These values were all calculated using similar methods. The sources of information for the other carbon dioxide–paraffin systems were as follows: carbon dioxide–propane, Poettman and Katz (*12*); carbon dioxide–isobutane, Besserer and Robinson (*4*); carbon dioxide–*n*-butane Olds et al. (*11*); carbon dioxide–isopentane, Besserer and Robinson (*6*); carbon dioxide–*n*-pentane, Besserer and Robinson (*5*); carbon dioxide–*n*-hexane, Gupta and Friesen (*9*); carbon dioxide–*n*-octane, Schneider et al. (*14*); carbon dioxide–*n*-decane, Reamer and Sage (*13*).

It will be noted from this figure that the data on the Henry constants for carbon dioxide in most of the paraffin hydrocarbons follows a consistent pattern. A possible exception is in the case of carbon dioxide in *n*-octane where the low-temperature data lie outside the curve for *n*-decane. The value obtained in this work for carbon dioxide in *n*-heptane at 250 °F appears a bit low.

The experimental data were subjected to a consistency test using the method of Christiansen and Fredenslund (*7*). Of the 63 points used in the test, 53 met the criterion that $|Y_{calcd} - Y_{exptl}| \leq 0.010$. At 399.3 °F, only two of the seven data points met the criterion, probably because of the inability of the equation of state to properly describe the fugacity of both phases so near the critical region.

Glossary

K_{CO_2}	equilibrium ratio for carbon dioxide
K_{nC_7}	equilibrium ratio for normal heptane
M	molecular weight
n	refractive index
n_L	refractive index of liquid
n_V	refractive index of vapor
P	pressure
R_{LL}	molal refractivity as defined by the Lorentz–Lorenz, relationship
R_{LL}^0	molal refractivity at zero pressure
V_L	liquid molal volume
V_V	vapor molal volume
x	mole fraction of component in the liquid phase
y	mole fraction of component in the vapor phase
ρ	density

Literature Cited

(1) Benedict, M., Webb, G. B., Rubin, L. C., *J. Chem. Phys.*, **8**, 334 (1940).
(2) Besserer, G. J., Robinson, D. B., *Can. J. Chem. Eng.*, **49**, 651 (1971).
(3) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **18**, 137 (1973).
(4) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **18**, 298 (1973).
(5) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **18**, 416 (1973).
(6) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **20**, 93 (1975).
(7) Christiansen, L. J., Fredenslund, A., *AIChE J.*, **21**, 49 (1975).
(8) Fredenslund, A., Mollerup, J., Christiansen, L. J., *Cryogenics*, **13**, 414 (1973).
(9) Gupta, B. N., Friesen, R. D., unpublished data, University of Alberta, 1968, 1972.
(10) Ng, H. J., Robinson, D. B., "The Equilibrium Phase Properties of the Toluene-Carbon Dioxide System", submitted to *J. Chem. Eng. Data*.
(11) Olds, R. H., Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **41**, 475 (1949).
(12) Poettman, F. H., Katz, D. L., *Ind. Eng. Chem.*, **37**, 847 (1945).
(13) Reamer, H. H., Sage, B. H., *J. Chem. Eng. Data*, **8**, 508 (1963).
(14) Schneider, G., Alivani, Z., Heim, W., Howarth, E., Franch, E. V., *Chem.-Ing.-Tech.*, **39**, 649 (1967).
(15) Smyth, C. P., Engel, E., Wilson, E. B., Jr., *J. Am. Chem. Soc.*, **51**, 1736 (1929).
(16) Wan, S. W., Dodge, B. F., *Ind. Eng. Chem.*, **32**, 95 (1940).

Equilibrium Phase Properties of the Nitrogen–Isobutane System

Harish Kalra, Heng-Joo Ng, Rogel D. Miranda, and Donald B. Robinson*

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada, T6G 2G6

The compositions of the equilibrium vapor and liquid phases have been experimentally determined for the nitrogen–isobutane binary system at temperatures of 0, 50.1, 99.9, 150.0, 199.7, and 250.0 °F and at pressures up to the critical point for the system or to about 3000 psia. Refractive index measurements for each of the equilibrium phases were also made at temperatures of 0, 50.1, and 99.9 °F. The experimental data were used to calculate the equilibrium phase molar volumes at these conditions and to calculate the equilibrium ratio for nitrogen and isobutane in the binary system. The Henry constant for nitrogen in isobutane was calculated at each temperature.

