature limit was never reached but, for practical purposes, is probably about 150°K. The highest temperature at which measurements were made was about 120°K., which required about 200-w. heat input out of 1,100 w. available.

Thermal isolation of the system was achieved by evacuation of the cryostat to a pressure below 10^{-4} mm. Hg. All outer surfaces of the copper bar and nitrogen tank were chrome plated and highly polished to minimize radiation. Two heat shields made of thin copper sheet, plated and polished on both sides, were placed between the cold assembly and the ambient walls. The nitrogen tank and copper bar were suspended from the top of the cryostat by three very thin stainless steel rods in order to minimize conduction.

Visual observation of the cell was made through opposing windows in the outer shell with corresponding slits in the heat shields and copper bar.

Equilibrium Cell

The equilibrium cell was designed to permit visual observation of the system at liquid-nitrogen temperatures and pressures well above atmospheric. This cell (see Figure 2) was constructed from an 8-in. length of 1½-in. diameter heavy-wall Pyrex tubing. This glass tube was wet at both ends with very pure indium metal and sealed into troughs in copper end plates. These seals were leak-free at liquid nitrogen temperatures from 10^{-5} mm. Hg. up to over 20 atm.

The indium seals were not expected to flow at low temperatures; rather, the difference in thermal expansion of the

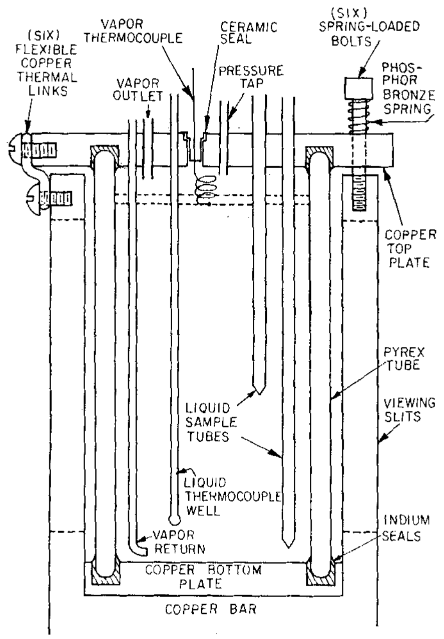

Fig. 2. Equilibrium cell.

Pyrex tube and the copper bar (about 0.020 in. between ambient and operating temperature) was taken up by letting the top plate of the equilibrium cell float free, held down by six heavy phosphor-bronze springs. The tension on each spring was adjusted to be uniform as well as adequate for the high-pressure operations.

Agitation of the liquid phase (or phases) in the cell was carried out by vapor recirculation. Vapor was pumped out the top of the cell and bubbled back in at the bottom. The up-flowing vapor was demisted by a series of very fine copper mesh screens near the top of the cell.

The construction of the cell is discussed in detail elsewhere (8).

Vapor Recirculation

The vapor-recirculation technique served a dual purpose. The recirculated vapor bubbling through the liquid in the cell provided excellent agitation and allowed the system to reach equilibrium faster; furthermore, the recirculation stream provided easy access to the vapor phase for sampling.

Vapor recirculation (see Figure 3) was carried out by means of a specially designed, positive-displacement, noncontaminating pump. The pumping action was achieved by squeezing along a rubber tube with rollers. By matching the pressure inside and outside the tube the pump could be run at any pressure desired. The gas, while being pumped, came in contact with only the rubber tube.

The pump was driven by a variable-speed drive to permit operation in the range of 10 to 1,000 cc./min. vapor recirculation. The usual recirculation rate was about 100 cc./min.

Vapor samples were first isolated in a section of the recirculation line and then bled into previously evacuated sample vessels. The recirculating vapor was returned and cooled through long copper tubes in the cryostat.

Temperature and Pressure

Temperatures were measured at both the top and the bottom of the equilibrium cell by iron-constantan thermocouples. Each was calibrated at four fixed points: the ice point, sublimation point of dry ice, boiling point of oxygen, and boiling point of nitrogen; the temperatures measured were accurate to about ± 0.05°K.

