Vapor-Liquid Equilibria in Methane–Hydrocarbon Systems

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Experiment determinations of the compositions of coexisting liquid and vapor phases were made for these systems: methane–*n*-pentane, methane–isopentane, methane–neopentane, methane–isopentane–*n*-pentane, and methane–neopentane–*n*-pentane. The pressures and temperatures covered the ranges of 300–500 psia to critical pressures of about 2500 psia and from 160° to 280° F. Experiments were made in a fixed-volume stirred cell. Samples of the phases were analyzed by chromatograph. A correlation employing the B-W-R equation of state to predict vapor phase fugacity coefficients, Hildebrand's regular solution theory, and a modified form of the Chao-Seader expression to calculate the liquid phase fugacity coefficient is presented. Comparison of observed with calculated *K* values indicates an average absolute percent deviation within 10%.

Two methods for predicting equilibrium vaporization ratios which have been widely used by the design engineer are the NGPA Equilibrium Ratio value charts (*11*) and the Kellogg charts (*10*). Both methods have been used with a varying degree of success; however, each method is restricted to mixtures of paraffins, olefins, or combinations thereof.

Since the development of these correlations, effort has been directed toward the formulation of generalized correlations. A primary approach has been to relate the phase behavior of mixtures to experimentally determined properties of pure components and binary systems which comprise the multicomponent mixture.

A number of experimental investigations have been reported for several binary methane–hydrocarbon mixtures, but data for the methane–pentane systems are incomplete. Methane, *n*-pentane, and isopentane are important naturally occurring compounds in hydrocarbon mixtures. Neopentane, because of its molecular symmetry is of theoretical interest to the scientist whose ultimate goal is to correlate macroscopic thermodynamic functions with microscopic properties or intermolecular forces.

Boomer *et al.* (*4*) have determined compositions and densities of the two-phase region at 25° C and pressures ranging from 35 to 135 atm for a system containing impure methane and a mixture of isopentane and *n*-pentane.

Sage *et al.* (*14*) have experimentally determined the specific volumes of six mixtures of methane and *n*-pentane for seven different temperatures between 100° and 460° F at pressures up to 5000 psia. They have, in addition, determined the compositions of the vapor and liquid phases throughout the two-phase region for several temperatures between 100° and 340° F and pressures from the vapor pressure of *n*-pentane to the critical pressure of the mixture.

Experimental data for the methane–isopentane binary system have been reported by Amick *et al.* (*1*). They report coexisting phase compositions for temperatures ranging from 160° to 340° F and pressures from 400 to 1000 psia, but with considerable scatter in the data.

No experimental information has been found on the methane–neopentane system. Experimental work related to the pure compound, neopentane (2,2-dimethyl propane) has been reported by Beattie *et al.* (*2*), and more recently by Heichelheim *et al.* (*8*).

The purpose of this paper is to report equilibrium vaporization data near the critical region for the methane–isopentane binary system and to report the compositions of both the vapor and liquid phases throughout the two-phase region for the methane–neopentane binary system. Equilibrium ratio data for each component in the methane–isopentane–*n*-pentane ternary system and the methane–neopentane–*n*-pentane ternary system are investigated to extend our knowledge of more complex systems of methane in mixtures of pentane isomers.

Finally, these experimental data are used to determine the reliability of a generalized correlation for predicting vapor-liquid equilibrium behavior at pressures up to the critical.

EQUIPMENT

The apparatus used in this study is similar to that described by Brainard (*5*), but with modifications in the sampling equipment and procedures to accommodate the methane–pentane systems. Figure 1 presents a simplified flow diagram of the apparatus used in this research. Temperature of the constant-temperature bath surrounding the equilibrium cell and both pressure locks is determined with a calibrated mercury in a glass thermometer. It is believed that the overall uncertainty in temperature is ±0.5° F. The equilibrium pressure is measured with a calibrated Heise pressure gauge. It is believed that the equilibrium pressures are known to within ±3 psia.

Sampling System. Vapor and liquid samples are removed from the equilibrium cell and contained by means of pressure locks. Each lock is made up of two valves (valves 5, 6, 7, 8 in Figure 1) and a 6-in. nipple, ¼-in. od by 0.083-in. id Type 316 stainless steel. Sixteen-gauge Chromel A wire was inserted in the 6-in. nipple to minimize the dead volume. The valves were manufactured by Autoclave Engineers Inc. (Catalogue No. 30VM-4071) with a stellite stem. The pressure locks are totally immersed in the constant-temperature bath fluid. A Toepler pump is used to transfer the vapor and liquid samples to the collection section. The glass collection section consists of expansion flasks, a ground glass joint thermometer, and a closed-end mercury manometer.

