The Equilibrium Phase Properties of the Nitrogen–*n*-Pentane System

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Vapor and liquid equilibrium phase compositions and refractive indices have been determined for the nitrogen–*n*-pentane system at 39.7, 99.6, 160.0, and 220.0 °F and at pressures from the vapor pressure of *n*-pentane to about 3000 psia. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The equilibrium phase densities were calculated from the measured phase composition and refractive index using the Lorentz–Lorenz molar refractivity relationship.

Virtually all modern design procedures involving the determination of the thermodynamic properties of multicomponent fluid systems make use of binary interaction parameters for each possible binary pair that can be made up from the various molecular species in the multicomponent system. In most instances, the binary interaction parameters for paraffin hydrocarbon–paraffin hydrocarbon pairs are negligible, but the interaction parameters for paraffin hydrocarbon–non-paraffin hydrocarbon pairs or for non-hydrocarbon pairs are normally not negligible and have an appreciable effect on predicted behavior of the multicomponent system.

The object of the work undertaken in this study was to obtain experimental data on the equilibrium phase properties of binary mixtures of nitrogen and *n*-pentane over a sufficiently wide range of pressure, temperature, and composition so that the binary interaction and other parameters for the system could be calculated. Studies on the phase behavior of this system have been reported earlier by Kurata and Swift (*8*) but no work has been reported at the higher temperatures.

Experimental Method

A detailed description of the experiment and methods used in this work has been reported earlier by Besserer and Robinson (*2, 3*). Briefly, the equilibrium cell was of the variable volume movable piston type consisting of two cylinder–piston end sections and a central windowed section. The function of the pistons was to separate the cell contents from the silicone oil used as a hydraulic fluid, and to provide a means for varying the cell volume. The function of the windowed section was to permit visual observation of the cell contents and to provide a means for taking refractive index measurements of the liquid and vapor phases. These optical measurements were made using a telescope fitted with an autocollimating eyepiece and mounted on a precision rotary table centered under a point on the front surface of the cell window. The light source was provided by a helium–neon ruby laser.

The system temperature was measured with a calibrated iron–constantan thermocouple relative to an ice junction. The temperature is believed known to ±0.1 °F. The pressure was measured with a calibrated 0–3000 psi Heise gauge equipped with a 316 stainless steel bourdon tube. The measurements are believed known to within ±0.1% of full scale.

Samples of both the liquid and vapor phases were expanded through micro-metering valves into an evacuated manifold at a pressure of about 100 mmHg. The pressure in the manifold was measured with a differential pressure transducer. Two samples of each phase were taken and triplicate analyses were run on each sample. The gas chromatograph used for the analysis was a Hewlett-Packard Mode 700 equipped with a thermal conductivity cell detector. The column used was 3 ft long by ⅛ in. diameter packed with Porapak QS and maintained at 175 °C. Calibration of the unit was done using pure components over sample loop pressure up to about 150 mmHg where response was linear with sample size. The relative response factors for converting area fractions to mole fractions were 2.1832 for nitrogen and 1.0000 for *n*-pentane. The compositions are believed known to at least ±0.005 mole fraction.

Materials. The nitrogen used in this work was obtained from a local supplier and was stated to have a minimum purity of 99.99 mole %. A sample of the material was analyzed on a silica gel column, and no impurity peaks were detected. The *n*-pentane was pesticide grade obtained from the Fisher Scientific Co. having a purity of not less than 99.9 mole %. This was used without further treatment.

Experimental Results. The behavior of binary mixtures of nitrogen and *n*-pentane was studied at temperatures of 39.7, 99.6, 160.0, and 220.0 °F and at pressures between the vapor pressure of *n*-pentane and about 3000 psia. Equilibrium phase compositions and refractive index measurements were made at 10–12 pressures within this interval at each of the four temperatures. The results of these measurements together with the calculated equilibrium ratios for each component in the binary system and the calculated phase molal volumes are given in Table I.

A graphical representation of the phase compositions as a function of pressure at each of the four temperatures is given in Figure 1. A section of the saturated liquid data is shown in expanded form in Figure 2 in order to clarify the behavior of the system at low pressures when the solubility of nitrogen in *n*-pentane is low. The calculated equilibrium ratios are shown in Figure 3.

