

Equilibrium-Phase Properties of Propane-Carbonyl Sulfide System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the propane-carbonyl sulfide system at 20°, 60°, 100°, 140°, and 180°F from the vapor pressure of propane to the vapor pressure of carbonyl sulfide. Although azeotropic tendencies existed toward the higher concentration range for each component, no azeotrope was found at any temperature up to 180°F. The equilibrium ratios were calculated for each component at each temperature from the phase composition data. The equilibrium-phase densities were calculated from the measured phase composition and refractive index data by use of the Lorentz-Lorenz molar refractivity relationship.

In recent years, increasing concern has been expressed over the presence of sulfur compounds in products derived from the processing of coal, petroleum, and natural gas and in the effluents arising from plants manufacturing these products. Considerable experimental and theoretical work has been reported on the behavior of hydrogen sulfide in the presence of other components found in these materials, but relatively little work appears to have been done on mixtures containing other commonly occurring sulfur compounds such as carbon disulfide, carbonyl sulfide, and the lighter mercaptans. In particular, as far as the authors can ascertain, no previous work has been reported on the phase behavior of carbonyl sulfide-paraffin hydrocarbon systems.

As a first step in a study of these systems, it was decided to investigate the equilibrium-phase properties of the propane-carbonyl sulfide system. This was chosen because of the difficulties that are encountered in the separation of these two compounds by the usual distillation procedures. The similarity in vapor-pressure relationships and critical temperatures of the materials leads to low relative volatilities and azeotropic tendencies. Consequently, process design calculations involving these components become difficult in the absence of reliable experimental data.

Experimental

The experimental equipment and procedures used in this work were essentially the same as those described in earlier papers by Besserer and Robinson (1, 2). The sample of fluid under investigation was placed in a variable volume cell in which the vapor and liquid mixture was confined between two movable pistons. The pressure of the cell contents and the location of the phases within the cell were varied by altering the relative position of the pistons using a double-acting two-cylinder Ruska pump. The refractive index of either phase viewed in an observation port was calculated from measurements made using a special window and mirror arrangement and an autocollimating telescope. These made it possible to obtain the minimum angle of deviation of a ruby laser ray passed through the window and cell contents, reflected off the mirror, and back out through the window.

Experiments were carried out at each of five temperatures at 20°, 60°, 100°, 140°, and 180°F and at a series of pres-

ures ranging from the vapor pressure of propane to the vapor pressure of carbonyl sulfide at each temperature. At each experimental condition, samples of both liquid and vapor were withdrawn for analysis, and refractive index measurements were made on each phase. The temperature was measured with a calibrated pair of iron constantan thermocouples with the reference junction kept in an ice bath, and it is believed known to $\pm 0.1^\circ\text{F}$. The pressure was measured with a calibrated Heise gauge, and each measurement was also checked with a 1500-psi strain gauge transducer. Pressure measurements are 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 6-ft by $\frac{1}{8}$ -in. diameter stainless-steel tube packed with Porapak QS maintained at a temperature of 75°C. Samples of liquid or vapor were expanded directly from the equilibrium cell to a pressure of 0.2 atm through a micrometering valve into an evacuated line. Two samples of each phase were taken at each condition, and triplicate analyses were run on each sample. These analyses were repeatable to ± 0.004 mole fraction. The signal from the chromatograph was detected by an on-line IBM 1800 computer, and peak integrations were obtained by available software and checked by an electronic integrator. The chromatograph was calibrated using pure components in a 1-cc sample loop at pressures less than 0.3 atm. The response was linear in this pressure range. The response factor of propane relative to carbonyl sulfide was 0.995 for converting area fraction to mole fraction.

Materials

Matheson Gas Products instrument grade carbonyl sulfide was used in this work. Since the purity of the liquid phase was only 97.6 mol %, further purification was necessary before tests could be conducted. This was carried out in two stages. The first consisted of venting the vapor phase four or five times from a liquid sample cooled by liquid nitrogen. The second consisted of venting the vapor phase slowly from a sample confined in the equilibrium cell. The resulting liquid had a minimum purity of 99.5 mol %. The major remaining contaminant was carbon disulfide.

The propane used in this work was also Matheson Gas Products instrument grade, and the liquid phase was 99.9 + mol % propane. This was used without further purification.

