Vapor–Liquid Equilibrium in Binary and Ternary Mixtures of Nitrogen, Argon, and Methane

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Vapor–liquid equilibrium values are reported for binary and ternary mixtures of nitrogen, argon, and methane at 122.89 K. The experimental results are successfully correlated with the Peng–Robinson equation of state.

Introduction

Vapor–liquid equilibrium (VLE) values are required in technological applications and are fundamental to separation operations. In this work we report VLE data on the three binary mixtures and the ternary system of nitrogen, argon, and methane at 122.89 K. The experimental VLE values on the binary mixtures were correlated with the Peng–Robinson equation of state, and used to predict the VLE values for the binary system. The predicted values were then compared with the experimental results. Calculated pressure and vapor composition from the equation are compared with the ternary mixture data.

Knapp (*1*) gives references to VLE measurements on the three binary mixtures, which contain seven sets of N_2 + Ar and N_2 + CH_4 each, and five sets of Ar + CH_4. Although the temperature range of the data reported above is rather broad, and only one set of data for Ar + CH_4 is at 123 K, Sprow and Prausnity (*2*) and Gravelle and Lu (*3*) reported VLE data on ternary mixtures of N_2, Ar, and CH_4 at 90.67 and 123.4 K, respectively. Hence, this work may be considered as a supplement to Gravelle's work.

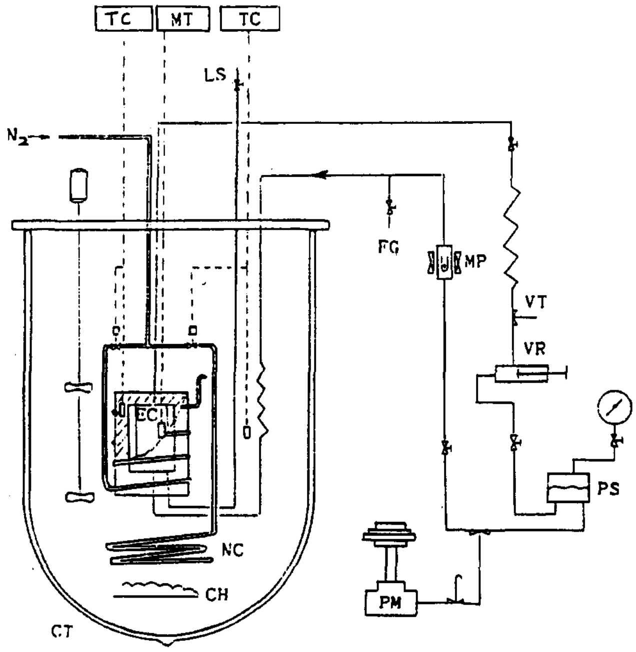

Figure 1. Schematic diagram of the experimental apparatus: (CH) control heater, (NC) nitrogen vaporization coil, (CT) cryostat, (PM) plug-type pressure meter, (EC) equilibrium cell, (PS) pressure sensor, (FG) feed gas, (TC) temperature controller, (LS) liquid sampling tube, (VR) volume regulator, (MP) magnetic pump, (VT) vapor sampling tube, (MT) measuring temperature meter.

Table I. Experimental Values and Calculated Deviations for Nitrogen (1) + Argon (2) at T = 122.89 K (k_{12} = –0.010 60)

experimental value			calculated deviation	
P/MPa	x_1	y_1	100[P(calc) – P]/P	y_1(calc) – y_1
1.484	0.0506	0.0851	1.16	–0.0007
1.600	0.1248	0.1959	0.51	–0.0016
1.728	0.2068	0.2975	–0.18	0.0032
1.760	0.2410	0.3376	0.75	0.0037
1.865	0.3117	0.4196	0.38	0.0000
2.006	0.3895	0.4945	-1.21	0.0040
2.008	0.4079	0.5222	0.00	–0.0059
2.156	0.5144	0.6237	0.09	–0.0104
2.286	0.5994	0.7118	–0.27	–0.0266
2.453	0.7092	0.7979	–0.50	–0.0248
2.587	0.8067	0.8530	0.08	–0.0041
2.734	0.8974	0.9214	–0.04	–0.0027
2.839	0.9705	0.9765	0.57	–0.0004
average absolute deviation			0.44	0.0068

Table II. Experimental Values and Calculated Deviations for Nitrogen (1) + Methane (2) at T = 122.89 K (k_{12} = 0.034 99)

experimental value			calculated deviation	
P/MPa	x_1	y_1	100[P(calc) – P]/P	y_1(calc) – y_1
0.422	0.0511	0.4339	–0.24	0.0007
0.676	0.1270	0.6524	–0.90	–0.0055
0.867	0.1923	0.7306	–0.23	–0.0017
1.027	0.2516	0.7768	0.10	–0.0023
1.311	0.3748	0.8345	1.70	–0.0027
1.617	0.4975	0.8730	–0.81	–0.0056
1.936	0.6760	0.9130	2.35	–0.0064
1.938	0.6501	0.9030	–0.63	–0.0018
2.266	0.7904	0.9369	–0.98	–0.0055
2.580	0.9121	0.9656	0.00	–0.0015
average absolute deviation			0.80	0.0034