Discussion

The molar volumes of the equilibrium phases were calculated by the Lorentz–Lorenz refractivity relationship

$$R_{\mathrm{LL}}{}^{0} = \frac{M}{\rho}\frac{n^2 - 1}{n^2 + 2}$$

The development of this relationship has been described in detail in the original articles (*9, 10*) and its application to determining the density of binary systems is explained in the more recent articles by Besserer and Robinson (*2*), and Miranda et al. (*11*). In applying the relationship to mixtures, the assumption is made that the molal refractivity is additive. The justification for this is based largely on the work of Keilich (*7*) and Smyth et al. (*12*). The reliability of the method is reviewed in some detail in the recent article by Miranda et al. (*11*).

The pure component molal refractivity of *n*-pentane was obtained by using experimentally measured values of the refractive index at each of the experimental temperatures at pressures up to about 3000 psia. These measurements were then used together with density values for pure *n*-pentane obtained from the Benedict–Webb–Rubin equation of state (*1*) with recently developed constants (*5*) to calculate the molal refractivity. At the wavelength of 6328 Å used in this work, the values of $R_{\mathrm{LL}}{}^{0}$ ranged from 25.14 mL g-mol^{-1} at 40 °F to 25.41 mL g-mol^{-1} at 220 °F. Corrections for the effect of pressure were applied, but these were generally very small and amounted to about 1.2% at the highest pressures.

Table I. Experimental Equilibrium Phase Properties for the Nitrogen-*n*-Pentane System

Pressure	Composition[a]		Refractive index[b]		Molar volume[c]		Equilibrium constant	
P	x	y	n_L	n_V	V_L	V_V	K_{N_2}	$K_{nC_5H_{12}}$
				39.7 °F				
241	0.025	0.981	1.3635	1.0057	1.77	20.4	39.2	0.0195
601	0.055	0.990	1.3606	1.0132	1.74	8.52	18.0	0.0106
1004	0.104	0.988	1.3570	1.0219	1.68	5.17	9.50	0.0134
1508	0.149	0.988	1.3528	1.0329	1.63	3.44	6.63	0.0141
2008	0.194	0.988	1.3489	1.0438	1.58	2.60	5.09	0.0149
2504	0.223	0.987	1.3456	1.0543	1.55	2.10	4.43	0.0167
3006	0.251	0.985	1.3409	1.0648	1.52	1.79	3.92	0.0200
				99.6 °F				
36.3	0.0027	0.577	1.3453	1.0028	1.90	112	214	0.424
65.3	0.0055	0.757	1.3452	1.0033	1.89	69.1	138	0.244
113	0.011	0.856	1.3450	1.0037	1.89	47.9	77.8	0.146
199	0.020	0.913	1.3438	1.0053	1.88	28.1	45.7	0.0888
310	0.031	0.940	1.3427	1.0074	1.87	18.5	30.3	0.0619
421	0.043	0.950	1.3425	1.0096	1.85	13.7	22.1	0.0522
599	0.061	0.960	1.3400	1.0133	1.83	9.55	15.7	0.0426
922	0.095	0.968	1.3369	1.0197	1.79	6.25	10.2	0.0354
1222	0.125	0.970	1.3342	1.0257	1.76	4.76	7.76	0.0343
1526	0.155	0.970	1.3313	1.0322	1.72	3.80	6.26	0.0355
1822	0.185	0.969	1.3284	1.0383	1.69	3.21	5.24	0.0380
2222	0.223	0.967	1.3246	1.0466	1.64	2.66	4.34	0.0425
2624	0.258	0.964	1.3195	1.0551	1.61	2.29	3.74	0.0485
3010	0.288	0.961	1.3153	1.0632	1.58	2.02	3.34	0.0548
				160.0 °F				
60	0.0022	0.323	1.3233	1.0052	2.02	86.1	147	0.678
119	0.0086	0.622	1.3227	1.0063	2.02	47.4	72.3	0.381
206	0.019	0.770	1.3218	1.0081	2.00	27.3	40.5	0.234
311	0.032	0.838	1.3210	1.0103	1.99	18.4	26.2	0.167
446	0.048	0.877	1.3196	1.0126	1.97	13.4	18.3	0.129
612	0.066	0.901	1.3178	1.0160	1.95	9.81	13.7	0.106
933	0.104	0.924	1.3131	1.0223	1.91	6.52	8.88	0.0848
1338	0.146	0.930	1.3086	1.0306	1.86	4.65	6.37	0.0820
1771	0.196	0.931	1.3032	1.0399	1.80	3.57	4.75	0.0858
2345	0.252	0.930	1.2956	1.0525	1.74	2.73	3.69	0.0936
3014	0.330	0.922	1.2858	1.0681	1.65	2.17	2.79	0.1164
				220.0 °F				
118	0.0032	0.179	1.3005	1.0105	2.17	49.8	55.9	0.824
144	0.0079	0.320	1.2996	1.0109	2.17	41.1	40.5	0.685
187	0.015	0.470	1.2989	1.0119	2.16	31.6	31.3	0.538
276	0.035	0.609	1.2963	1.0136	2.14	22.3	17.4	0.405
542	0.071	0.774	1.2925	1.0188	2.10	11.8	10.9	0.243
955	0.124	0.845	1.2861	1.0277	2.04	6.71	6.81	0.177
1531	0.196	0.858	1.2760	1.0407	1.97	4.41	4.38	0.177
2046	0.266	0.862	1.2664	1.0541	1.90	3.29	3.24	0.188
2644	0.339	0.852	1.2532	1.0716	1.83	2.57	2.51	0.224
3016	0.400	0.837	1.2404	1.0851	1.79	2.25	2.09	0.272