Introduction

Nitrogen is commonly found in natural gases and other reservoir fluids and consequently its presence must be considered whenever the thermodynamic properties or phase behaviors of these fluids are being evaluated. Most modern equations of state or generalized correlation procedures make use of binary interaction parameters between unlike molecules such as nitrogen and paraffin hydrocarbons. The phase behavior of many of the nitrogen–hydrocarbon binaries has been determined and consequently the necessary binary interaction parameters and Henry's constants are known. However, no data have been found in the literature on the behavior of the nitrogen–isobutane binary system. For this reason it was considered worthwhile to study the equilibrium phase properties of this system at temperatures in the 0–250 °F range at pressures up to about 3000 psia.

Experimental Method

The experimental methods used in this work were similar to those used for the studies on nitrogen in normal pentane and nitrogen in isopentane recently reported by Kalra et al. (*8*) and Krishnan et al. (*10*). The work at 50.1 and 99.9 °F was carried out in a double piston-type variable volume cell which permitted the removal of both equilibrium liquid and vapor samples and also the direct measurement of the refractive index of each phase. The working pressure of the cell was 3000 psia and the working volume ranged from about 10 to 175 mL. This equipment and the method of operation have been described in detail by Besserer and Robinson (*2, 3*).

The work at 0 °F was carried out in a double-windowed constant-volume cell which also permitted the removal of equilibrium vapor and liquid samples and the measurement of the refractive index of each phase. Equilibrium was attained by agitating with an externally coupled Teflon-coated magnet. The working pressure of this cell was about 4000 psia and the

working volume was approximately 250 mL. The construction and operating details of this cell have been described in detail by Kalra and Robinson (7).

The experimental measurements at the three highest temperatures were made in a constant volume visual cell recently described by Ng and Robinson (11). This cell had a working volume of about 150 mL and could be used to about 3000 psia in a temperature range from 100 to 600 °F. The pressures and temperatures were measured using techniques similar to those used at the lower temperatures.

The system temperature was measured by a single-junction iron constantan thermocouple relative to the ice point. The thermocouple juncton was in direct contact with the working fluids and the temperature is believed known to ±0.1 °F. The pressure was measured with a series of calibrated Heise gauges appropriate for the pressures encountered during the experimental measurements for each isotherm. The pressures are believed known to ±0.15% of the highest pressure for any isotherm.

The phase compositions were obtained using Hewlett-Packard Model 700, Model 5750B, and Model 5830A gas chromatographs equipped with thermal conductivity cells. The chromatographic columns were $1/8$ in. in diameter and 3 ft long and were packed with Porapak QS. These were maintained at a temperature of 140 °C. The relative response factor of nitrogen for converting from peak area to mole fraction was 1.6612 compared to 1.0000 for isobutane. This factor was obtained by using pure component samples in a 0.5-mL sample loop at pressures less than about 0.3 atm. Over this range, the response was linear with sample size and compositions are believed known to within ±0.005 mol fraction.

The sequence followed in carrying out the study was as follows. The equilibrium cells were cleaned, pressure tested, and evacuated. Isobutane was then added until a sufficient quantity of liquid was present in the cell and nitrogen was added from a cylinder until the pressure reached the desired value. The cell and its contents were then brought to the desired temperature and equilibrium was established. This condition was easily recognized by the stability of the pressure after mixing and at the three lower temperatures by the nature of the refractive index lines. At this point refractive index readings were taken and samples were drawn for analyses. At least two samples of each phase were withdrawn and triplicate analyses were run on each sample. Thus at least six analyses were averaged for each experimental data point.

Materials

The nitrogen used in this work was obtained from a local supplier and was stated to have a minimum purity of 99.99 mol %. An analysis of the material on a silica gel column did not reveal any impurities. The isobutane was Phillips Petroleum Research grade with a reported purity of 99.9+ mol %. This was used without further treatment.

