nesium chloride in the NaCl-$MgCl_2$ system; yet, the excess free energy of mixing is much less.

In conclusion, the behavior of the sodium chloride-manganous chloride system is only moderately complicated in that quadratic terms in the Harned expressions are sufficient to give an accurate description of the activity coefficients and that estimates of trace activity coefficients from single salt data are in reasonable agreement with experimental values.

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Equilibrium-Phase Properties of *n*-Pentane-Carbon Dioxide System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the *n*-pentane-carbon dioxide system at 40.1°, 100.2°, 159.8°, and 220.0°F from the vapor pressure of *n*-pentane to pressures in the critical region. 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 by use of the Lorentz-Lorenz molar refractivity relationship.

As a continuation of a program to provide data on binary systems of interest to the petroleum and natural gas industry, the behavior of the *n*-pentane-carbon dioxide system was studied. This system was studied earlier by Poettman and Katz (*5*) in the temperature range from about 80° to 280°F, but it was suspected that substantial errors might exist in the data.

The first indication of this possibility arose when a considerable discrepancy existed between the data for the *n*-butane-carbon dioxide system reported in the same work and the data of Olds et al. (*4*) and data taken by Besserer and Robinson (*1*). In this system the liquid-phase compositions were generally too lean in *n*-butane, thus suggesting the possibility of some consistent error in the liquid-phase compositions. From this it was reasoned that a similar error might exist in the *n*-pentane-carbon dioxide data. The second indication was that the Henry's Law constant for carbon dioxide dissolved in *n*-pentane, defined by

$$H = \lim_{x \to 0} \frac{f}{x}$$

was about 30% lower than would have been expected by comparison with values of the constant for other carbon dioxide-paraffin binaries.

Experimental

The experimental equipment and procedure were described in detail in earlier papers by Besserer and Robinson (*1, 3*). Experiments were carried out at each of four temperatures which were nominally 40°, 100°, 160°, and 220°F. At each temperature, measurements of equilibrium-phase compositions and refractive indices were made at a series of pressures between the vapor pressure of *n*-pentane and the vapor pressure of carbon dioxide or the critical pressure for the system. The temperature was measured with a calibrated pair of iron-constantan thermocouples with the reference junction kept in an ice bath and is believed known to ±0.1°F. The pressure was measured with a strain gauge pressure transducer calibrated against the vapor pressure of carbon dioxide at 70°F and is believed known to ±3 psi.

The phase compositions were determined with a Hewlett-Packard Model 700 gas chromatograph equipped with a thermal conductivity cell detector. The column used was a 3-ft by ⅛-in. diameter stainless steel column packed with Poropak QS maintained at 170°C. The response factors for conversion from area fraction to mole fraction were 1.903 for *n*-pentane compared to 1.000 for carbon dioxide. These factors were obtained by calibration by use of pure component samples in a 1-cc sample loop at pressures up to 0.3 atm. The compositions are believed known to ±0.004 mole fraction.

Materials

The carbon dioxide used in the experiments was obtained from Canadian Liquid Air and the *n*-pentane was pesticide grade obtained from the Fisher Scientific Co. Both had a purity of better than 99.9 mol %.

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Table I. Experimental Equilibrium-Phase Properties for n-Pentane–Carbon Dioxide System