[a] Mole fraction nitrogen. [b] Relative to vacuum at 6328 Å. [c] ft^3 $lb\text{-}mol^{-1}$ calculated from the refractive index and composition data.

Table II. Consistency Test of Nitrogen-*n*-Pentane Experimental Data

Temp, °F	No. of exptl points	Points passing test
40	7	7
100	14	13
160	11	9
220	10	5

Table III. Henry's Constants at Zero Pressure for Nitrogen in *n*-Pentane

	Henry's constant, psia	
Temp, °F	Graphical	Analytical
40	9670	9620
100	9170	9210
160	8280	8310
220	6840	6690

A similar procedure was used in obtaining the refractivity of pure nitrogen; however, the variation with pressure or temperature was so slight that no correction was justified and the constant value of 4.44 mL g-mol^{-1} reported by Besserer and Robinson (*4*) was used throughout.

The calculated molal volumes of the saturated liquids and vapors are given in Table I. The reliability of these figures depends on the accuracy of the experimental composition and refractive index measurements and on the pure component molal refractivities. The composition measurements are estimated to be within 0.005 mole fraction and the refractive indices were measurable to within 0.0001. The molal refractivity of the pure components is estimated to be within ±0.1% for the liquid and ±2.0% for the vapor. The reliability of the molal volumes of the saturated liquid is thought to be within about 0.5%. The reliability for the saturated vapor phase is thought to be within about 1 or 1.5% but, in cases where the refractive indices are close to unity, the error could be as high as 5%.

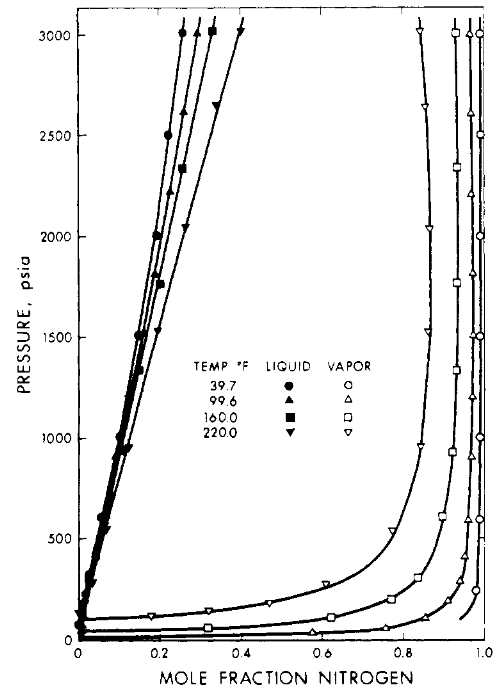

Figure 1. Pressure-equilibrium phase composition diagram for the nitrogen–*n*-pentane system.