Experimental Results

The phase behavior of mixtures of nitrogen and isobutane was studied at temperatures of 0, 50.1, 99.9, 150.0, 199.7, and 250.0 °F. The experimental phase-composition data were used to calculate the vapor–liquid equilibrium ratios. The phase compositions together with the refractive indices of each phase were used to calculate the molar volumes of each equilibrium phase at the three lower temperatures. All of the experimental measurements and the calculated results are given in Table I. Example pressure–composition diagrams are shown graphically at three temperatures in Figure 1 and the calculated equilibrium ratios are shown in Figure 2. The lines shown for the equilibrium ratio for nitrogen at 150 and 250 °F are not complete and the points are not shown on the figure because of the congestion
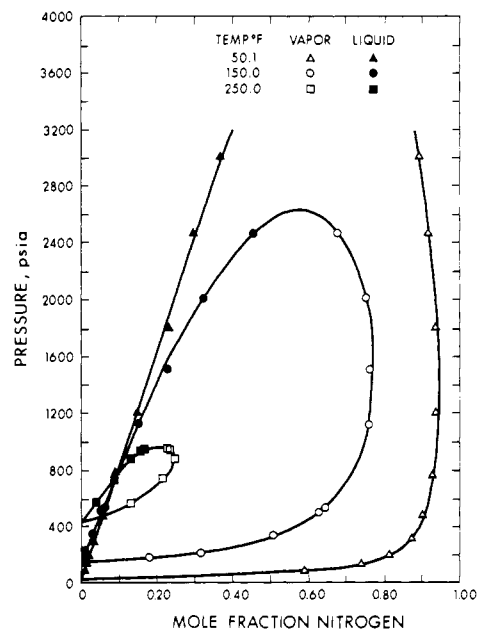

Figure 1. Pressure–equilibrium phase composition diagram for the nitrogen–isobutane binary system at three temperatures.
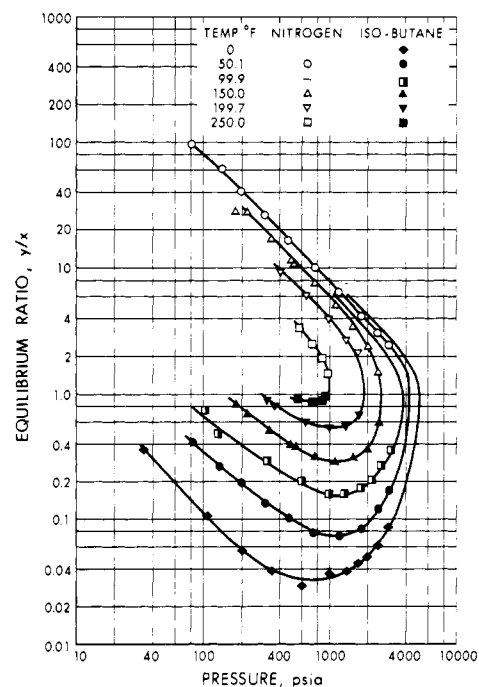

Figure 2. Equilibrium ratios for isobutane and nitrogen in the isobutane–nitrogen binary system.

with the other curves, particularly at the lower pressures. These points are, however, available in Table I.

Discussion

The equilibrium phase composition and refractive index data for the binary mixtures at the three lowest temperatures were used to calculate the equilibrium vapor- and liquid-phase densities using the Lorentz–Lorenz refractivity relationship as explained by Besserer and Robinson (2). In applying the relationship to mixtures, the assumption is made that the molal refractivity is additive on a molal average basis. The justification for this is based largely on the work of Smyth et al. (12) and Keilich (9).

The pure component molal refractivity of isobutane was obtained by using experimentally measured values of the refractive index at each of the experimental temperatures and