Composition Determination. A Perkin-Elmer Vapor Fractometer (Model No. 154-D) equipped with a thermal conductivity cell as the sensing device is used for the separation and analysis of the vapor and liquid samples. The column

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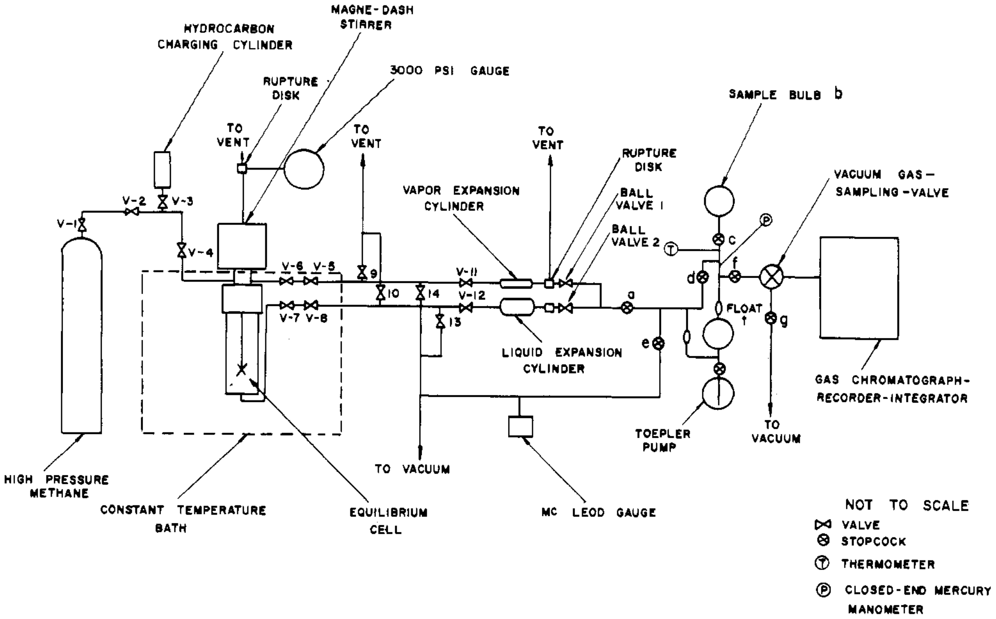

Figure 1. Schematic diagram of experimental equipment

used in all aspects of this work is 14 ft of ¼-in. tubing packed with squalane (20%) on a Chemisorb support.

The gas sample is introduced into the Fractometer by means of a Perkin-Elmer precision gas sampling valve (Catalogue No. 008-0659).

A Perkin-Elmer printing integrator (Model No. 194-B) was used to integrate the area under the resultant chromatographic curves. After two successive samples indicated that equilibrium was reached, a minimum of two samples was taken and at least two analyses were made for each sample. In all cases duplicate samples differed by less than 0.75%.

The chromatographic technique was calibrated against 12 different blends of reference standards which encompassed expected sample compositions. A typical result is:

Actual composition of blend, mole %		G.c. analyses, mole %	
Methane	Neopentane	Methane	Neopentane
66.7	33.3	66.8	33.2
		66.6	33.4
		66.7	33.3
		66.8	33.2
		66.8	33.2
		Av 66.8	33.2

MATERIALS

Research-grade pentanes were donated by the Phillips Petroleum Co. The purities of the components as verified by chromatographic analysis are: methane, 99.3% (0.6% nitrogen, 0.1% ethane); *i*-pentane, 99.9%; *n*-pentane, 99.9%; and neopentane, 99.8%.

RESULTS

The experimental data obtained in this research are presented in Tables I and II. Some of the experimental data are presented in Figures 2 through 6. The experimental phase equilibrium data for the methane–*n*-pentane system are compared with those of Sage *et al.* in Figure 2. The agreement between that and this work is quite good.

Figure 3 shows the pressure-composition data at a temperature of 160° F, for the methane-isopentane binary system. Included in Figure 3 are the experimental data reported by Amick *et al.* (*1*).

Figure 4 gives the ternary composition diagram for three pressures. It shows the decrease of the two-phase region with increased pressure. The data for the methane–*n*-pentane binary system in Figure 4 are those of Sage *et al.* (*14*).

Figure 5 is the pressure-composition curve for one isotherm at which experimental data were obtained for the methane-neopentane binary system.