Results

The experimentally measured equilibrium-phase compositions and refractive indices, together with the calculated phase densities and equilibrium ratios, are given in Table I. Representative isothermal pressure-composition diagrams at three temperatures of 20°, 100°, and 180°F are shown graphically in Figure 1. The calculated equilibrium ratios are shown for each of these temperatures in Figure 2, and representative values of the experimental refractive indices and calculated densities are given in Figures 3 and 4, respectively.

The phase densities were calculated from the equilibrium-phase compositions and refractive indices by use of the Lorentz-Lorenz (8, 9) molar refractivity relationship as explained in earlier papers by Besserer and Robinson (1, 2). Although Keilich (7), in a theoretical study of molar refractivities of dense mixtures, has shown that the molar refractivity is addi-

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tive only in perfect gases, the magnitude of the nonadditive terms in real systems has been shown experimentally to be exceedingly small. Smyth et al. (12), for example, studied the refractive index and density of several binary liquid mixtures containing a wide variety of compounds such as alcohols,

bromides, chlorides, and paraffin hydrocarbons. In every case the maximum deviation from the molal additivity rule was less than 0.1%. Since the materials used in the study included compounds having dipole moments greater than that of water and, in fact, three times that of carbonyl sulfide, it was con-

Table I. Equilibrium-Phase Properties for Propane-Carbonyl Sulfide System

Press, psia	Composition ^a		Refractive index ^b		Molar volume ^c		Equilibrium constant	
	x	y	n _L	n _V	V _L	V _V	K _{COS}	K _{C₃H₈}
20°F								
55.8	0.0000	0.000	1.3128	1.0047	1.298	82.7	...	1.0000
57.6	0.0691	0.102	1.3176	1.0046	1.276	80.7	1.475	0.965
58.8	0.110	0.156	1.3212	1.0047	1.253	78.7	1.419	0.948
60.8	0.194	0.261	1.3260	1.0048	1.221	75.7	1.346	0.917
65.4	0.387	0.474	1.3417	1.0045	1.130	76.7	1.226	0.858
69.3	0.574	0.643	1.3527	1.0045	1.063	75.2	1.121	0.837
70.3	0.623	0.680	1.3571	1.0046	1.039	73.1	1.091	0.849
72.9	0.744	0.809	1.3702	1.0047	0.980	70.5	1.045	0.847
74.6	0.877	0.897	1.3792	1.0047	0.941	68.7	1.023	0.840
75.1	0.911	0.925	1.3834	1.0049	0.925	66.4	1.015	0.843
75.8	0.953	0.961	1.3867	1.0052	0.911	61.6	1.008	0.840
76.0	0.970	0.975	1.3890	1.0052	0.904	61.3	1.005	0.843
76.5	1.000	1.000	1.3883	1.0062	0.901	60.0	1.000	...
60°F								
109.5	0.000	0.000	1.2938	1.0088	1.384	42.9	...	1.000
110.8	0.0427	0.063	1.2968	1.0087	1.357	43.3	1.480	0.979
113.0	0.101	0.143	1.3020	1.0087	1.324	42.6	1.418	0.953
118.4	0.223	0.286	1.3081	1.0089	1.276	40.9	1.281	0.919
121.2	0.280	0.349	1.3116	1.0091	1.249	39.6	1.244	0.905
126.0	0.391	0.460	1.3197	1.0091	1.201	39.1	1.177	0.887
129.0	0.471	0.534	1.3263	1.0093	1.161	37.8	1.134	0.881
136.8	0.717	0.753	1.3429	1.0098	1.068	34.3	1.051	0.871
139.4	0.817	0.841	1.3518	1.0094	1.026	33.9	1.030	0.866
140.4	0.856	0.875	1.3570	1.0094	0.998	33.6	1.022	0.869
141.6	0.916	0.927	1.3604	1.0094	0.988	33.2	1.012	0.871
142.0	0.945	0.952	1.3640	1.0094	0.973	33.0	1.007	0.877
142.5	1.000	1.000	1.3666	1.0098	0.960	32.6	1.000	...
100°F								
190.5	0.0000	0.000	1.2722	1.0155	1.494	24.4	...	1.000
194.5	0.0715	0.103	1.2778	1.0157	1.444	23.9	1.442	0.966
196.2	0.0969	0.138	1.2763	1.0159	1.445	23.6	1.419	0.955
200.0	0.144	0.197	1.2791	1.0161	1.423	23.1	1.371	0.938
207.5	0.230	0.294	1.2832	1.0164	1.386	22.4	1.280	0.916
220.8	0.390	0.462	1.2925	1.0168	1.313	21.3	1.185	0.882
228.0	0.506	0.571	1.2994	0.0169	1.263	20.7	1.129	0.869
238.0	0.733	0.769	1.3171	1.0171	1.317	19.9	1.049	0.865
240.8	0.797	0.823	1.3221	1.0170	1.127	19.8	1.033	0.872
244.5	0.922	0.931	1.3340	1.0168	1.068	19.7	1.009	0.893
245.5	1.000	1.000	1.3412	1.0174	1.035	18.8	1.000	...
140°F								
306.5	0.000	0.000	1.2465	1.0271	1.657	14.4	...	1.000
313.5	0.0784	0.103	1.2522	1.0265	1.604	14.5	1.310	0.974
319.0	0.130	0.166	1.2541	1.0270	1.582	14.1	1.273	0.959
325.0	0.200	0.244	1.2651	1.0271	1.549	13.9	1.221	0.945
332.0	0.273	0.324	1.2621	1.0269	1.508	13.9	1.186	0.930
339.0	0.339	0.393	1.2653	1.0274	1.476	13.5	1.159	0.918
345.5	0.392	0.608	1.2661	1.0278	1.465	13.2	1.138	0.911
366.0	0.699	0.730	1.2923	0.0271	1.283	13.0	1.044	0.898
371.5	0.843	0.858	1.3077	0.0276	1.198	12.5	1.017	0.907
373.6	0.941	0.947	1.3182	1.0261	1.145	12.3	1.006	0.908
374.5	1.000	1.000	1.3151	1.0280	1.147	12.1	1.000	...
180°F								
475.4	0.000	0.000	1.210	1.0491	1.99	7.94	...	1.000
478.5	0.063	0.080	1.2226	1.0490	1.85	8.13	1.273	0.982
485.0	0.137	0.170	1.2240	1.0481	1.82	8.14	1.224	0.964
495.0	0.221	0.263	1.2292	1.0480	1.77	8.10	1.187	0.947
506.0	0.314	0.361	1.2352	1.0487	1.71	7.91	1.148	0.932
522.5	0.454	0.503	1.2443	1.0472	1.63	8.06	1.107	0.911
538.0	0.592	0.629	1.2563	1.0461	1.54	8.15	1.062	0.910
554.0	0.730	0.756	1.2601	1.0462	1.46	8.05	1.036	0.902
560.0	0.790	0.809	1.2693	1.0464	1.45	7.97	1.024	0.911
566.0	0.896	0.905	1.2805	1.0447	1.38	8.21	1.010	0.914
568.0	0.949	0.954	1.2871	1.0444	1.35	8.21	1.005	0.913
568.5	1.000	1.000	1.2863	1.0444	1.35	8.18	1.000	...