Press,	Composition[a]		Refractive index[b]		Molar volume[c]		Equilibrium constant	
P	x	y	n_L	n_V	V_L	V_V	K_{CO_2}	$K_{n-C_5H_{12}}$
40.1°F								
4.3	0.0000	0.0000	...	...	...	...	...	1.0000
33	0.0290	0.8528	1.36351	1.00134	1.770	167.7	29.407	0.1516
82	0.0856	0.9449	1.35896	1.00282	1.714	64.92	11.039	0.0603
160	0.1834	0.9709	1.35070	1.00554	1.615	31.00	5.294	0.0356
247	0.3179	0.9803	1.33867	1.00874	1.476	19.18	3.084	0.0289
325	0.4858	0.9846	1.32271	1.01208	1.293	13.73	2.027	0.0299
397	0.6255	0.9872	1.29879	1.01554	1.164	10.60	1.578	0.0342
471	0.8229	0.9894	1.25805	1.01962	0.9734	8.350	1.202	0.0599
501	0.8998	0.9862	1.23952	1.02143	0.8931	7.716	1.096	0.1377
538	0.9623	0.987	1.22184	1.02371	0.8286	7.061	1.026	0.3448
544	0.9791	0.990	1.21521	1.02439	0.8162	6.865	1.011	0.4785
565	1.0000	1.0000	1.21037	1.02343	0.7878	6.222	1.000	...
100.2°F								
15.3	0.0000	0.0000	...	...	...	...	...	1.0000
67	0.0344[d]	0.7421	1.34385	1.00324	1.860	84.63	21.573	0.2671
123	0.0739[e]	0.8598	1.34008	1.00497	1.822	44.55	11.635	0.1514
230	0.1689	0.9202	1.33219	1.00855	1.724	22.75	5.448	0.0960
316	0.2379	0.9401	1.32481	1.01113	1.657	16.69	3.952	0.0786
428	0.3357	0.9527	1.31379	1.01565	1.560	11.52	2.838	0.0712
528	0.4223	0.9550	1.30170	1.01998	1.480	8.975	2.261	0.0779
636	0.5321	0.9575	1.28507	1.02551	1.375	6.993	1.799	0.0908
770	0.6674	0.9663	1.25720	1.03397	1.264	5.142	1.448	0.1013
859	0.7702	0.9692	1.23091	1.04127	1.189	4.207	1.258	0.1340
904	0.8109	0.9699	1.21954	1.04561	1.160	3.803	1.196	0.1592
948	0.8553	0.9704	1.20320	1.05077	1.147	3.415	1.135	0.2046
986	0.8763	0.9701	1.19265	1.05602	1.156	3.101	1.107	0.2417
1015	0.8963	0.9745	1.18115	1.06060	1.174	2.836	1.087	0.2459
1071	0.9416	0.9724	1.15956	1.07705	1.195	2.250	1.033	0.4726
159.8°F								
42	0.0000	0.0000	...	...	...	...	...	1.0000
60	0.0072[f]	0.2708	1.32377	1.00494	2.012	98.63	37.611	0.7345
92	0.0268	0.5195	1.32258	1.00612	1.989	61.28	19.384	0.4937
95	0.0283	0.5367	1.32228	1.00565	1.989	64.98	18.965	0.4768
127	0.0444	0.6420	1.32019	1.00675	1.976	47.38	14.459	0.3746
214	0.0979	0.7763	1.31543	1.00947	1.922	27.43	7.930	0.2480
326	0.1631	0.8427	1.30881	1.01342	1.857	17.13	5.167	0.1880
437	0.2249	0.8728	1.30147	1.01752	1.800	12.35	3.881	0.1641
571	0.3026	0.8936	1.29136	1.02278	1.730	9.099	2.953	0.1526
720	0.3897	0.9040	1.27896	1.02964	1.651	6.842	2.320	0.1573
854	0.4698	0.9105	1.26510	1.03682	1.587	5.435	1.938	0.1688
1003	0.5623	0.9127	1.24571	1.04698	1.525	4.247	1.623	0.1995
1085	0.6111	0.9125	1.23205	1.05398	1.510	3.702	1.493	0.2250
1202	0.6830	0.9045	1.20840	1.06810	1.509	2.996	1.324	0.3013
1300	0.7425	0.8914	1.17879	1.09000	1.592	2.344	1.201	0.4217
1337	0.7796	0.8694	1.15468	1.11209	1.718	1.981	1.115	0.5926
220.0°F								
94	0.0000	0.0000	...	...	...	...	...	1.0000
132	0.0119[g]	0.2568	1.29803	1.01095	2.171	45.25	21.580	0.7522
214	0.0482[h]	0.5092	1.29401	1.01341	2.138	28.43	10.564	0.5157
341	0.1115	0.6668	1.28707	1.01742	2.080	17.80	5.980	0.3750
486	0.1797	0.7410	1.27874	1.02288	2.019	12.09	4.124	0.3157
653	0.2548	0.7854	1.26785	1.03014	1.961	8.523	3.082	0.2880
850	0.3452	0.8094	1.25344	1.03979	1.895	6.193	2.345	0.2911
1055	0.4367	0.8162	1.23405	1.05336	1.856	4.572	1.869	0.3263
1286	0.5601	0.8000	1.20093	1.07860	1.855	3.214	1.428	0.4546
1397	0.6447	0.7674	1.17415	1.10571	1.900	2.545	1.190	0.6547