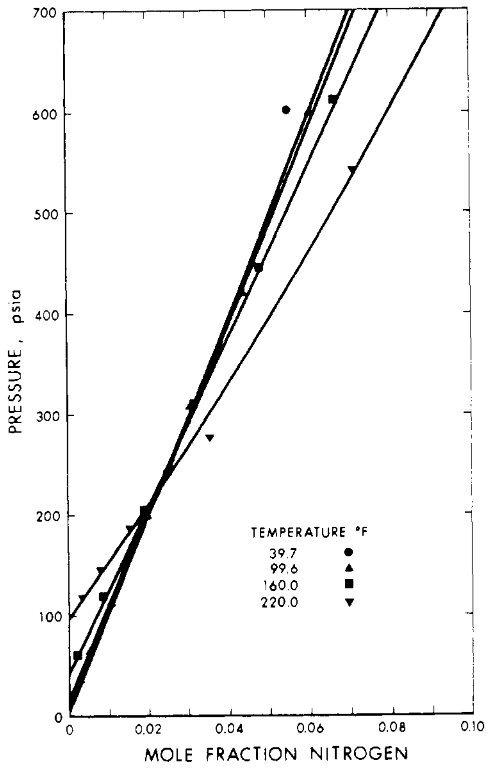

Figure 2. Pressure-equilibrium phase composition diagram for the nitrogen–*n*-pentane system at low nitrogen concentrations.

The entire set of *p–x–y* data at each isotherm was subjected to the thermodynamic consistency test proposed by Christiansen and Fredenslund (*6*). In this method the vapor composition in equilibrium with each experimental liquid composition is calculated by the method of orthogonal collocation within a thermodynamic framework which is internally consistent. The calculated vapor compositions are compared with the experimentally measured values and, if the absolute difference between the calculated and measured values is within the experimental error bounds, the data are considered to be consistent.

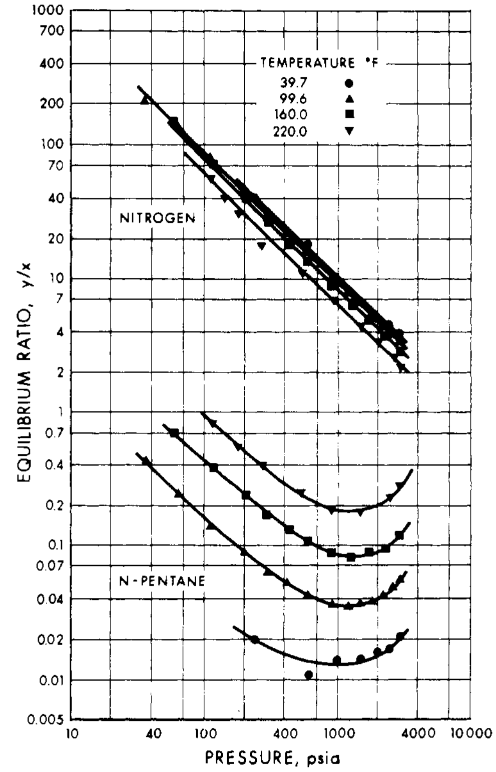

Figure 3. Equilibrium ratios for nitrogen and *n*-pentane in the nitrogen–*n*-pentane binary system.

The results of these tests are given in Table II. This shows that generally the data are consistent according to the test, although the percentage of points passing the test decreases as temperature increases. Since the experimental techniques and equipment were the same for all temperatures, it is possible that some of the apparent lack of consistency at the higher temperatures may be caused by inadequacies in the method of calculating fugacity coefficients. Visual inspection of the *p–x–y* data indicates that two of the points at 220 °F are subject to some experimental error.

In addition to carrying out the above consistency test, Henry's constant for nitrogen in *n*-pentane was calculated at each temperature. The values were determined graphically by plotting f_2^0/x_2 vs. x_2 and extrapolating to zero solute concentration, and analytically using the method of Christiansen and Fredenslund (*6*). The results of these determinations are given in Table III where it will be noted that the two methods agree well except at 220 °F where a difference of about 2% exists.

Acknowledgment

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Glossary

f_2^0	fugacity of solute at zero pressure, psia
K_{N_2}	equilibrium ratio for nitrogen
$K_{nC_5H_{12}}$	equilibrium ratio for *n*-pentane
M	molecular weight
n	refractive index
n_L	refractive index of liquid
n_V	refractive index of vapor
P	pressure, psia
R_{LL}^0	Lorentz–Lorenz molal refractivity at zero pressure, mL g-mol^{-1}

V_L molal volume of liquid, ft^3 lb-mol^{-1}
V_V molal volume of vapor, ft^3 lb-mol^{-1}
x mole fraction of component in liquid phase
x_2 mole fraction of solute in liquid phase
y mole fraction of component in vapor phase
ρ molal density, g-mol mL^{-1}

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Volume Changes on Mixing Normal Alkanes with Branched Alkanes

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Excess volumes at 25 °C are reported for the systems *n*-pentane + 2,6-dimethylheptane, *n*-hexane + 2,5-dimethylhexane, *n*-heptane + 2,4-dimethylpentane and *n*-octane + 2,3-dimethylbutane. The results are compared with the predictions of a generalized principle of congruence.

