TABLE A1. FUNCTIONS FOR EQUATION (A1)

T_R	$\phi(T_R)$	System	$1 - \frac{\epsilon_{12}}{\epsilon_{11}}$
0.6	0.39	Methane-H_2	0.58
0.7	0.58	Ethane-H_2	0.55
0.8	0.99	Propane-H_2	0.55
0.9	2.10	Benzene-H_2	0.65
0.95	3.56	*n*-Octane-H_2	0.51
		n-Dodecane-H_2	0.51

TABLE A2. CONSTANTS FOR SATURATED LIQUID

	Ωa	Ωb
Hydrogen	0.4278	0.0694
Methane	0.4546	0.0872
Ethane	0.4347	0.0827
Propane	0.4138	0.0802
Benzene	0.4100	0.0787
n-Octane	0.3900	0.0739

$$\Omega a_{ij} = \tfrac{1}{2}(\Omega a_i + \Omega a_j) \tag{A8}$$

$$v_{cij} = \tfrac{1}{2}(v_{ci} + v_{cj}) \tag{A9}$$

$$z_{cij} = 0.291 - 0.04(\omega_i + \omega_j) \tag{A10}$$

$$T_{cij} = (T_{ci}T_{cj})^{1/2}(1 - k_{ij}) \tag{A11}$$

$$k_{ij} = 1 - \left[\frac{(v_{ci}^{1/3}v_{cj}^{1/3})^{1/2}}{(v_{ci}^{1/3} + v_{cj}^{1/3})/2}\right]^3 \tag{A12}$$

The molar liquid volumes of solvents at saturation, v_1's, are calculated by a method discussed elsewhere (Chueh and Prausnitz, 1969; Prausnitz and Chueh, 1968).

Values of $\bar{v}_2^{\infty(P_1^s)}$ calculated from Equation (A6) are found to be in good agreement with both experimental data and those calculated from Equation (A1).

Partial Molar Compressibility of Hydrogen

The partial molar compressibility of hydrogen is given by

$$\bar{\beta}_2 = -\frac{1}{\bar{v}_2}\left(\frac{\partial \bar{v}_2}{\partial P}\right)_{T,x} = -\frac{1}{\bar{v}_2}\left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1}\right]_{T,x}$$

$$= \frac{1}{\bar{v}_2}\left(\frac{\partial P}{\partial V}\right)^{-2}_{T,n_1,n_2}\left[\frac{\partial}{\partial n_2}\left(\frac{\partial P}{\partial V}\right)_{T,n_1,n_2}\right]_{T,P,n_1} \tag{A13}$$

Substitution of Equations (A3) to (A6) into Equation (A13) gives partial molar compressibility of hydrogen at infinite dilution,

$$\bar{\beta}_2^{\infty} = \frac{QA - QB - QC}{QD}$$

$$QA = \frac{a_1(2\bar{v}_2^{\infty} + b_2) + 2a_{12}(2v_1 + b_1)}{T^{0.5}v_1^2(v_1 + b_1)^2}$$

$$QB = \frac{2a_1(2v_1 + b_1)[\bar{v}_2^{\infty}(v_1 + b_1) + v_1(\bar{v}_2^{\infty} + b_2)]}{T^{0.5}v_1^3(v_1 + b_1)^3}$$

$$QC = \frac{RT[(v_1 - b_1) - 2(\bar{v}_2^{\infty} - b_2)]}{(v_1 - b_1)^3}$$

$$QD = \bar{v}_2^{\infty}\left[\frac{a_1(2v_1 + b_1)}{T^{0.5}v_1^2(v_1 + b_1)^2} - \frac{RT}{(v_1 - b_1)^2}\right]^2 \tag{A14}$$

where subscript 1 refers to solvent and 2 refers to hydrogen. The meanings of symbols are the same as in Equation (A6).

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Liquid-Vapor Equilibria at 112.00 K for Systems Containing Nitrogen, Argon, and Methane

Liquid-vapor phase equilibria measurements were made at 112.00 K on the binary systems nitrogen-argon, nitrogen-methane, and argon-methane and the ternary system nitrogen-argon-methane. Values of g^E, the excess Gibbs free energy, have been calculated from the experimental data for all the systems studied. The data and derived g^E values for the binary systems were compared with the results of previous investigations with satisfactory agreement.