Finally, Figure 6 presents a ternary composition diagram of the methane, neopentane, and *n*-pentane system. It demonstrates the shrinkage of the two-phase region with increased pressure and the relative independence of the binary components with pressure on a methane-free basis for the liquid phase. Methane–*n*-pentane data illustrated in Figure 6 are those of Sage *et al.* (*14*).

Although the reproducibility of the measurements, in particular the determination of composition, indicates adequate technique in analysis of vapor and liquid phase samples, consideration must also be given to the uncertainty of the experimental technique–*i.e.*, certainty of equilibration and the withdrawal of representative samples from the cell. By making several runs at the same temperature and essentially the same pressure for the methane–*n*-pentane binary system and the methane–isopentane–*n*-pentane ternary system (Tables I and II) the reproducibility of the system can be determined. These results indicate a reproducibility within less than 1.0%.

ANALYTICAL CORRELATION PROCEDURE

The ultimate goal of phase equilibrium thermodynamics is to develop reliable and accurate methods to predict vapor-liquid phase behavior of complex mixtures. However, such methods can only be deemed reliable when subjected to direct comparison with experimental data. The correlation procedure adopted for the calculation of the equilibrium vaporization ratio, *K*, for the components investigated in this research is a modified form of the Chao-Seader correlation (*7*).

Table I. Experimental Data Binary Systems

Pressure, psia	Temp, °F	Mole fraction methane	
		Vapor	Liquid
	System: Methane-*n*-Pentane		
1001	220	0.805	0.247
1005	220	0.814	0.248
1023	220	0.806	0.253
1231	220	0.810	0.306
1260	220	0.816	0.310
1265	220	0.812	0.324
1501	220	0.808	0.382
1502	220	0.808	0.380
1777	220	0.788	0.456
1999	220	0.740	0.532
	System: Methane–Isopentane		
502	160	0.841	0.142
755	160	0.872	0.218
1001	160	0.885	0.283
1253	160	0.879	0.351
1505	160	0.869	0.418
1759	160	0.853	0.489
1992	160	0.821	0.545
2191	160	0.741	0.633
499	220	0.710	0.118
759	220	0.765	0.192
1001	220	0.741	0.262
1256	220	0.788	0.331
1503	220	0.774	0.396
1721	220	0.746	0.454
1899	220	0.686	0.566
	System: Methane–Isopentane (*Continued*)		
511	280	0.520	0.092
759	280	0.603	0.161
1001	280	0.636	0.231
1267	280	0.651	0.315
1277	280	0.643	0.330
1517	280	0.581	0.488
	System: Methane–Neopentane		
310	160	0.667	0.085
511	160	0.761	0.153
763	160	0.797	0.232
1005	160	0.819	0.312
1273	160	0.813	0.391
1281	160	0.813	0.398
1521	160	0.784	0.482
1709	160	0.727	0.560
1748	160	0.685	0.603
308	220	0.395	0.051
503	220	0.563	0.117
748	220	0.639	0.197
1008	220	0.670	0.282
1251	220	0.654	0.377
1434	220	0.585	0.471
506	280	0.280	0.068
755	280	0.407	0.163
1004	280	0.416	0.281