^a Mole fraction COS. ^b Relative to vacuum at 6328 Å. ^c Ft³/lb-mol calculated from refractive index and composition data.

cluded that any possible nonadditive terms in the density calculations for propane-carbonyl sulfide mixtures could be neglected without introducing an appreciable error.

To calculate the refractivity of pure propane, experimental refractive index measurements were made at each experimental temperature from the vapor pressure to about 1000 psia. The density values for propane were obtained at each experimental condition from the Benedict-Webb-Rubin equation of state with recently determined coefficients. These had been shown to reproduce the densities within an rms error of $\pm 0.42\%$ over a temperature range of 32–460°F, at pressures to 10,000 psia (10). The molar refractivities at zero pressure at each of the experimental temperatures are given in Table II. A correction was applied for the actual pressure at each experimental point, but in general, these corrections were very small. At all temperatures up to 140°F, the correction was less than 0.4%. The maximum correction occurred at the highest pressure for the 180° isotherm where it amounted to 1.7%.

The refractivity of carbonyl sulfide was calculated from refractive index measurements made in this work and from the saturated liquid densities for carbonyl sulfide reported by Partington and Neville (11). No other density measurements at higher pressures for carbonyl sulfide could be found, and consequently, a pressure correction term could not be applied for this material. The values calculated at each temperature are given in Table II.

In estimating the overall accuracy of the density calculations, the pressure correction was assumed to be of the same order as that for propane.