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SCOPE

Low temperature phase equilibria data are valuable in process design calculations and in the testing and formulation of liquid solution correlations and theories. The objective of this study was to provide consistent liquid-vapor phase equilibria data for a ternary system and its constituent binaries. The nitrogen-argon-methane system was selected since all of these simple components are of

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considerable interest in cryogenic processing applications and in theoretical studies. A temperature of 112 K was chosen so that one of the constituents (nitrogen) would be at a high reduced temperature ($T/T_c = 0.887$), while the other components remained well below their critical temperatures.

A vapor-recirculation type equilibrium cell was used, with separate liquid and vapor samples taken and analyzed chromatographically. Activity coefficients and excess Gibbs free energies were calculated from the P-T-y-x experimental data. A number of previous investigators have studied phase equilibria for the binary mixtures over considerable ranges of temperatures both below and above 112 K. The only previous results for the ternary mixture are at the methane triple point (90.68 K).

CONCLUSIONS AND SIGNIFICANCE

A self-consistent set of liquid-vapor phase equilibria data has been obtained at 112.00 K for the system N_2-Ar-CH_4 including the constituent binaries. These data are in good agreement with earlier work on the binary systems.

Phase equilibria data are scarce for systems containing three or more simple species, particularly for conditions where one component is at a high reduced temperature. The present data, combined with earlier results for N_2-Ar-CH_4 should contribute to the experimental basis for testing and improving correlations involving multicomponent phase equilibria prediction. The composition dependence of the liquid mixture excess Gibbs free energy, which was extracted from the data, should provide a guide for the development of improved theories of liquid mixtures.

EXPERIMENTAL PROCEDURE

The phase equilibria measurements were made in a closed-loop, vapor recirculation system. Since the vapor-recirculation pump and the cryostat have been discussed in detail elsewhere (Hiza and Duncan, 1969; Duncan and Hiza, 1970) and fairly complete descriptions of the general experimental method have also been published (Kidnay et al., 1971; Miller et al., 1972), only those aspects of the measurements peculiar to the nitrogen-argon-methane system will be discussed here.

For the ternary mixture an experimental run was started by establishing in the cryostat the operating temperature of 112.00 K used in all of the runs, and then partially filling the equilibrium cell with liquid methane. Argon was then added to bring the system to a preselected argon-methane liquid composition. The vapor recirculation pump was started and, after equilibrium conditions were established, a sample was withdrawn. In most cases, the liquid and vapor samples were withdrawn simultaneously. However, for three runs the liquid and vapor samples were taken independently and at slightly different pressures. Analysis of the sample established a data point for the argon-methane binary system. Nitrogen was then added and after re-establishment of equilibrium, a sample was again withdrawn for analysis, thus establishing a data point for the nitrogen-argon-methane ternary system. The procedure of adding nitrogen and sampling was repeated until the total system pressure approached the vapor pressure of nitrogen (16.233 atm or 1.6448 MN/m^2) at which point the run was discontinued and the contents of the cryostat vented. Subsequent experimental runs were made using the same procedure, but starting with different ratios of argon to methane. Five runs were made starting with argon-methane liquid mole percents of approximately 10-90, 30-70, 50-50, 70-30, 90-10.

The binary systems nitrogen-methane and nitrogen-argon were measured by partially filling the equilibrium cell with methane or argon, and then adding nitrogen incrementally until the vapor pressure of nitrogen was approached. The liquid and vapor samples were determined in independent runs at nearly equivalent pressures.

Both the liquid and vapor samples for all of the runs were analyzed with a gas chromatograph using a thermal conductivity detector. Helium carrier gas was used, and the separation was obtained with a 6-ft. column containing molecular sieve 13X and a 3-ft. column containing molceular sieve 5A in series. The chromatograph was calibrated using samples of pure argon, pure nitrogen, and pure methane introduced into the chromatograph at pressures from 60 to 620 mm Hg (0.008 to 0.083 MN/m^2). The calibrations were checked by use of nearly equimolar mixtures of argon-methane and nitrogen-methane prepared by weight. When analyzing samples from the equilibrium cell, the compositions of all of the components in the mixture were determined chromatographically, and the sum of the compositions thus determined was normalized to 100%.