Pressures were measured with two 16-in. Heise Bourdon tube gauges, one 0 to 30 lb./sq. in. abs. for low pressures and the other 0 to 300 lb./sq. in. gauge for high pressures. The low-pressure gauge was checked against a mercury barometer and found accurate to ± 0.01 lb./sq. in.; the high-pressure gauge was checked with a dead-weight tester and was accurate to ± 0.3 lb./sq. in.

Liquid Sampling

Liquid samples were taken by means of extended needle valves as shown in Figure 4. This method offered the advantage of virtually no dead space, so that the sampling device did not need to be flushed with sample, and the amount of sample taken could be as small as desired. These valves worked by drawing a very small amount of liquid into an evacuated area through a fine hole. The liquid then flashed and could be bled into an evacuated sample vessel. The samples taken were very small to minimize the effect of the equilibrium; in general, the volume of liquid removed represented less than 0.1% of the volume of the system. The liquid sampling device is discussed in detail elsewhere (8).

Analytic Procedure

All analyses were done on a Beckman GC-2A gas chromatograph equipped with a 6-ft. silica gel adsorption column with helium used as carrier gas at 30 lb./sq. in. gauge for the nitrogen–carbon tetrafluoride system and 20 lb./sq. in. gauge for the argon-ethane system. The column temperature was 100°C. and the filament current was 200 ma. Results were recorded on a Wheelco 8000 series millivolt recorder and peak areas measured by an attached disk integrator. The instruments were calibrated by a series of mixtures of known composition. Analyses of binary mixtures were reproducible to about 0.5% in mole fraction for an equimolar mixture and to about 0.2% for a dilute mixture. The amount of sample used was about 1 cc. of vapor at S.T.P.

Materials

The materials used were:

	Supplier	Purity %
Argon	Linde	99.995
Nitrogen	Matheson	99.998
Ethane	Phillips	99.96
Carbon tetrafluoride	DuPont	99.8

The carbon tetrafluoride was purified by the standard procedure of alternate freezing and melting under vacuum in order to remove oxygen and nitrogen, the major impurities, as recommended by the supplier. All materials were then further purified by passing through a silica-gel trap at dry ice temperatures.

RESULTS

As a check on the apparatus, phase splitting was observed for an approximately equimolar mixture of methane and carbon tetrafluoride at 94.0°K. This result is in good agreement with the data of Croll and Scott (3), who reported an upper critical solution temperature of 94.5°K. at $x_{CF_4} = 0.43$. This measurement served as a check on the visibility of liquid-phase separation; the transition was quite apparent and reproducible.

The two systems investigated for phase separation were argon-ethane and nitrogen-carbon tetrafluoride. In both cases only a single liquid phase existed over the tempera-

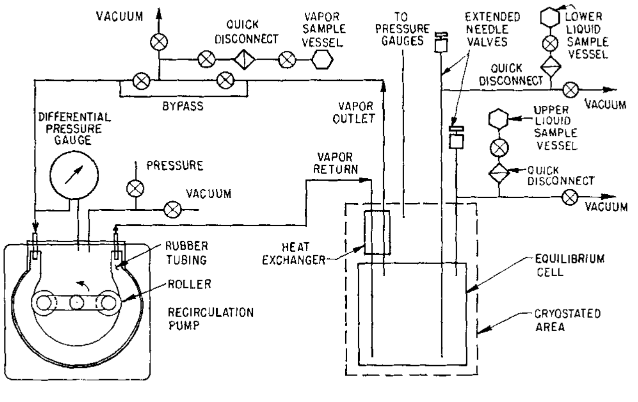

Fig. 3. Sampling and vapor recirculation system.