Table I. Equilibrium Phase Properties for the Nitrogen–Isobutane System

pressure, psia	composition[a] liquid x	vapor y	refractive index[b] liquid n_L	vapor n_V	molar volume[c] liquid V_L	vapor V_V	equilibrium constant nitrogen K_{N_2}	isobutane $K_{iC_4H_{10}}$
				0.0 °F				
33.7	0.0071*[d]	0.651	1.3351	1.0008	1.59	297	91.6	0.352
60.7	0.0066	0.802	1.3355	1.0007	1.59	260	122	0.199
109.0	0.0143	0.892	1.3358	1.0049	1.58	30.5	62.4	0.109
206	0.0251*	0.947	1.3396	1.0043	1.55	29.9	37.7	0.0544
357	0.0445	0.963	1.3354	1.0115	1.54	10.6	21.6	0.0388
601	0.0758	0.973	1.3327	1.0150	1.51	7.89	12.8	0.0289
1002	0.119	0.968	1.3267	1.0253	1.48	4.72	8.14	0.0359
1411	0.165	0.967	1.3215	1.0351	1.44	3.40	5.86	0.0390
1687	0.197	0.964	1.3173	1.0408	1.42	2.95	4.89	0.0445
2013	0.238	0.962	1.3135	1.0533	1.38	2.27	4.04	0.0501
2511	0.290	0.957	1.3057	1.0626	1.34	1.95	3.30	0.0608
2973	0.334*	0.943	1.2983	1.0818	1.31	1.56	2.82	0.0856
				50.1 °F				
82.5	0.0062*	0.588	1.3270	1.0044	1.63	62.4	94.8	0.415
135.5	0.0122	0.739	1.3261	1.0056	1.63	38.5	60.6	0.264
200	0.0198	0.812	1.3252	1.0069	1.63	27.1	41.0	0.192
310	0.0335	0.874	1.3235	1.0094	1.62	17.2	26.1	0.131
477	0.0556	0.904	1.3210	1.0132	1.60	11.3	16.3	0.102
759	0.0899	0.929	1.3168	1.0196	1.58	7.13	10.3	0.078
1213	0.149	0.938	1.3093	1.0310	1.53	4.37	6.31	0.073
1804	0.230	0.936	1.2987	1.0472	1.47	2.86	4.07	0.083
2464	0.295	0.916	1.2856	1.0669	1.44	2.12	3.11	0.119
3008	0.369*	0.894	1.2724	1.0858	1.39	1.75	2.43	0.168
				99.9 °F				
103.5	0.0056*	0.259	1.3087	1.0100	1.73	39.9	46.3	0.745
169.5	0.0136*	0.525	1.3074	1.0015	1.73	25.6	38.5	0.482
317	0.0332	0.717	1.3050	1.0145	1.72	15.2	21.6	0.292
591	0.0679	0.818	1.3002	1.0213	1.69	8.43	12.0	0.196
966	0.114	0.859	1.2929	1.0309	1.67	5.29	7.54	0.159
1323	0.171	0.870	1.2864	1.0405	1.62	3.94	5.10	0.157
1790	0.237	0.869	1.2749	1.0543	1.58	2.95	3.66	0.172
2221	0.308	0.858	1.2648	1.0591	1.53	2.39	2.79	0.205
2651	0.371	0.836	1.2486	1.0870	1.52	2.01	2.25	0.261
3013	0.436	0.803	1.2303	1.1075	1.51	1.76	1.84	0.350
				150.0 °F				
182	0.0065	0.180				27.7		0.826
227	0.0111*	0.314				28.3		0.694
339	0.0297*	0.505				17.0		0.511
505	0.0547	0.628				11.5		0.393
532	0.0634	0.644				10.2		0.380
1121	0.151*	0.759				5.03		0.284
1514	0.228	0.764				3.35		0.306
2012	0.324*	0.751				2.32		0.368
2470	0.458	0.676				1.48		0.598
				199.7 °F				
306	0.005*	0.103				22.8		0.901
394	0.026*	0.243				9.35		0.777
654	0.074*	0.445				6.02		0.599
988	0.138	0.542				3.92		0.531
1354	0.214*	0.566				2.64		0.552
1724	0.233*	0.505				2.17		0.646
				250.0 °F				
566	0.040	0.131				3.30		0.905
740	0.088	0.215				2.46		0.860
883	0.130	0.247				1.90		0.866
934	0.158	0.231				1.47		0.912
942	0.166	0.230				1.39		0.923

[a] Mole fraction nitrogen. [b] Relative to vacuum at 6328 Å. [c] $ft^3\ lb^{-1}\ mol^{-1}$ calculated from refractive index and composition data. [d] Values marked with an asterisk did not pass the Christiansen–Fredenslund consistency test.

pressures up to about 3000 psia. These measurements were used together with density values calculated for pure isobutane using the Benedict–Webb–Rubin equation of state (1) with coefficients reported by Bishnoi and Robinson (4) to calculate the molal refractivity at each temperature. These values are presented in Table II.

A procedure similar to the above was used for pure nitrogen. In earlier work (8, 10) it had been assumed that a single average value for the refractivity of pure nitrogen could be used over the range of temperatures and pressures being encountered; however, in this work new measurements of the refractive index were made at the experimental temperatures. The measured refractive indices were used with density values obtained from the Benedict–Webb–Rubin equation as explained above to calculate the refractivity of nitrogen at each temperature. These values are also reported in Table II.