TABLE 1. N_2 + Ar AT 112.00 K

Pressure† MN/m^2	atm	y_{N_2}	y_{Ar}	x_{N_2}	x_{Ar}	γ_{N_2}	γ_{Ar}	g^E joules/mole
0.8378	8.268	0.1706	0.8294	—	—			
0.8510	8.399	—	—	0.1107	0.8894	0.958	1.017	9.6
0.9669	9.543	0.3717	0.6283	—	—			
0.9773	9.645	—	—	0.2452	0.7551	1.058	1.014	22.6
1.0520	10.382	0.4808	0.5192	—	—			
1.0590	10.452	—	—	0.3385	0.6616	1.056	1.017	27.6
1.1975	11.818	0.6383	0.3617	—	—			
1.2122	11.963	—	—	0.5124	0.4876	1.021	1.059	35.6
1.2989	12.819	0.7327	0.2674	—	—			
1.3075	12.904	—	—	0.6243	0.3757	1.017	1.068	32.6
1.4012	13.829	0.8197	0.1804	—	—			
1.4060	13.876	—	—	0.7355	0.2644	1.014	1.075	27.2
1.5095	14.898	0.9048	0.0953	—	—			
1.5100	14.903	—	—	0.8529	0.1471	1.010	1.063	16.3

† 1 atm. = 1.01325 bars = 0.101325 MN/m^2

The adjustment of the sum of the compositions to 100% corrects for the small uncontrollable shifts in the sensitivity that occur in the analytical equipment.

The temperature in the system was measured and controlled with an accuracy of ± 0.05 K using a calibrated platinum resistance thermometer. The pressures were measured with a 0-20 bar bourdon tube gauge having an accuracy of ± 0.1% of the full scale reading. The chromatographic analyses are believed accurate to ± 1% of the measured values.

RESULTS

The experimental liquid and vapor phase compositions are presented in Tables 1, 2, and 3 and plotted for the

TABLE 2. $N_2 + CH_4$ AT 112.00 K

Pressure† MN/m²	atm	y_{N_2}	y_{CH_4}	x_{N_2}	x_{CH_4}	γ_{CH_4}	γ_{N_2}	g^E joules/mole
0.1862	1.838	0.4478	0.5522	—	—			
0.1838	1.814	—	—	0.0338	0.9662	0.982	2.069	6.7
0.2192	2.163	0.5311	0.4689	—	—			
0.2181	2.152	—	—	0.0545	0.9456	1.036	1.812	61.1
0.4027	3.974	0.7476	0.2523	—	—			
0.4013	3.961	—	—	0.1336	0.8665	1.009	1.822	81.6
0.4335	4.278	0.7660	0.2339	—	—			
0.4285	4.229	—	—	0.1505	0.8495	1.011	1.773	89.1
0.5559	5.486	0.8190	0.1810	—	—			
0.5485	5.413	—	—	0.2170	0.7830	1.043	1.639	130.5
0.6990	6.900	0.8626	0.1374	—	—			
0.6985	6.894	—	—	0.3082	0.6918	1.072	1.493	159.4
0.9229	9.108	0.9041	0.0959	—	—			
0.9120	9.001	—	—	0.4701	0.5299	1.182	1.282	191.2
0.9460	9.336	0.9086	0.0914	—	—			
0.9490	9.366	—	—	0.5172	0.4829	1.255	1.202	190.8
1.0852	10.710	0.9287	0.0713	—	—			
1.0847	10.705	—	—	0.6103	0.3896	1.312	1.156	181.1
1.1970	11.813	0.9433	0.0566	—	—			
1.1960	11.804	—	—	0.7068	0.2932	1.473	1.088	161.1
1.2960	12.791	0.9552	0.0448	—	—			
1.2957	12.788	—	—	0.7811	0.2189	1.609	1.055	136.0