[a] Mole fraction carbon dioxide. [b] Relative to vacuum at 6328 Å. [c] Ft³/lb mol calculated from refractive index and composition data. [d] Smoothed value, 0.043. [e] Smoothed value, 0.089. [f] Smoothed value, 0.010. [g] Smoothed value, 0.017. [h] Smoothed value, 0.054.

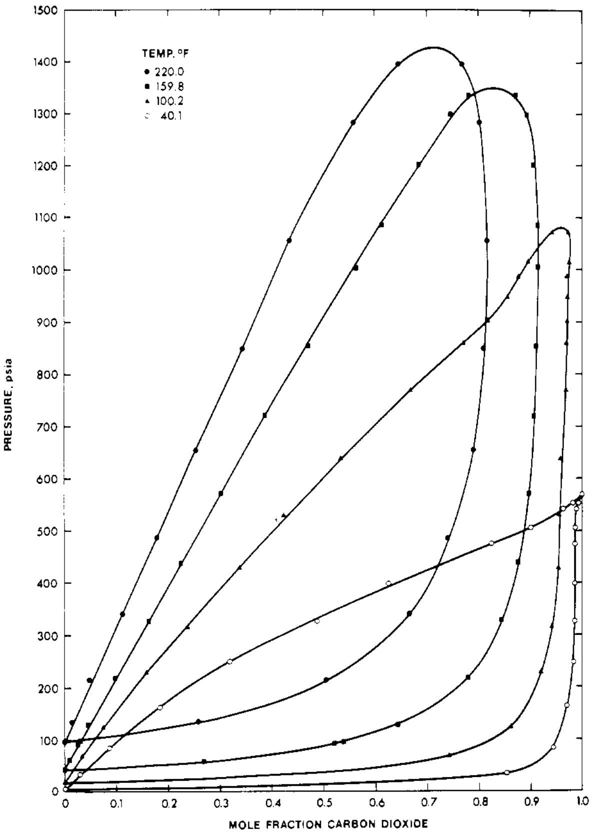

Figure 1. Pressure-equilibrium phase composition diagram for *n*-pentane-carbon dioxide system

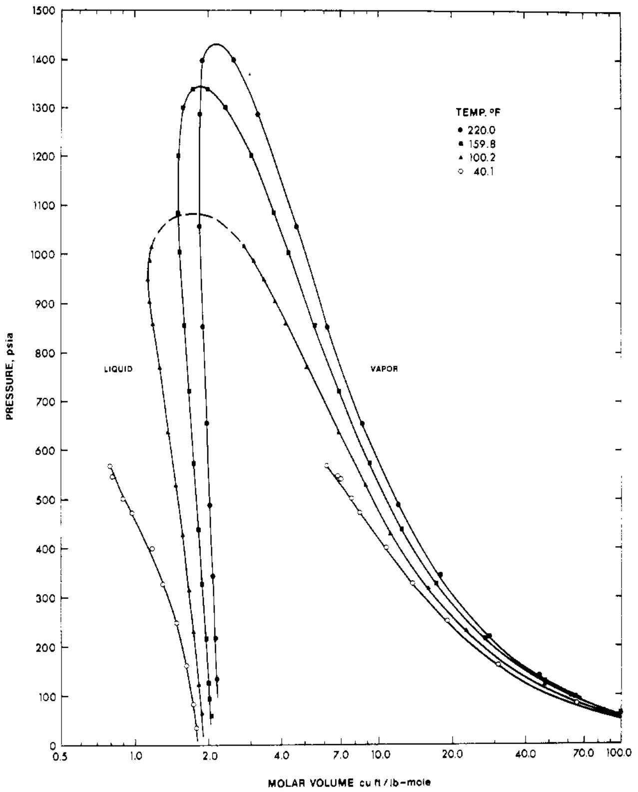

Figure 3. Pressure-equilibrium phase molar volume diagram for *n*-pentane-carbon dioxide system