Table II. Experimental Data Ternary Systems

System: Methane–Neopentane–*n*-Pentane

Pressure, psia	Temp, °F	Compositions, mole fraction					
		Vapor			Liquid		
		C_1	neo-C_5	*n*-C_5	C_1	neo-C_5	*n*-C_5
503	160	0.8451	0.0577	0.0972	0.1407	0.2165	0.6429
751	160	0.8714	0.0459	0.0827	0.2058	0.1997	0.5945
1006	160	0.8787	0.0406	0.0807	0.2781	0.1760	0.5459
1251	160	0.8778	0.0404	0.0818	0.3375	0.1641	0.4985
1505	160	0.8699	0.0410	0.0891	0.3998	0.1482	0.4520
1759	160	0.8546	0.0429	0.1025	0.4607	0.1314	0.4079
2013	160	0.8052	0.0536	0.1413	0.5500	0.1112	0.3388
2120	160	0.7753	0.0591	0.1655	0.6019	0.0976	0.3005
			System: Methane–Isopentane–*n*-Pentane				
504	160	0.8712	0.0395	0.0892	0.1386	0.2227	0.6387
755	160	0.8939	0.0305	0.0755	0.2114	0.2058	0.5828
1003	160	0.8971	0.0296	0.0733	0.2738	0.1888	0.5374
1493	160	0.8890	0.0307	0.0803	0.4057	0.1536	0.4408
1975	160	0.8488	0.0405	0.1107	0.5038	0.1290	0.3672
1995	160	0.8419	0.0422	0.1159	0.5210	0.1229	0.3561
2268	160	0.7585	0.0632	0.1783	0.5934	0.1039	0.3027
			System: Methane–Isopentane–*n*-Pentane				
507	220	0.7445	0.0701	0.1854	0.1202	0.2198	0.6599
753	220	0.7878	0.0577	0.1545	0.1867	0.2047	0.6086
995	220	0.8096	0.0510	0.1394	0.2513	0.1876	0.5611
1263	220	0.8100	0.0509	0.1391	0.3191	0.1716	0.5093
1519	220	0.8006	0.0527	0.1466	0.3887	0.1540	0.4573
1765	220	0.7706	0.0613	0.1681	0.4537	0.1391	0.4072
2047	220	0.7470	0.0652	0.1878	0.5552	0.1117	0.3331
539	280	0.5633	0.1162	0.3205	0.0998	0.2196	0.6806
541	280	0.5682	0.1197	0.3120	0.1030	0.2321	0.6649
757	280	0.6292	0.1020	0.2687	0.1642	0.2143	0.6215
760	280	0.6303	0.0967	0.2730	0.1622	0.2017	0.6361
1001	280	0.6623	0.0866	0.2510	0.2311	0.1866	0.5822
1031	280	0.6646	0.0910	0.2444	0.2417	0.1956	0.5628
1253	280	0.6738	0.0809	0.2452	0.3064	0.1644	0.5291
1255	280	0.6745	0.0870	0.2385	0.3042	0.1797	0.5161
1565	280	0.6156	0.0994	0.2850	0.4533	0.1384	0.4083

Chao and Seader express K in terms of rigorously defined thermodynamic quantities.

$$K_i \equiv \frac{y_i}{x_i} \equiv \frac{\nu_i^0\gamma_i}{\phi_i} \tag{1}$$

where ν_i^0 is the liquid-phase fugacity coefficient and is defined as f_i^0/P, γ_i is the liquid phase activity coefficient, and ϕ_i is the vapor phase fugacity coefficient.

Equation of State. A good equation of state is necessary in deriving thermodynamic functions to represent experimental vapor-liquid equilibrium data. For this work the equation presented by Benedict *et al.* (3) was chosen to