† 1 atm. = 1.01325 bars = 0.101325 MN/m²

TABLE 3. $N_2 + Ar + CH_4$ AT 112.00 K

Pressure† MN/m²	atm	x_{Ar}	x_{N_2}	x_{CH_4}	y_{Ar}	y_{N_2}	y_{CH_4}	γ_{Ar}	γ_{N_2}	γ_{CH_4}	g^E joules/mole
*0.4500	4.441	—	—	—	0.8535	0.0060	0.1405	—	—	—	—
*0.4452	4.394	0.4946	0.0015	0.5040	—	—	—	1.089	1.438	1.059	67
0.5088	5.021	0.4841	0.0422	0.4738	0.7232	0.1531	0.1236	1.057	1.463	1.102	83
0.7060	6.968	0.4181	0.1876	0.3943	0.4548	0.4609	0.0843	1.023	1.319	1.168	114
0.9100	8.981	0.3382	0.3595	0.3024	0.2950	0.6455	0.0594	1.009	1.189	1.279	130
1.1100	10.955	0.2530	0.5380	0.2090	0.1900	0.7691	0.0408	1.010	1.103	1.428	121
1.3169	12.997	0.1585	0.7234	0.1181	0.1077	0.8672	0.0251	1.028	1.045	1.679	91
*0.6880	6.790	0.8837	0.0011	0.1151	0.9724	0.0021	0.0255	1.013	1.001	1.189	29
0.7460	7.362	0.8462	0.0574	0.0962	0.8522	0.1248	0.0229	0.992	1.221	1.356	32
0.9100	8.981	0.7031	0.2180	0.0789	0.6025	0.3802	0.0173	0.992	1.154	1.431	50
1.1148	11.002	0.5094	0.4341	0.0566	0.3797	0.6084	0.0119	1.007	1.085	1.546	59
1.3115	12.943	0.3119	0.6546	0.0334	0.2155	0.7765	0.0080	1.043	1.031	1.895	51
*0.1752	1.729	0.0944	0.0016	0.9039	0.4297	0.0172	0.5531	1.192	1.603	1.000	16
0.3055	3.015	0.0831	0.0612	0.8558	0.2276	0.4590	0.3134	1.216	1.896	0.997	49
*0.5613	5.540	0.6895	0.0017	0.3089	0.9165	0.0052	0.0782	1.026	1.345	1.159	59
0.9090	8.971	0.4959	0.3003	0.2038	0.4260	0.5313	0.0427	0.993	1.170	1.364	100
1.1165	11.019	0.3578	0.5024	0.1397	0.2663	0.7040	0.0296	1.006	1.086	1.556	98
1.3142	12.971	0.2251	0.6916	0.0834	0.1520	0.8299	0.0181	1.021	1.045	1.716	75
*0.3209	3.167	0.3081	0.0000	0.6919	0.7629	0.0002	0.2369	1.151	—	0.975	24
0.5162	5.094	0.2795	0.1144	0.6061	0.4218	0.4315	0.1466	1.082	1.541	1.034	85
0.7174	7.080	0.2387	0.2543	0.5071	0.2510	0.6552	0.0937	1.002	1.402	1.022	91
0.9095	8.976	0.1880	0.4156	0.3964	0.1644	0.7592	0.0764	1.011	1.209	1.253	159
1.1190	11.044	0.1372	0.5960	0.2667	0.0998	0.8508	0.0494	0.984	1.109	1.360	132
1.3140	12.968	0.0878	0.7595	0.1527	0.0384	0.9408	0.0208	0.661	1.078	1.080	30
*0.1542	1.522	—	—	—	0.3588	0.0040	0.6372	—	—	—	—
*0.1545	1.525	0.0690	0.0003	0.9307	—	—	—	1.206	1.761	0.993	6
*0.3135	3.094	—	—	—	0.7377	0.0029	0.2594	—	—	—	—
*0.3143	3.102	0.2945	0.0005	0.7049	—	—	—	1.141	1.504	1.027	54

* Plotted as binary $Ar + CH_4$.
† 1 atm = 1.01325 bars = 0.101325 MN/m².

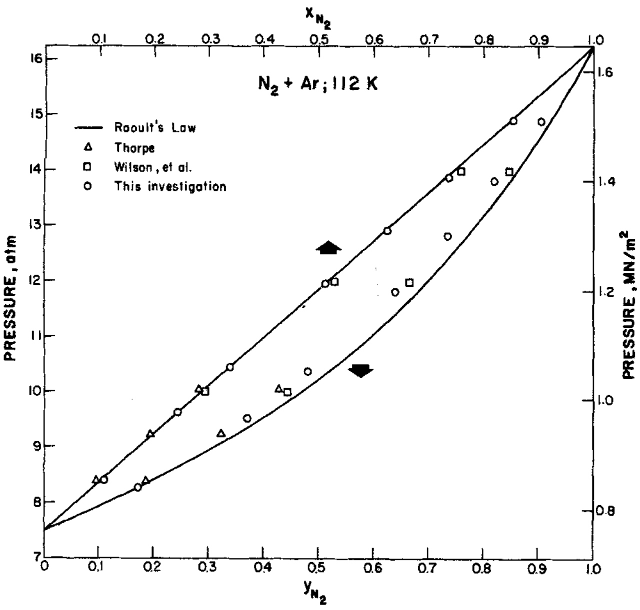

Fig. 1. Pressure-composition diagram for nitrogen + argon.