Discussion

The critical temperature of carbonyl sulfide has been reported to be 221.2°F by Ilosvay (6) and Hempel (5) and 216.2°F by Partington and Neville (11). The critical temperature of propane is 206.3°F (4). In view of the closeness of these critical temperatures, it was expected prior to completing the experimental work that a minimum boiling azeotrope would form. However, although azeotropic tendencies were observed from the pressure-composition diagrams at both the carbonyl sulfide and propane-rich ends, no azeotrope was found at any temperature below 180°F.

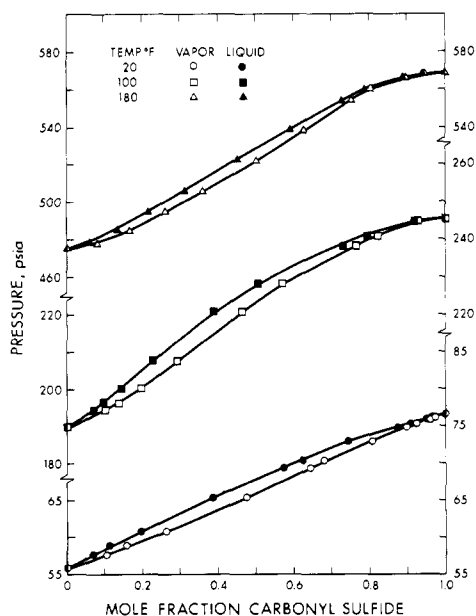


Figure 1. Pressure-equilibrium phase composition diagram for propane-carbonyl sulfide system at 20°, 100°, and 180°F

Certain difficulties were encountered with the experimental work because of the behavior of the carbonyl sulfide in the equilibrium cell. Carbonyl sulfide is described in the literature as a colorless gas, but the liquid used in this investigation was transparent and had a bright cherry red color. This increased the difficulties experienced in making the refractive index measurements with the ruby laser. Decomposition of the carbonyl sulfide to give sulfur and carbon monoxide was suspected, but there was no evidence of carbon monoxide or, in fact, of any other impurity at any time during the chromatographic analyses. When the cell was dismantled for cleaning, there was no evidence of a residue, but the ends of the normally opaque white teflon pistons used to confine the contents of the cell had turned to an ebony black where they had been in contact with carbonyl sulfide. So far, the reasons for the red color and the black teflon have not been found.

The reliability of the calculated molal volumes of the saturated liquid and vapor phases 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 0.004 mole fraction, and the refractive indices are measurable to

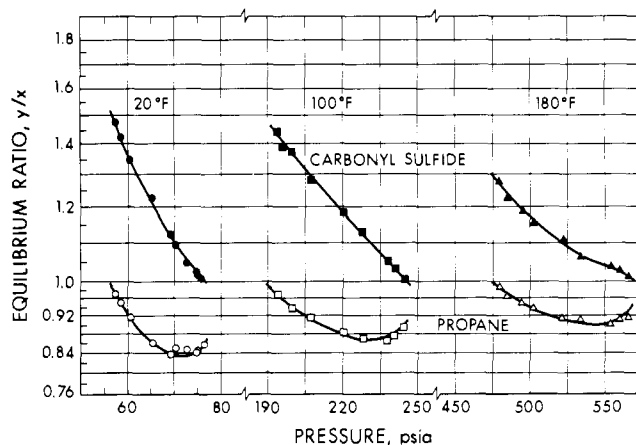


Figure 2. Equilibrium ratios for propane and carbonyl sulfide in propane-carbonyl sulfide binary system at 20°, 100°, and 180°F

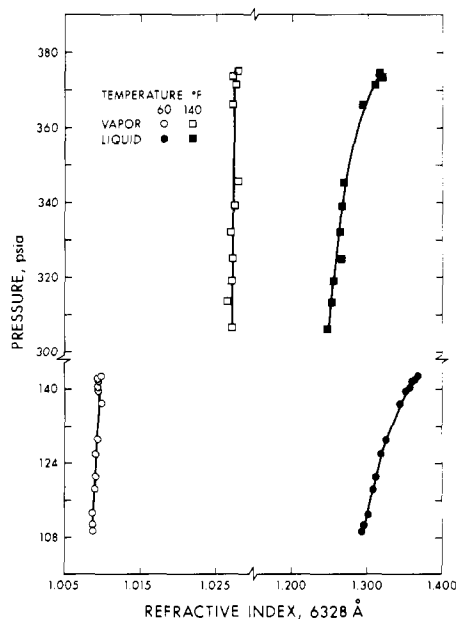


Figure 3. Pressure-equilibrium phase refractive index diagram for propane-carbonyl sulfide system at 60° and 140°F