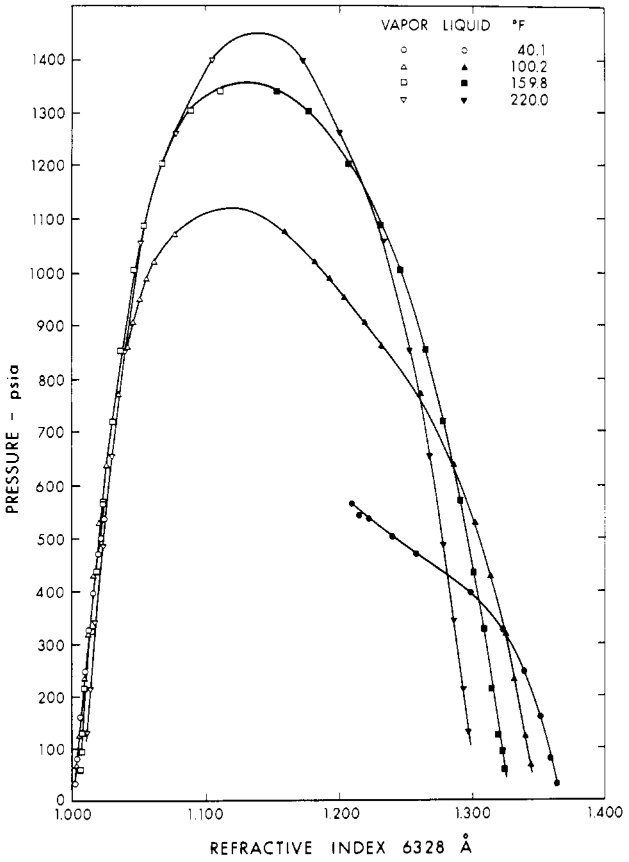

Figure 2. Pressure-equilibrium phase refractive index diagram for *n*-pentane-carbon dioxide system

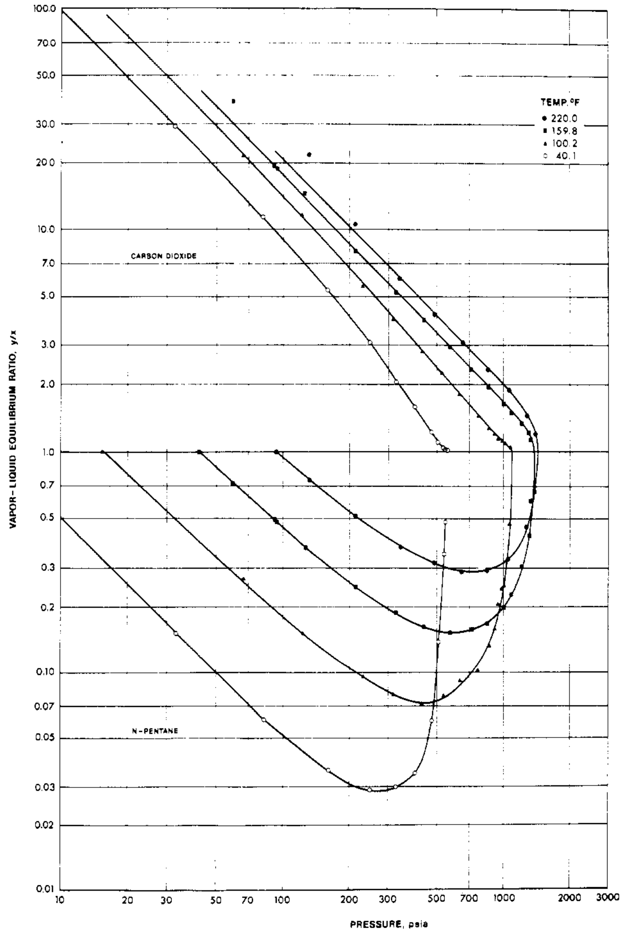

Figure 4. Equilibrium ratios for *n*-pentane and carbon dioxide in *n*-pentane-carbon dioxide binary system