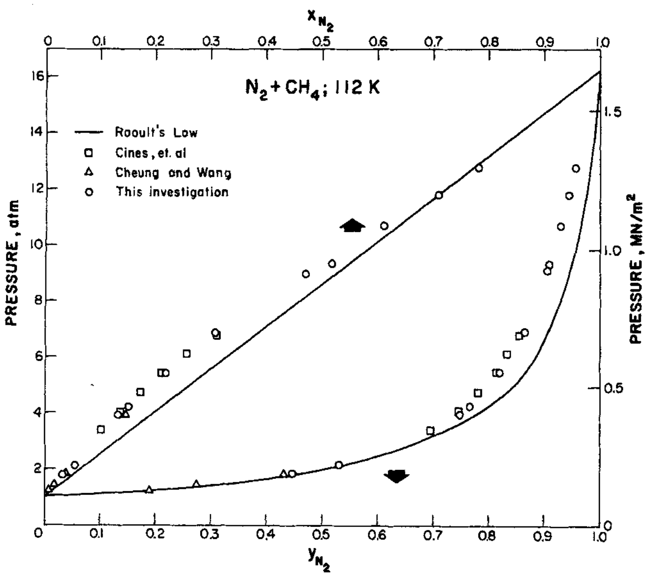

Fig. 2. Pressure-composition diagram for nitrogen + methane.

binary systems in Figures 1, 2, and 3. The small amount of nitrogen present in the argon-methane binary (Table 3) is not large enough to significantly affect its phase equilibrium properties.

It is highly desirable, whenever possible, to compare new experimental data with the results of earlier investigations. Unfortunately, no experimental measurements have been made at 112.00 K for either the nitrogen-methane or nitrogen-argon binary systems or for the ternary system, but some comparisons are possible by interpolating the data of other investigations at 112.00 K.

For the nitrogen-argon system, some of the data of Thorpe (1968) and Wilson et al. (1965) can be interpolated at 112.00 K. These interpolated data are compared with Raoult's law and the results of this research in Figure 1. The agreement between the various sets of measurements is within 2% in composition and, as would be expected, deviations from Raoult's law are small.

Figure 2 compares the results of this research for nitrogen-methane with interpolated values from Cines et al. (1953) and from Cheung and Wang (1964). Again, the agreement between the various data sets is within 2% in composition. The deviations from Raoult's law attain larger values in this system.

The argon-methane system of Figure 3 is the only binary in which no interpolation was necessary for a comparison. Duncan and Hiza (1972) measured liquid phase compositions at 112.00 K for this system, and their results are in excellent agreement with the work reported here. Once again, deviations from Raoult's law are very small. It should be noted that Duncan and Hiza (1972) employed the same equilibrium apparatus as used in this work, but they used a different chromatograph with an independent calibration for the analysis.

The data for the ternary system at pressures of approximately 9, 11, and 13 atm are shown in Figures 4, 5, and 6. Since the only other measurements on the nitrogen-argon-methane system were made at the triple point of methane (90.68 K) by Sprow and Prausnitz (1966), no intercomparison of data is possible.

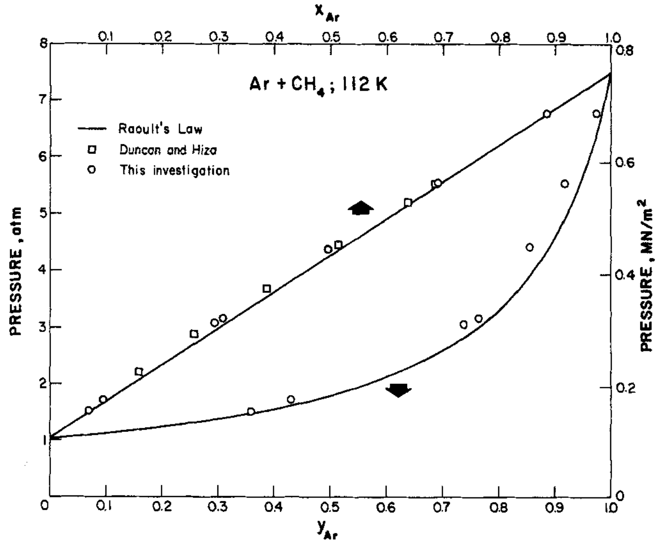

Fig. 3. Pressure-composition diagram for argon + methane.