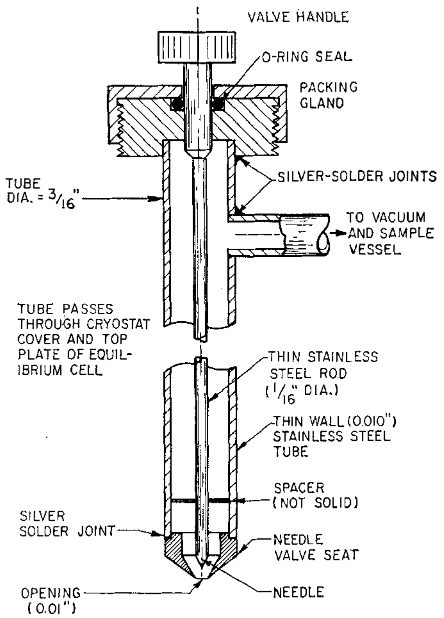

Fig. 4. Extended needle valve liquid-sampling device.

ture range investigated. Pressure, temperature, and vapor and liquid composition data were obtained; these are presented in Tables 3 and 4.

ANALYSIS OF RESULTS

Activity coefficients for argon in the argon-ethane system and for nitrogen when mixed with carbon tetrafluoride were calculated from the equation of equilibrium:

$$x_i \gamma_i P_i^s \phi_i^s \exp\left[\frac{v_i(P - P_i^s)}{RT}\right] = y_i \phi_i P \qquad (3)$$

Pure-component vapor pressure and liquid volume data are available (*4, 7, 26*); the vapor-phase nonidealities were calculated from the virial equation with Pitzer's correlation (*14*) for virial coefficients, and the pure-component fugacity coefficient was calculated from a new correlation (*15*) based on Pitzer's method. Because of the disparity of volatilities in both systems, the vapor mole fractions of the heavy components were too small for meaningful analysis. As a result it was not possible to check the data for thermodynamic consistency.

Since both systems are mixtures of molecules of somewhat different volume, the activity coefficients are best correlated in terms of a Scatchard type of equation for excess Gibbs energy:

$$g^E = A_{12}\,(x_1 v_1 + x_2 v_2)\,\Phi_1 \Phi_2 \qquad (4)$$

where Φ is the volume fraction of component i. From the experimentally measured values of γ, the exchange energy density A_{12} was calculated over the temperature range investigated. For each system the exchange energy density varies only slightly with temperature according to the equations

Argon-ethane $A_{12} = (7.0 + 0.021\,T)$ cal./cc.
Nitrogen–carbon tetrafluoride $A_{12} = (5.2 + 0.023\,T)$ cal./cc.

The uncertainty in A_{12} is estimated to be ± (0.5 to 1.0) cal./cc.

TABLE 3. ARGON-ETHANE EQUILIBRIUM DATA

T, °K.	P, atm.	x_A	y_A
81.44	0.4050	0.312	0.999+
84.76	0.6379	0.445	0.998
90.00	1.1722	0.611	0.999
99.10	2.484	0.581	0.999+
102.98	3.321	0.499	0.999
113.52	6.818	0.660	0.998

From these results good estimates can be made of the consolute temperatures of the solutions, on the assumption that they could be supercooled sufficiently without solidification. The values found are

	U.C.S.T., °K.	
	Calculated from experimental results	Predicted from regular solution theory (*13*)
Argon-ethane	81	69
Nitrogen–carbon tetrafluoride	63	94

The calculated values of the U.C.S.T. based on experimental results may be one or two degrees too high, owing to the slight effect of ordering near the consolute point.

These results, as well as those presented earlier, again point out the weakness of the regular solution theory in predicting critical solution phenomena for simple mixtures. An outstanding example may be found in a comparison of the results found for the argon-ethane system with those quoted earlier for oxygen-ethane mixtures. Although argon and oxygen have quite similar configurational and critical properties, their mixtures with ethane show very different behavior. From a comparison of the predicted and experimental U.C.S.T. for oxygen with ethane (49° and 108°K., respectively), one would expect the U.C.S.T. for the argon mixture to be much higher than it actually is, but the regular solution prediction for the latter system is only about 15% low. Apparently the geometric mean assumption is much better for argon-ethane than for oxygen-ethane interactions.

It is apparent that one cannot expect good predictions of critical solution phenomena from the simple regular solution theory. As mentioned earlier, this theory has two shortcomings: it does not take into account order-disorder effects, which, while negligible under ordinary conditions, may be important near the consolute point, and it assumes that the interaction between unlike molecules is given by the geometric mean of the interactions between the like molecules.