Table III. Experimental Values and Calculated Deviations for Argon (1) + Methane (2) at 122.89 K (k_{12} = 0..026 33)

experimental value			calculated deviation	
P/MPa	x_1	y_1	100[P(calc) – P]/P	y_1(calc) – y_1
0.335	0.0729	0.3299	–0.60	–0.0090
0.385	0.1142	0.4238	0.53	0.0070
0.503	0.2071	0.5976	0.00	–0.0052
0.592	0.2775	0.6777	–0.68	–0.0056
0.708	0.3799	0.7554	–0.14	–0.0012
0.721	0.4025	0.7619	1.69	0.0069
0.838	0.4924	0.8209	–0.36	–0.0023
0.928	0.5808	0.8600	0.66	–0.0016
1.038	0.6732	0.8932	–0.10	0.0008
1.132	0.7635	0.9267	0.63	–0.0017
1.263	0.8813	0.9634	1.20	–0.0007
1.342	0.9468	0.9843	1.28	–0.0011
average absolute deviation			0.66	0.0036

Experimental Section

A forced-recirculation apparatus is employed in this work. A schematic diagram of the apparatus is shown in Figure 1. It consists of a visual equilibrium cell, an electromagnetic

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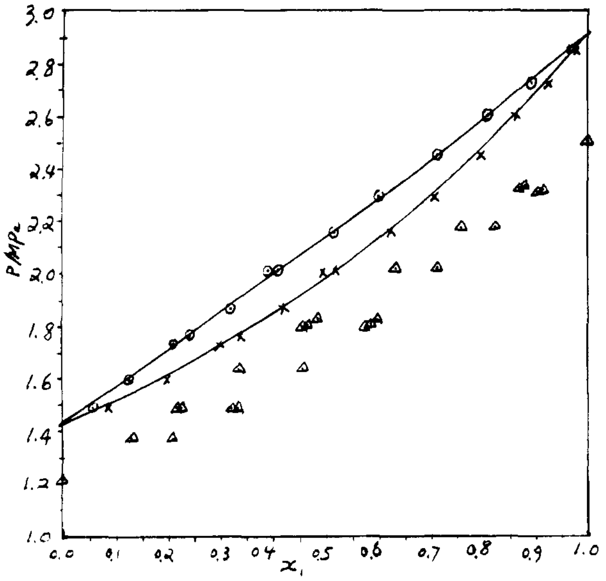

Figure 2. Pressure P as a function of the liquid (⊙) and vapor (×) mole fractions for N_2 (1) + Ar (2) at 122.89 K: (—) calculated from the Peng-Robinson equation, (△) liquid and vapor mole fractions from Narinskii (*5*) at 119.97–120.00 K.

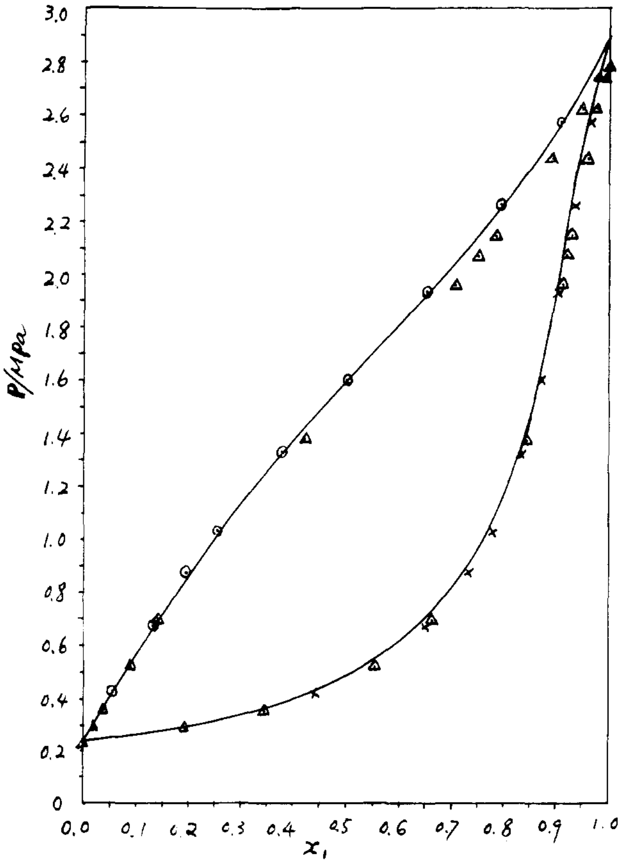

Figure 3. Pressure P as a function of the liquid (⊙) and vapor (×) mole fractions for N_2 (1) + CH_4 (2) at 122.89 K: (—) calculated from the Peng-Robinson equation, (△) liquid and vapor mole fractions from Stryjek et al. (*6*) at 122.04 K.

pump, nitrogen vaporization coils, a cryostat and its temperature control system, sampling facilities, and pressure measuring devices. In this manner, the bath temperature is regulated to within 0.2 K of the desired value, and the cell temperature is controllable to ±0.05 K.