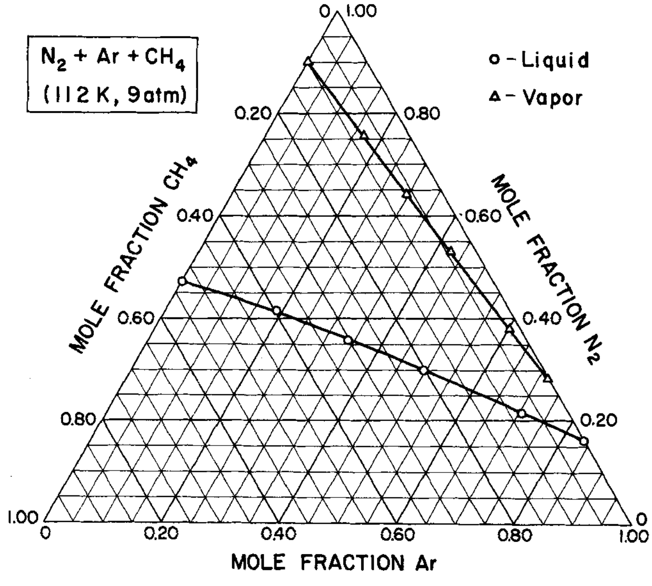

Fig. 4. Phase diagram for nitrogen + argon + methane at 9 atm (0.91 MN/m²).

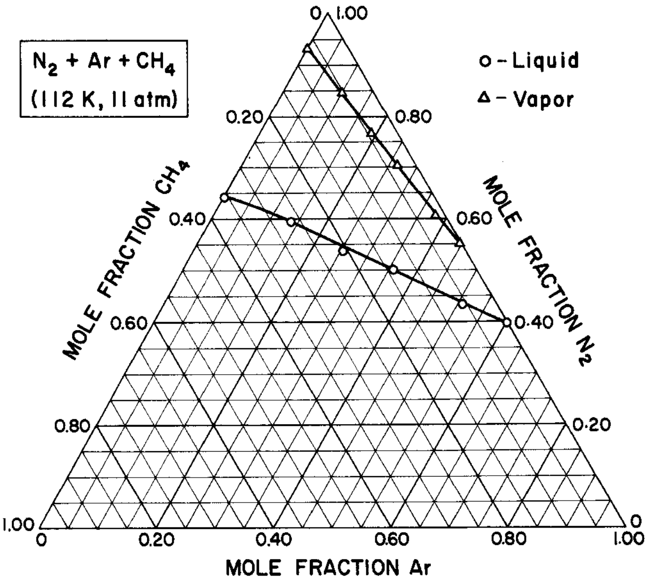

Fig. 5. Phase diagram for nitrogen + argon + methane at 11 atm ($1.11\ MN/m^2$).

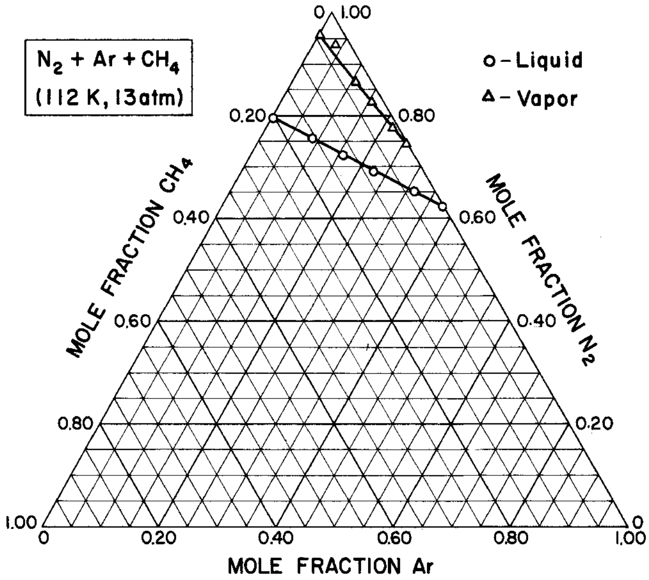

Fig. 6. Phase diagram for nitrogen + argon + methane at 13 atm ($1.32\ MN/m^2$).

CALCULATION OF EXCESS GIBBS FREE ENERGIES

Gas phase fugacity coefficients were calculated from the virial equation truncated after the second term

$$\ln\varphi_i = \frac{2}{v}\,(y_i B_{ii} + y_j B_{ij}) - \ln\left(\frac{Pv}{RT}\right) \qquad (1)$$

Virial coefficients were estimated from the correlation of Pitzer and Curl (1957), except in the case of pure methane. The second virial coefficient for methane at 112 K was taken to be $-323\ cm^3\ mole^{-1}$, as determined by Byrne, Jones, and Staveley (1968). Cross virial coefficients were obtained using the following mixing rules

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

$$v_{cij} = \frac{1}{8}\,(v_{ci}^{1/3} + v_{cj}^{1/3})^3, \qquad (3)$$

$$\omega_{ij} = \frac{1}{2}\,(\omega_i + \omega_j), \qquad (4)$$

with k_{ij} values of 0.02 for CH_4 + Ar, 0.03 for CH_4 + N_2 and 0.00 for Ar + N_2.