The second shortcoming is the more serious one. Even a small deviation from the geometric mean assumption can

TABLE 4. NITROGEN-CARBON TETRAFLUORIDE EQUILIBRIUM DATA

T, °K.	P, atm.	x_{N_2}	y_{N_2}
69.57	0.2919	0.452	0.999+
69.90	0.2746	0.268	0.999+
75.81	0.6036	0.185	0.999
78.06	0.3523	0.067	0.999
85.28	1.7350	0.516	0.999
81.51	1.1214	0.238	0.999
81.83	0.6244	0.113	0.996
85.28	1.7350	0.479	0.999
89.96	1.1419	0.105	0.998
95.33	3.668	0.329	0.997
107.94	8.506	0.564	0.992
116.24	1.9189	0.025	0.963

have a large effect on the consolute temperature, as pointed out by Reed (*21*), Scott (*23*), and others. This can be shown by rewriting Equation (1) in the more general form

$$\text{U.C.S.T.} = \frac{2x_1x_2v_1^2v_2^2}{R(x_1v_1 + x_2v_2)^3}\left[(\delta_1 - \delta_2)^2 + 2k_{12}\delta_1\delta_2\right] \quad (5)$$

where k_{12} is a constant, independent of temperature, characteristic of the binary system 1-2 and defined by

$$c_{12} = (1 - k_{12})(c_{11}c_{22})^{1/2} \quad (6)$$

The geometric mean assumption sets $k_{12} = 0$. However, even if k_{12} is very small compared with unity, the effect on U.C.S.T. can be large. For example if $\delta_1 = 5$ and $\delta_2 = 8$, U.C.S.T. is increased by about 9% if $k = 0.01$ and by about 18% if $k_{12} = 0.02$. According to London's theory of dispersion forces for nonpolar molecules, $k_{12} \geqq 0$, and this inequality is supported by experimental results.

A good estimate of k_{12} can be made from second virial coefficient data for the 1-2 binary system. For example, Douslin and co-workers have measured volumetric properties for gaseous methane–carbon tetrafluoride mixtures (*5*) as well as those for the pure components (*6*). From their measurements near room temperature, $k_{12} = 0.073$, a very large deviation from the geometric mean. When one uses this value in Equation (5), the calculated U.C.S.T. for the methane–carbon tetrafluoride system is 104°K., a large improvement over the value calculated from Equation (1). (See Table 2.)

CONCLUSIONS

1. An apparatus has been designed and constructed for the investigation of phase equilibria at cryogenic temperatures and moderate pressures.

2. Vapor-liquid equilibrium measurements have been made on the argon-ethane system in the range 82° to 114°K. and on the nitrogen–carbon tetrafluoride system from 70° to 116°K. No liquid-liquid phase splitting was observed.

3. In the temperature range investigated, the exchange energy density of the argon-ethane system is 8.5 to 9.5 cal./cc., and for the nitrogen–carbon tetrafluoride system it is 6.5 to 8.0 cal./cc.

5. Upper critical solution temperatures calculated from the experimental data are 81°K. for argon-ethane and 63°K. for nitrogen–carbon tetrafluoride.

5. Prediction of upper critical solution temperature by regular solution theory is impaired by the theory's neglect of the order-disorder phenomenon and, more seriously, by the geometric mean assumption for the intermolecular forces between dissimilar molecules.

6. These results, as well as others, point out the need for further experimental study of solutions of simple molecules since such studies are necessary to form the basis for a realistic theory of solutions.

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NOTATION

A_{12} = exchange energy density
c = cohesive energy density (δ^2)
g = molar Gibbs energy
P = pressure
R = gas constant
T = temperature, K°
U = internal energy
v = molar volume
x = liquid mole fraction
y = vapor mole fraction

Greek Letters

γ = activity coefficient
δ = solubility parameter
ϕ = fugacity coefficient
Φ = volume fraction

Superscripts

s = saturated
E = excess

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