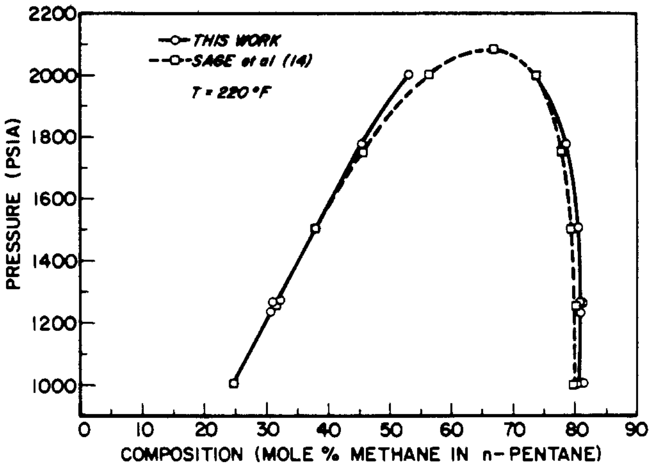

Figure 2. Pressure composition phase diagram for methane–*n*-pentane system

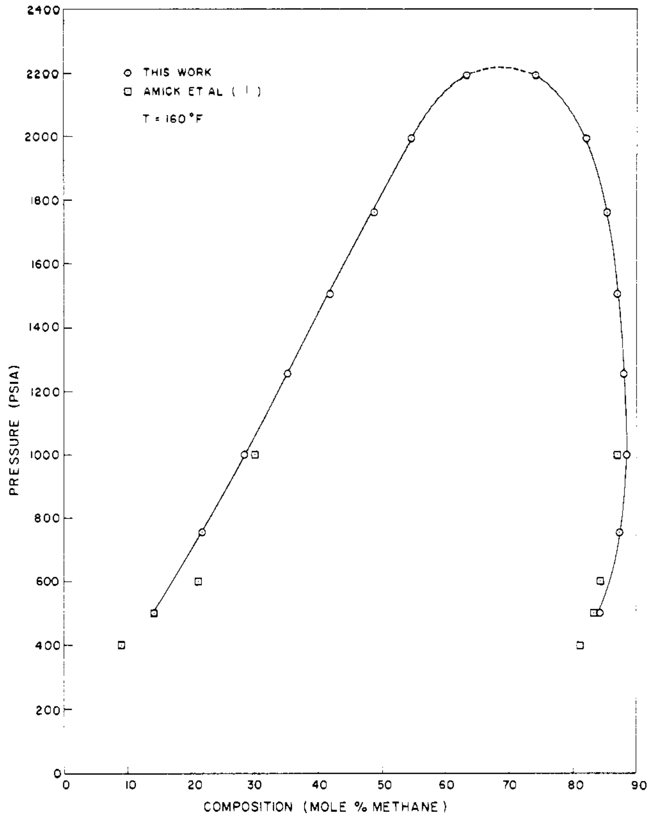

Figure 3. Pressure composition phase diagram for methane–isopentane system

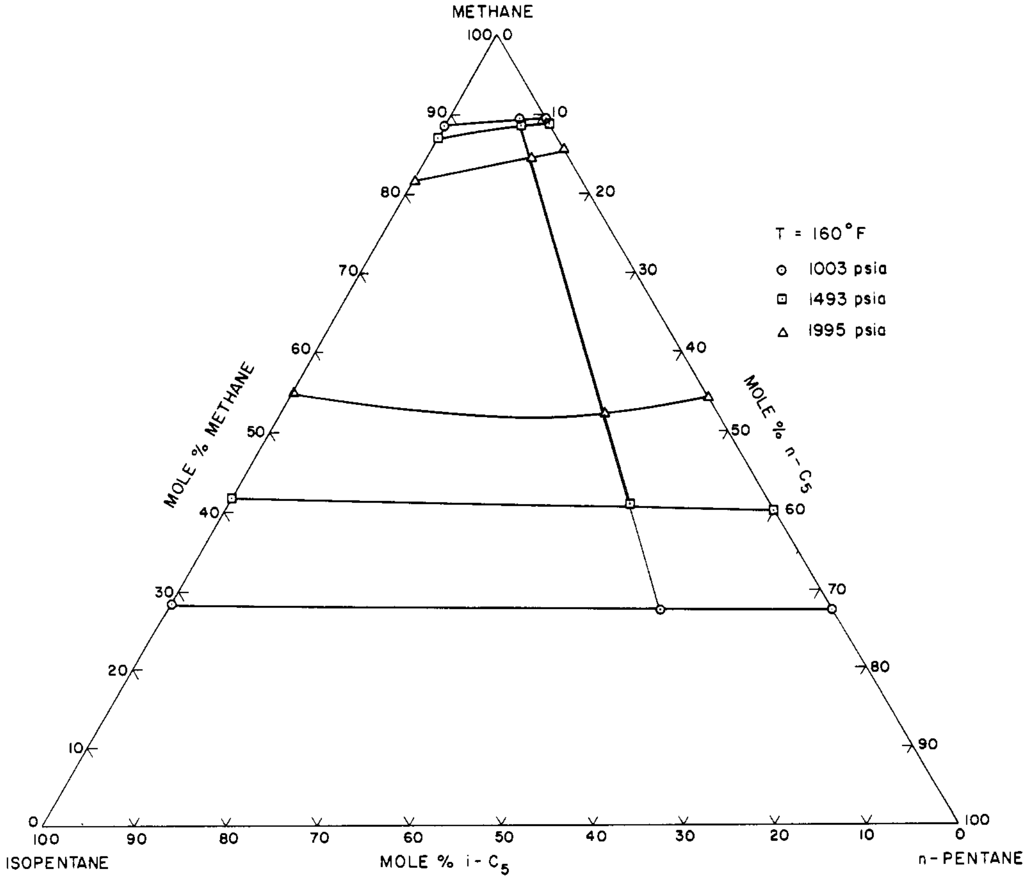

Figure 4. Ternary phase diagram for methane isopentane–*n*-pentane system

evaluate the specific volume of the vapor phase, and the vapor phase fugacity coefficient, ϕ_i. There are two reasons for selecting this equation as opposed to other equations of state. First the B-W-R equation can be used to predict thermodynamic properties in the critical region. Second, constants used to describe the behavior of the vapor-phase region have been determined for all the pure components studied in this research.