The principle of congruence is a very useful tool for predicting the properties of hydrocarbon mixtures. As originally formulated by Brønsted and Koefoed (*1*), the principle asserts that at a given temperature the properties of mixtures of *n*-alkanes depend only on the average chain length $\bar{n}$

$$\bar{n} = \sum_i x_i n_i \tag{1}$$

where x_i is the mole fraction of component i and n_i is its chain length. The principle has been extended with some success to other homologous series (*2*) and has been found applicable to gaseous mixtures as well (*3, 7*).

Theoretical justification for the principle of congruence was provided by Longuet-Higgins (*4*). His model for the interactions between long-chain molecules of similar type leads to a generalization of the congruence principle: "if two mixtures, each containing chain molecules of the type $A(X)_nB$, are such that the molecules of the two mixtures can be divided into identical sets of fragments by cutting the chains in suitable places, then these mixtures will have identical equations of state and identical solvent properties."

The systems *n*-pentane + 2,6-dimethylheptane, *n*-hexane + 2,5-dimethylhexane, *n*-heptane + 2,4-dimethylpentane, and *n*-octane + 2,3-dimethylbutane might be expected to satisfy the

Table I. Excess Volumes, V^E_m, at 25 °C

x	V^E_m/cm^3 mol^{-1}	x	V^E_m/cm^3 mol^{-1}	x	V^E_m/cm^3 mol^{-1}	x	V^E_m/cm^3 mol^{-1}
	n-Pentane + 2,6-Dimethylheptane				*n*-Heptane + 2,4-Dimethylpentane		
0.0263	−0.037	0.4805	−0.260	0.0317	−0.0114	0.4623	−0.0347
0.0625	−0.080	0.4869	−0.258	0.0716	−0.0161	0.5043	−0.0347
0.1081	−0.127	0.5230	−0.252	0.1671	−0.0240	0.5205	−0.0340
0.1614	−0.172	0.5445	−0.248	0.2290	−0.0280	0.5488	−0.0348
0.2169	−0.207	0.5568	−0.245	0.2941	−0.0314	0.6004	−0.0338
0.2769	−0.234	0.6249	−0.221	0.3509	−0.0333	0.6590	−0.0315
0.3306	−0.251	0.6933	−0.192	0.3533	−0.0315	0.7326	−0.0274
0.3637	−0.258	0.7654	−0.156	0.4011	−0.0334	0.8132	−0.0214
0.3804	−0.258	0.8333	−0.118	0.4114	−0.0344	0.9062	−0.0128
0.4188	−0.263	0.8982	−0.075	0.4465	−0.0341		
0.4336	−0.261	0.9611	−0.029				
	n-Hexane + 2,5-Dimethylhexane						
0.0446	−0.0030	0.5248	−0.0232		*n*-Octane + 2,3-Dimethylbutane		
0.1010	−0.0072	0.5434	−0.0222	0.0496	−0.021	0.5352	−0.129
0.1750	−0.0126	0.5878	−0.0217	0.0944	−0.039	0.5434	−0.124
0.2419	−0.0165	0.5925	−0.0221	0.2083	−0.077	0.5861	−0.129
0.3252	−0.0203	0.6305	−0.0209	0.2534	−0.089	0.6012	−0.122
0.3925	−0.0221	0.6704	−0.0200	0.2992	−0.100	0.6749	−0.115
0.4228	−0.0224	0.7299	−0.0176	0.3691	−0.114	0.7567	−0.100
0.4519	−0.0225	0.8041	−0.0144	0.4190	−0.115	0.8537	−0.070
0.4656	−0.0230	0.8842	−0.0078	0.4337	−0.123	0.9234	−0.046
0.4811	−0.0228	0.9512	−0.0029	0.4893	−0.122	0.9593	−0.023
0.5128	−0.0228			0.4933	−0.128		