Table II. Lorentz-Lorenz Molar Refractivities at Zero Pressure, mL (g-mol)$^{-1}$

temp, °F	$R_{LL}°$	
	isobutane	nitrogen
0.0	20.6	4.53
50.1	20.7	4.75
99.9	20.8	4.46
149.9	20.6	4.56
199.7	20.9	4.60
250.0	20.9	4.60

The calculated molal volumes of the equilibrium liquids and vapors are included in Table I. The reliability of these values 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 within ±0.0001. The molal refractivity of the pure components is thought to be within ±1.3% for the liquid and ±1.1% for the vapor. Thus the reliability of the molal volumes of the saturated liquids is thought to be within about ±1.3%. Similarly, the reliability of the saturated-vapor densities is within about ±1.3% except in cases where the refractive indices are close to unity and the error may be as high as 5%.

The Henry constant for nitrogen dissolved in isobutane is of interest in some generalized methods for predicting the phase behavior of multicomponent systems containing these and other compounds. The data obtained in this work were used to calculate the Henry constants using the method and program described by Christiansen and Fredenslund (5). The values of the vapor-phase fugacity of nitrogen divided by the liquid-phase concentration were plotted as a function of the liquid-phase concentration and extrapolated to zero pressure. A Poynting correction was applied to these values to get the Henry constant at zero pressure for each temperature. These values are presented in Table III.

A comparison of the Henry constants obtained from the extrapolations with the values for other light paraffins and olefins recently presented by Grauso et al. (6) showed them to be in good agreement on the basis that the Henry constant for a dissolved gas tends to increase as molecular weight increases.

The experimental data were also subjected to the thermodynamic consistency test recommended by Christiansen and Fredenslund (5). The data obtained at 250 °F were not included in this analysis because the region covered is so close to the critical for isobutane that the consistency program does not converge properly. Of the 47 points subjected to the test, 31 met the criterion that $|y_{calcd} - y_{exptl}| \leq 0.010$. Of the 16 points failing to pass the test, 6 were for cases where the liquid phase contained less than 0.015 fraction of nitrogen.

The points which failed to pass the test are indicated in Table I by an asterisk. It will be noted that the consistency seems

Table III. Henry's Constants at Zero Pressure for Nitrogen in Isobutane

temp, °F	Henry's constant, psia	temp, °F	Henry's constant, psia
0	7010	150	5920
50	8220	200	4000
100	7510	250	1990

to decrease as the temperature increases. This may not be entirely correct and therefore misleading because the experimental techniques are the same at all temperatures. Actually the estimated thermodynamic properties needed in the relationships that are used to predict the vapor composition from the experimental liquid compositions may be less reliable at the higher temperatures nearer the critical region for isobutane, particularly when the nitrogen, the more volatile component, is highly supercritical. Thus the difference between the experimental and predicted y values would tend to increase.

Glossary

$f°$	fugacity of pure component referred to zero pressure
$H°$	Henry's constant referred to zero pressure
K	equilibrium ratio
n_L	refractive index of liquid
n_V	refractive index of vapor
P	pressure
V_L	liquid molal volume
V_V	vapor molal volume
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase
$R_{LL}°$	molal refractivity at zero pressure

Literature Cited

(1) Benedict, M., Webb, G. B., Rubin, L. C., *J. Chem. Phys.*, **8**, 334 (1940).
(2) Besserer, G. J., Robinson, D. B., *Can. J. Chem. Eng.*, **49**, 651 (1971).
(3) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **18**, 298 (1973).
(4) Bishnoi, P. R., Miranda, R. D., Robinson, D. B., *Hydrocarbon Process.*, **53**, 197 (1974).
(5) Christiansen, L. J., Fredenslund, A., *AIChE J.*, **21**, 49 (1975).
(6) Grauso, L., Fredenslund, A., Mollerup, J., *Fluid Phase Equilib.*, **1**, 13 (1977).
(7) Kalra, H., Robinson, D. B., *Cryogenics*, **15**, 409 (1975).
(8) Kalra, H., Robinson, D. B., Besserer, G. J., *J. Chem. Eng. Data*, **22**, 215 (1977).
(9) Keilich, S., *Physica (Utrecht)*, **28**, 1116 (1962).
(10) Krishnan, T. R., Kalra, H., Robinson, D. B., *J. Chem. Eng. Data*, **22**, 282 (1977).
(11) Ng, H.-J., Robinson, D. B., submitted for publication in *J. Chem. Eng. Data*.
(12) Smyth, C. P., Engel, E. W., Wilson, E. B., Jr., *J. Am. Chem. Soc.*, **51**, 1736 (1929).