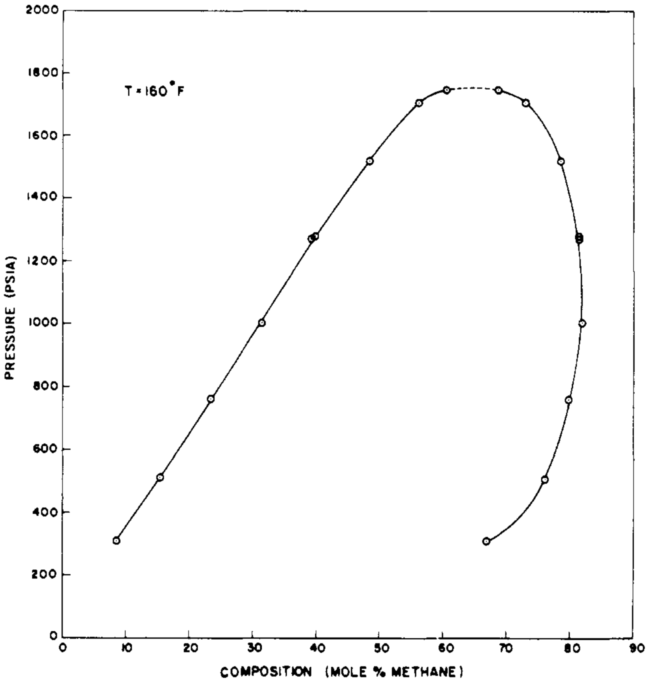

Figure 5. Pressure composition phase diagram for methane–neopentane system

Vapor Phase Fugacity Coefficient. The relationship between the fugacity coefficient and pressure, temperature, and volume is given by Equation 2.

$$RT \ln \phi_i = \int_{\underline{V}}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,\underline{V},n_j} - \frac{RT}{\underline{V}} \right] d\underline{V} - \ln z \tag{2}$$

Substitution of the B-W-R equation into Equation 2 yields an expression for the vapor phase fugacity coefficient, ϕ_i. In the case of this research, the constants used for the B-W-R equation of state were obtained from the literature. The constants for methane, isopentane, and *n*-pentane were reported by Benedict *et al.* (*3*) and for neopentane by Canjar *et al.* (*6*).

Activity Coefficient. Prausnitz *et al.* (*13*) have recommended that the Hildebrand-Scott (*9*) regular solution theory correlation for activity coefficient be used in nonpolar mixtures. For multicomponent systems, Hildebrand and Scott express activity coefficients in regular solutions by the following relations:

$$RT \ln \gamma_i = \underline{V}_i^L (\delta_i - \overline{\delta})^2 \tag{3}$$

The solubility parameter designated by the symbol δ_i is defined as

$$\delta_i = (\Delta E^{\underline{V}} / \underline{V}_i)^{1/2} \tag{4}$$

where ΔE at ordinary temperatures can be identified with the energy of vaporization or the energy required to vaporize the liquid to infinite volume, and V_i is the molal volume of constituent *i*. The symbol $\overline{\delta}$ designates the volume average value of the solubility parameter for the solution and is given mathematically as:

$$\overline{\delta} = \sum_i x_i \underline{V}_i \delta_i / \sum_i x_i \underline{V}_i \tag{5}$$