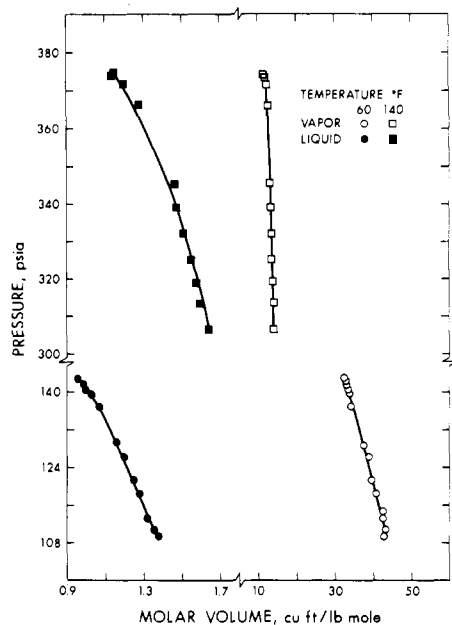


Figure 4. Pressure-equilibrium phase molar volume diagram for propane-carbonyl sulfide system at 60° and 140°F

Table II. Pure Component Lorentz-Lorenz Molar Refractivities

Temp, °F	R_{LL} , cc/g-mol	
	Propane	Carbonyl sulfide
20	15.88	13.27
60	15.80	13.43
100	15.85	13.58
140	16.17	13.98
180	16.63	15.01

± 0.0001 . The molar refractivity of the pure components is estimated to be within 0.45% for the liquid and 2.15% for the vapor. On the basis of these figures, the reliability of the molar volumes of the saturated liquid phase is expected to be within 0.7%. The reliability of the molar volumes of the saturated vapor phase is expected to be within about 1 or 2%, but at 20°F, where the refractive indices are close to unity, the error could be as high as 5%.

The entire set of pressure-composition data was subjected to a thermodynamic consistency test suggested by Christiansen and Fredenslund (3). In this method the vapor composition in equilibrium with the 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. If the absolute difference between the calculated and the measured values is within experimental error bounds, the data are considered to be consistent.

The method is based on the evaluation of the activity coefficients and the excess Gibbs free energy by a simultaneous solution of three equations using the orthogonal collocation

procedure. The vapor-phase fugacity coefficient ϕ_i is also evaluated using the Redlich-Kwong equation of state and the calculated vapor composition is then estimated from the equation

$$y_i = \frac{\gamma_i x_i f_i^0}{\phi_i P} \quad (1)$$

All of the data taken at the five temperatures totaling 50 points, when subjected to the consistency test as described above, indicated an unbiased estimate of the error variance to be 8.99×10^{-5} where the variance is defined as

$$\sigma^2 = \frac{\sum_{i=1}^n (y_{cal,i} - y_{exp,i})^2}{n - 1} \quad (2)$$

From these calculations it is concluded that the data are thermodynamically consistent.

Thermodynamic consistency tests of this type involve the use of equations of state which include properties and parameters based on data for the pure components. In view of the lack of reliable data on pure COS, it cannot be assumed, therefore, that any lack of agreement between predicted and experimental results means that the data are in error. A difference between a calculated and experimental vapor composition may result partly from an error in experimental measurements and partly from an error in prediction methods.

Nomenclature

- f^0 = fugacity of pure component liquid
- K_{COS} = equilibrium ratio for carbonyl sulfide
- $K_{C_3H_8}$ = equilibrium ratio for propane
- n = number of data points
- n_L = refractive index of liquid
- n_V = refractive index of vapor
- p = pressure, psia
- R_{LL} = Lorentz-Lorenz molar refractivity at zero pressure
- V_L = molar volume of liquid, ft³/lb mol
- V_V = molar volume of vapor, ft³/lb mol
- x = mole fraction of component in liquid phase
- y = mole fraction of component in vapor phase
- γ = liquid-phase activity coefficient
- ϕ = vapor-phase fugacity coefficient
- i = subscript denoting any component in a solution

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