Third virial coefficient terms were estimated to make relatively minor contributions at the pressures employed in this study. They were not included in the calculations due to the large uncertainties in third virial coefficients for argon and methane at 112 K.

Activity coefficients for the liquid phase at the saturation pressures were extracted from the experimental data by use of the equation

$$\gamma_i = \frac{P y_i \varphi_i}{p_i^0 \varphi_i^0 x_i \exp\left[\dfrac{v_i^L (P - p_i^0)}{RT}\right]} \qquad (5)$$

The pure fluid vapor pressures and liquid molar volumes used in these calculations are shown in Table 4.

Excess Gibbs free energies were calculated for each data point from

$$g^E = RT\,\Sigma\, x_i \ln \gamma_i\,. \qquad (6)$$

Values for both the activity coefficients and excess Gibbs free energies are presented in Tables 1, 2, and 3. Figure 7 gives the composition dependence of g^E for all three binary systems studied.

The nitrogen-argon-methane data can be presented as lines of constant g^E on a ternary composition diagram (Figure 8). This diagram should be considered as only semi-quantitative in nature. The number of ternary data points was insufficient to construct a diagram with an accuracy within the average experimental uncertainty.

For argon-methane the equimolar mixture value of 67.4 joules $mole^{-1}$ determined in this work is in close

TABLE 4. VAPOR PRESSURES AND MOLAL VOLUMES

	p_i^0, atm	v_i^L, $cm^3/mole$	Reference
CH_4	1.031	38.1	Prydz and Goodwin (1972); Goodwin (1971)
Ar	7.493	32.6	Gosman et al. (1969)
N_2	16.233	46.3	Strobridge (1962)

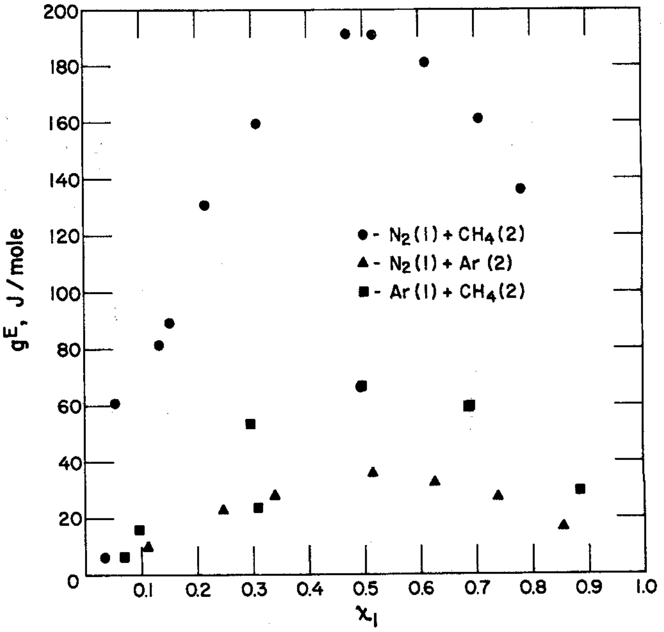

Fig. 7. Excess Gibbs free energy for the binary systems.

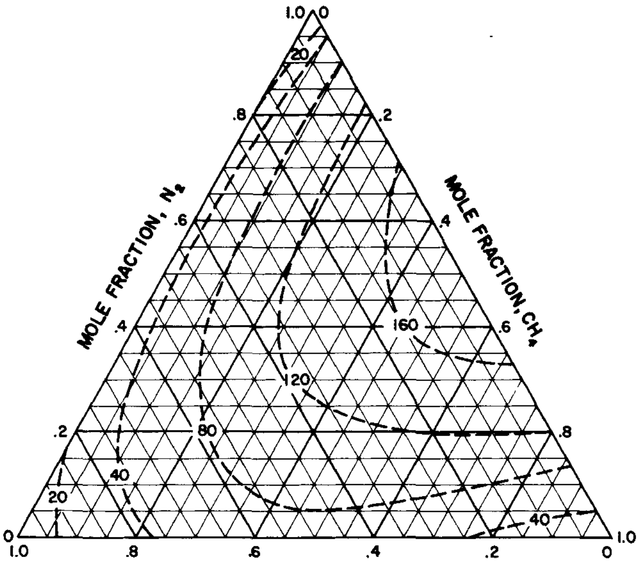

Fig. 8. Excess Gibbs free energy for the ternary system, J mole^{-1}.

agreement with the value 68.2 joules mole^{-1} measured by Duncan and Hiza (1972). Both values are well below the 75.8 joules mole^{-1} reported by Calado and Staveley (1972) at 115.77 K. They are also lower than the g^E of 76.2 joules mole^{-1} found by Mathot (1958) at 86.74 K and the g^E of 72.4 joules mole^{-1} found by Sprow and Prausnitz (1966) at 90.67 K. A decrease of g^E with temperature is consistent with the calorimetric h^E of 103.0 joules mole^{-1} measured by Lambert and Simon (1962) near 91 K.