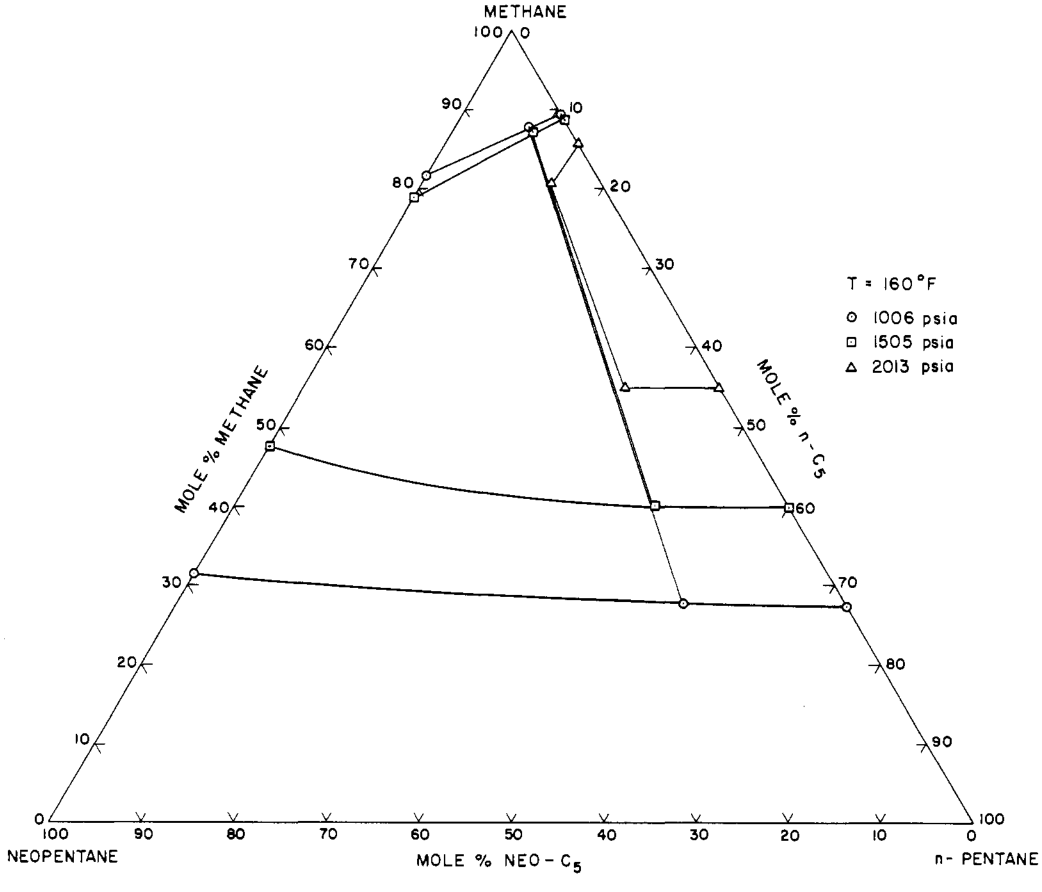

Figure 6. Ternary phase diagram for methane–neopentane-*n*-pentane system

The values of solubility parameters used in this work are presented by Chao *et al.* (*7*) for methane and *n*-pentane and by Hildebrand *et al.* (*9*) for neopentane and isopentane. Liquid molal volumes are also given by Chao *et al.* (*7*).

Fugacity Coefficient of Pure Liquid Component. The analytical expression given by Chao and Seader for the liquid-phase coefficient is:

$$\log \nu^{0} = \log \nu^{0} + \omega \log \nu^{1} \qquad (6)$$

The term $\nu^{(0)}$ is the fugacity coefficient of simple fluids characterized by a zero acentric factor. The term ν^{1} is a correction term and accounts for the departure of the properties of real fluids from those of simple fluids, and ω is defined as the acentric factor (*12*). Chao and Seader have expressed the quantities $\nu^{(0)}$ and $\nu^{(1)}$ as functions of reduced temperature and pressure. These terms have the following functional forms.

$$\log \nu^{0} = A_0 + A_1/T_r + A_2T_r + A_3T_r^2 + A_4T_r^3 + (A_5 + A_6T_r + A_7T_r^2)P_r + (A_8 + A_9T_r)P_r^2 - \log P_r \qquad (7)$$

and

$$\log \nu^{1} = -4.23893 + 8.65808\ T_r - (1.22060/T_r) - 3.15224\ T_r^3 - 0.025\ [P_r^{-0.6}] \qquad (8)$$

The coefficients in Equations 7 and 8, and values of ω are given by Chao and Seader (*7*).

A computer program was written to calculate equilibrium vaporization ratios from Equation 1. At the outset, Equations 3 and 6 were used to calculate the *K* values of the compounds studied in this work. After several trials, it became apparent that the calculated *K*-values for methane were always greater than observed values, and that this discrepancy increased with increasing pressure. Since the formulation of activity coefficients (Equation 3) is independent of pressure and the B-W-R equation is believed to be reliable in representing the P-V-T behavior of gaseous mixtures, the expression for liquid-phase fugacity coefficients was modified.

Since the acentric factor equals zero for methane, Equation 6 reduces to

$$\log \nu^{0} = \log \nu^{0}$$

The expression for $\log \nu^{0}$ was then divided by the quantity $(1 + P \times 10^{-4})$ where *P* is the total pressure (psia) of the system. Note that this quantity has no theoretical implications and that the simple pressure correction was introduced merely to produce a better fit of the experimental data.

Comparisons were made of the correlated equilibrium vaporization ratios with the observed *K* values. The average absolute deviation for the methane–*n*-pentane binary system is about 4%. For the methane–isopentane binary system, the average absolute percent deviation is about 8%. For the methane–neopentane–*n*-pentane ternary and the methane-isopentane–*n*-pentane ternary systems deviations are 6.3% and 6.0%, respectively. The methane–neopentane error averaged 11.6%.