Table II. Pure Component Lorentz-Lorenz Refractivities in cc/g mol at 6328 Å

	Temp, °F			
Component	40	100	160	220
Carbon dioxide	6.60	6.60	6.60	6.60
n-Pentane	25.14	25.23	25.32	25.41

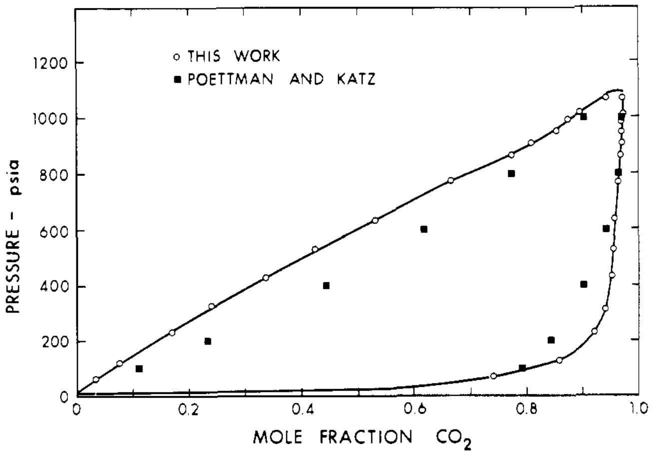

Figure 5. Pressure-equilibrium phase composition diagram for *n*-pentane-carbon dioxide system at 100°F

Results

The experimental measurements of the equilibrium-phase compositions and refractive indices, together with the calculated phase densities and vapor-liquid equilibrium ratios for both components are given in Table I. The vapor and liquid-phase envelopes at each of the four temperatures of 40.1°, 100.2°, 159.8°, and 220.0°F are shown as a function of pressure and composition in Figure 1. Figures 2–4 show the refractive indices, calculated phase densities, and the equilibrium ratios for both *n*-pentane and carbon dioxide.

The phase densities were calculated from the phase compositions and refractive indices by use of the Lorentz-Lorenz molar refractivity relationship described previously (*2*) and by assuming that the refractivities are additive. Justification for this assumption was given in an earlier paper by Besserer and Robinson (*1*) in which close agreement existed between the calculated phase densities for the *n*-butane-carbon dioxide system and the phase densities obtained by the direct volumetric measurements of Olds et al. (*4*). The molar refractivities of pure carbon dioxide and *n*-pentane which were used are shown in Table II.

The values for carbon dioxide were obtained by using the density data for pure carbon dioxide reported by Reamer et al. (*6*) and the refractive index data reported by Besserer and Robinson (*2*). The value of 6.60 cc/g mol is considered to be more reliable than the 6.65 cc/g mol reported earlier (*3*) from the low density data of Stoll (*8*). The values for *n*-pentane were obtained by using the density data for pure *n*-pentane reported by Sage and Lacey (*7*) and refractive index data obtained experimentally for *n*-pentane at each of the temperatures reported in this study at pressures up to 1500 psia.

The refractivities of carbon dioxide and *n*-pentane were essentially independent of pressure over the pressure interval of interest.

Discussion

As suspected previously, a considerable discrepancy was found between the measured phase compositions and the earlier data of Poettman and Katz (*5*). This is exemplified in Figure 5 which shows the two sets of data for the 100°F isotherm. The discrepancy in the carbon dioxide concentration in the liquid phase at a pressure of 500 psia is about 36%, and the discrepancy in the calculated equilibrium ratio for carbon dioxide is about 29%. The Henry's Law constant for carbon dioxide dissolved in *n*-pentane based on the data reported here is in agreement with the value one would expect by considering the values for carbon dioxide in other paraffin hydrocarbons.

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The authors acknowledge the work of Hans Rempis who took most of the experimental data reported herein.

Nomenclature

H = Henry's constant for carbon dioxide in *n*-pentane
f = fugacity of carbon dioxide
K_{CO_2} = equilibrium ratio for carbon dioxide
$K_{n\text{-C(5)H(12)}}$ = equilibrium ratio for *n*-pentane
n_L = refractive index of liquid
n_V = refractive index of vapor
P = pressure, psia
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
V_L = molar volume of liquid, ft^3/lb mol
V_V = molar volume of vapor, ft^3/lb mol

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