There are no reported g^E values for equimolar nitrogen-methane near 112 K; however, the data of Cines et al. (1953), as analyzed by Prausnitz and co-workers (1967) yields a value of 182.5 joules mole^{-1} at 112K. The present value of 192.6 joules mole^{-1} is in good agreement. Both of these g^E values are considerably higher than the values reported near 91 K (131.9 joules mole^{-1} by Sprow and Prausnitz (1966), and 141.5 joules mole^{-1} by Fuks and Bellemans (1967)).

The 35.6 joules mole^{-1} found here for equimolar nitrogen-argon is only slightly above values between 32.7 and 34.3 joules mole^{-1} reported by several investigators (Thorpe, 1968; Sprow and Prausnitz, 1966; Pool et al., 1962) between 83.82 and 90 K. Again, there are no reported g^E values near 112 K.

Considering the sensitivity of the calculated excess Gibbs free energies to slight differences in measured phase compositions, the agreement between the present data and previous work is satisfactory. It appears that g^E is not a strong function of temperature below 112 K for the argon-methane and nitrogen-argon systems. Not only are the deviations from ideal solution behavior much larger in the case of nitrogen-methane, but the temperature dependence is more important as well.

NOTATION

B = second virial coefficient
g^E = molar excess Gibbs free energy
k = geometric mean rule deviation parameter
P = total pressure
p^0 = vapor pressure
R = gas constant
T = temperature
T_c = critical temperature
v = molar volume
v_c = critical volume
v^L = liquid molar volume
x = mole fraction liquid phase
y = mole fraction vapor phase
γ = liquid phase activity coefficient
φ = gas phase fugacity coefficient
φ^0 = pure fluid gas phase fugacity coefficient at saturation
ω = acentric factor

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Miscible Displacement with Combined Free and Forced Convection: Laminar Flow in a Vertical Tube

An approximate analysis is given for miscible displacement in vertical tubes when density differences between the displaced and displacing fluids give rise to buoyancy forces which affect the velocity distribution significantly. The results of this analysis agree with the available experimental data fairly uniformly over the range of parameters studied experimentally.

By analogy with studies of heat transfer in vertical tubes it is concluded that both cases studied, when a lighter fluid displaces a heavier fluid in upflow, or when the heavier fluid is below the lighter fluid, are potentially unstable flows because buoyancy forces can create points of inflection in the velocity profile; stagnation at the wall also is predicted for upflow when the lighter fluid is on the bottom initially, and this has been observed to induce a sudden transition to turbulence in heat transfer systems.

Buoyancy forces reduce the extent of dispersion by flattening the velocity profile when the heavier fluid is on the bottom in upflow. The velocity profile is elongated and the dispersion coefficient is increased when the bottom fluid is lighter than the one it displaces in upflow.

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SCOPE

The concept of dispersion as introduced by G. I. Taylor (1953) has been used to model a wide variety of systems of practical interest such as tubular reactors, heat exchangers, chromatographs, displacement of fluids from porous media, distribution of thermal and material pollutants, etc. An objective of the present work is to describe how natural convection can influence the extent of dispersion in laminar flow in vertical tubes. Another objective is to determine whether natural convection effects in such flow can cause the kind of instabilities observed experimentally by Scheele and Hanratty (1962) when heat transfer in vertical flow causes significant density differences across the flow.

Consider two fluids which are at rest in vertical capillary tubes that are separated by a very thin partition. At time zero, the partition is removed and the fluids are instantaneously set in upward motion by a device which creates a constant volumetric flow rate. The bottom fluid may be heavier or lighter than the one it displaces. As the miscible displacement continues in time, a mixing zone develops in which the fluid density varies from point to point in the flow field due to concentration changes. This creates a coupling between the concentration and flow fields which makes a solution for either very difficult because the problem is both time dependent and nonlinear. It will be shown that the dispersion model provides an approximate method of solution for this complex problem of

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