Correlated *K* values and observed *K* values are in reasonably good agreement, except near the critical region. Inspection of the methane–neopentane binary system reveals the predicted methane *K* values to be in greater error than the predicted neopentane *K* values, especially at higher temperatures. This observation concurs with the temperature restriction for methane imposed on the Chao-Seader correlation. In other words, the Hildebrand equation cannot predict accurately, methane behavior at temperatures above 0.93 of the pseudocritical temperature of the equilibrium liquid mixture. It appears unlikely that the complex behavior of liquid mixtures composed of constituents with such different physical properties as methane and pentanes can be represented in the critical region by such relatively simplified expressions as Equations 3 and 6.

SUMMARY

Phase-equilibria data were obtained for the methane–isopentane binary system at temperatures of 160°, 220°, and 280° F and pressures from about 500 psia up to the critical pressure. Vapor-liquid equilibrium data have been obtained throughout the coexisting-phase region for the methane–neopentane binary system at pressures from about 300 psia to the critical region for temperatures of 160°, 220°, and 280° F. Equilibrium ratios have been experimentally determined for the methane–isopentane–*n*-pentane system for a temperature of 160°, and pressures from about 500 psia up to the critical region, and for the methane–neo-*n*-pentane ternary at 160° F and over the same range of pressures.

A correlation is presented which employs the B-W-R equation of state to predict vapor phase fugacity coefficients, Hildebrand's regular solution theory is applied to the liquid state, and an empirically modified Chao and Seader expression is used to calculate the liquid-phase fugacity coefficient. Comparison of the *K*-value correlation with all the experimental points determined in this work indicate an average absolute percent deviation within 10%.

LITERATURE CITED

(1) Amick, E. H., Jr., Johnson, W. B., Dodge, B. F., "P-V-T-X Relationships for the System: Methane-Isopentane," *Chem. Eng. Progr. Symp. Ser.*, **48**, 3, 65 (1952).

(2) Beattie, J. A., Douslin, D. R., Levine, S. W., "Vapor Pressure and Critical Constants of Neopentane," *J. Chem. Phys.*, **19**, 948 (1951).

(3) Benedict, M., Webb, G. B., Rubin, L. C., "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures," *Chem. Eng. Progr.*, **47**, 8, 419, 517, 609 (1951); *J. Chem. Phys.*, **8**, 334 (1940); *ibid.*, **10**, 747 (1942).

(4) Boomer, E. H., Johnson, C. A., Piercey, H. G. A., "Equilibria in Two-Phase Gas-Liquid Hydrocarbon Systems II. Methane and Pentane," *Can. J. Res.*, **B16**, 319 (1938).

(5) Brainard, A. J., "A Study of the Vapor-Liquid Equilibrium for the Quaternary System Hydrogen-Benzene-Cyclohexane-Normal Hexane," Doctoral Thesis, The University of Michigan, Ann Arbor, 1964.

(6) Canjar, L. N., Smith, R. F., Volianitis, E., Galluzzo, J. F., Cabarcos, M., "Correlation of Constants in the Benedict-Webb-Rubin Equation of State," *Ind. Eng. Chem.*, **47**, 6, 1028 (1955).

(7) Chao, K. C., Seader, J. D., "A General Correlation of Vapor-Liquid Equilibria in Hydrocarbon Mixtures," *AIChE J.*, **7**, 4, 598 (1961).

(8) Heichelheim, H. R., Kobe, K. A., Silberberg, I. H., McKetta, J. J., "Compressibility Factors of 2,2-Dimethylpropane (Neopentane)," *J. Chem. Eng. Data*, **7**, 4, 507 (1962).

(9) Hildebrand, J. H., Scott, R. L., "The Solubility of Nonelectrolytes," Dover Publ., New York, 1964.

(10) Kellogg Charts, "Liquid-Vapor Equilibrium in Mixtures of Light Hydrocarbons," M. W. Kellogg Co., New York, 1950.

(11) NGAA *K*-Value Charts, *Eng. Data Book*, Natural Gasoline Supply Men's Association, Tulsa, Okla., 1957.

(12) Pitzer, K. S., Lippman, D. Z., Curl, R. F., Jr., Huggins, C. M., Petersen, D. E., "The Volumetric and Thermodynamic Properties of Fluids II," *J. Amer. Chem. Soc.*, **77**, 3433 (1955).

(13) Prausnitz, J. M., Edmister, W. C., Chao, K. C., "Hydrocarbon Vapor-Liquid Equilibria and Solubility Parameter," *AIChE J.*, **6**, 2, 214 (1960).

(14) Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., "Phase Equilibria in Hydrocarbon Systems," *Ind. Eng. Chem.*, **34**, 9, 1108 (1942).

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