An electromagnetic pump is employed for recirculating the vapor through the liquid in the equilibrium cell in a closed system. The design is similar to that reported by Chang (*4*).

Table IV. Experimental Values and Calculated Deviations for N_2 (1) + Ar(2) + CH_4 (3) at T = 122.89 K

experimental value					calculated deviation		
P/MPa	x_1	x_2	y_1	y_2	100[P(calc) − P]/P	y_1(calc) − y_1	y_2(calc) − y_2
0.700	0.0751	0.1613	0.3761	0.3360	−1.74	−0.0197	0.0029
0.992	0.2015	0.1081	0.6267	0.1625	0.31	0.0012	−0.0043
1.269	0.3147	0.0990	0.7206	0.1167	0.32	0.0018	−0.0024
1.289	0.3266	0.0977	0.7257	0.1120	0.86	0.0057	−0.0015
1.581	0.4178	0.1850	0.7185	0.1778	0.00	−0.0020	−0.0029
1.880	0.5599	0.1513	0.7908	0.1282	−0.70	−0.0015	−0.0002
2.091	0.6408	0.1726	0.8058	0.1396	−0.68	−0.0024	−0.0014
2.235	0.7083	0.1446	0.8424	0.1129	−0.91	−0.0047	0.0006
2.441	0.8118	0.1001	0.8939	0.0761	−0.12	−0.0047	0.0015
average absolute deviation					0.63	0.0050	0.0020

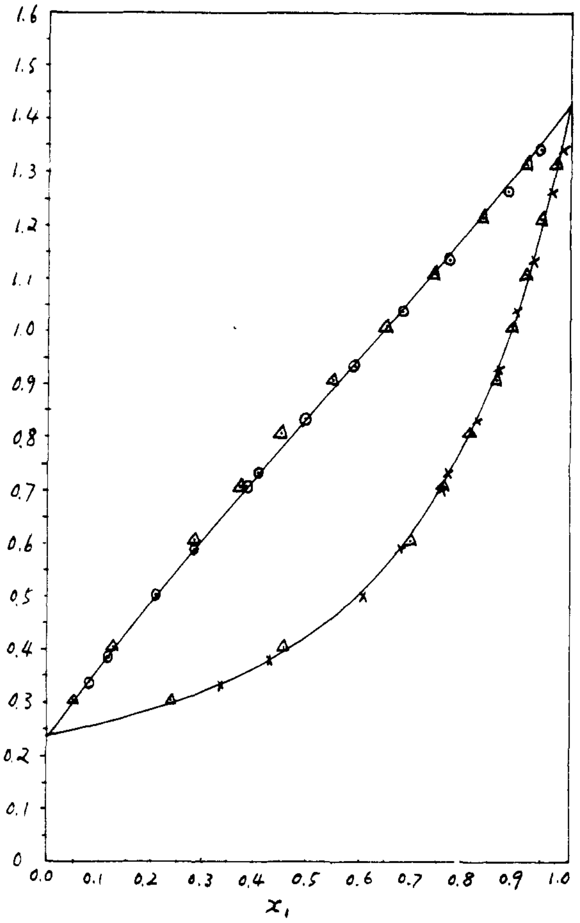

Figure 4. Pressure P as a function of the liquid (⊙) and vapor (×) mole fractions for Ar (1) + CH_4 (2) at 122.98 K: (—) calculated from the Peng-Robinson equation, (△) liquid and vapor mole fractions from Shatkaya and Zhiruova (*7*) at 123.05 K.

After reaching thermal equilibrium in the cell, the vapor is recirculated within the recirculation loop, which consists of the electromagnetic pump and the equilibrium cell described above, a volume regulator, a sampling loop, and a cooling coil. When the vapor passes through the volume regulator and the sampling loop, it is heated to room temperature, but it is cooled to the bath temperature again by passing through the cooling coil inside the cryostat before returning to the equilibrium cell.

The equilibrium temperature is measured by means of a thermocouple and a potentiometer. The pressure of the system is measured by means of a pressure gauge with an accuracy of ±0.16%; the range of the gauge is 0–6 MPa.

Analyses of samples were made with a Shimadzu Model GC-9a gas chromatograph. Research grade gases supplied by the Acadomia Metrology Sinica were used without any further purification. Minimum purities of these gases are as follows: nitrogen, 99.999 mol %; argon, 99.999 mol %; methane, 99.99 mol %.

Results

All equilibrium measurements are made at 122.89 K, and the results are presented in Tables I–IV. The binary pressure–composition results are shown in Figures 2–4.

The VLE data are correlated with the Peng–Robinson (PR) (*5*) equation. Tables I–III also present the three binary interaction parameters k_{ij} of the PR equation which were obtained by applying the method of least squares through optimization on the measured binary VLE data, and the calculated deviations of the correlation from the experimental data. By using the PR equation with these k_{ij} parameters, the vapor composition and the pressure for the ternary mixtures are predicted at the experimental temperature and liquid composition. The small deviations of the predicted values from experimental data shown in Table IV reflect the consistency between the measured binary data and the measured ternary results. The solid lines in Figures 2–4 show the calculated results by the PR equation.

Acknowledgment

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