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A Calorimetric Method for the Determination of Binary Phase Compositions at High Temperatures and Pressures

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ABSTRACT

The design and operation of supercritical separation equipment are dependent upon an accurate knowledge of phase equilibria among the components involved in the processes. Using high-pressure, high-temperature flow calorimeters, we have developed a method for determining phase splitting in binary mixtures from heat-of-mixing data taken in the region of the mixture critical locus. The flow calorimetric procedure for determining heats of mixing, phase equilibria, and the critical locus curve is described. The advantages and simplicity of using flow calorimetry to determine these data are discussed. Phase behavior of several binary CO_2-hydrocarbon systems is presented.

INTRODUCTION

The development of supercritical fluid processes has resulted in the need to better understand the behavior of mixtures in the critical region. In particular, supercritical separation processes involve mixtures in which one or more of the components is at a temperature and pressure exceeding the critical values of the component. Several reviews of theory and techniques involving supercritical separations have been published (1-5). For these

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operations to be effective, a detailed knowledge of enthalpies and phase equilibria at the temperatures and pressures of interest is required. Unfortunately, data for the supercritical region are not available for many mixtures and are difficult and time consuming to measure. In particular, excess enthalpy data for mixtures in this region are nearly nonexistent. In many cases, an imperfect theory is used to predict properties using parameters obtained from data at lower temperatures. This kind of extrapolation often yields values that are far from being correct. The high pressure, high temperature, flow calorimeters developed in our laboratory (6-8) have simplified measurement of excess enthalpy (H_m^E) data in supercritical regions. In addition, the straight line portions and discontinuities in the H_m^E curves have enabled us to determine gas and liquid phase compositions and, where there are sufficient data, critical locus curves.

The phase diagrams of binary systems display great variety and are dependent upon the physical characteristics of the pure components. The various classifications for binary phase diagrams and the characteristics of these diagrams are discussed in detail by Rowlinson and Swinton (9) and by Schneider (3). For a binary system, the critical locus curve is the locus of points in P-T-x space where gas and liquid phases just become indistinguishable from one another. As the critical locus curve is approached from within the two phase region along either an isobar or an isotherm, the compositions of the liquid and gas phases approach a single, critical composition.

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Several binary systems consisting of (CO_2 + a hydrocarbon) (10-23) or of (a hydrocarbon + a fluorohydrocarbon) (24-29) have been studied in our laboratory. Phase equilibria and/or critical locus data are available for four of these systems discussed in this paper: (CO_2 + pentane) (30), (CO_2 + decane) (31), (CO_2 + cyclohexane) (32), and (CO_2 + toluene) (33). In these cases, the binary systems have continuous critical loci with a pressure maximum.

This paper interprets the results of several of the studies noted above with respect to binary phase equilibria. An explanation of the shape of the H_m^E curves with respect to phase compositions is presented. The more extensive data taken for the (CO_2 + cyclohexane) and (CO_2 + toluene) systems have allowed determination of their critical locus curves, and these are compared with the curves reported in the literature.

EXPERIMENTAL

The main components of the flow calorimeter are shown in Figure 1. The apparatus has been described elsewhere in more detail.(6-8) The isothermal flow calorimeters span a temperature range of 263-773 K and can operate at pressures from 0.10 to 40.0 MPa. Temperature and pressure controls with the units are 0.01 K and 0.01 MPa,

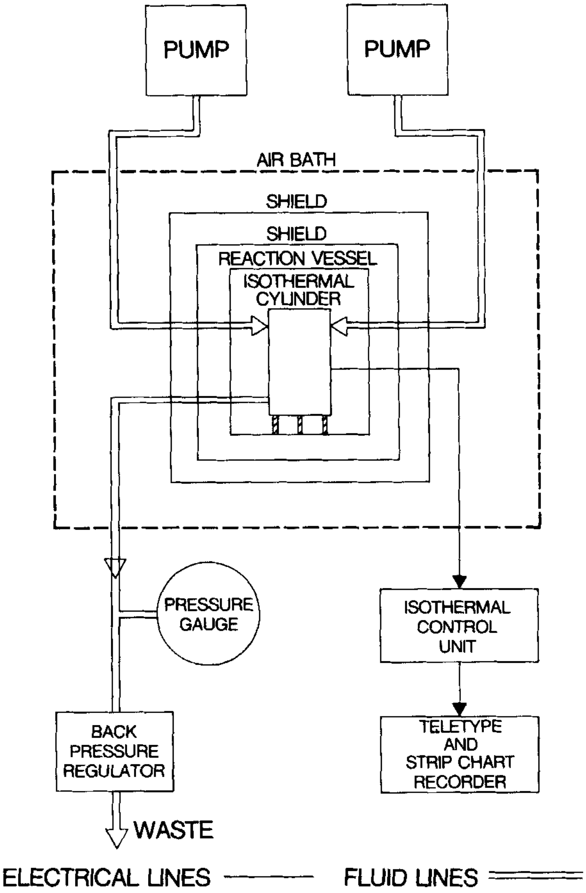

Figure 1. A block diagram of the main components of the flow calorimeter.

respectively. The main components of the flow calorimeter are the reaction vessel containing the isothermal cylinder and the equilibration coil in intimate contact with each other, the isothermal shields, the air bath, the flow circuit containing the high-pressure pumps, and the isothermal control unit.

A reaction is initiated by starting the pumps and letting the two reactants mix and flow together at a constant rate through the equilibration coil in the reaction vessel. A heat leak path provided by a Peltier cooler or by a constant temperature differential between the isothermal cylinder and the first isothermal

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shield removes energy from the equilibration coil at a constant rate. A controlled heater compensates for the heat leak as well as for energy liberated or absorbed by the reaction and maintains the equilibration coil at constant temperature. Differences in the rates of energy supplied to the heater before, during, and after the reaction are a direct measure of the enthalpy change during the reaction.

Previous results obtained using the calorimeters have been reproducible to 0.8 percent over a mole fraction range of $(0.2 < x < 0.8)$ (6). Reproducibility in the critical region was ±1 to ±2 percent mainly due to the difficulties in mixing the components in certain mole fraction regions.

The carbon dioxide (99.98 moles percent pure) used was supplied by Whitmore Oxygen Co., and was filtered prior to use through a Matheson gas purifier model 450 which also contains a molecular sieve dessicant. The hydrocarbons (> 99 moles percent pure, were supplied by Phillips Petroleum Co. or Aldrich Chemical Co.) were stored in sealed one liter bottles over approximately 50 cm^3 of Davison molecular sieves (0.3 nm effective pore diameter) and, just prior to use, were filtered through a Whatman filter (0.45 μm pore diameter) and degassed for 10 minutes in an ultrasonic bath.

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All runs were made in a steady state (fixed composition) mode. Flow rates in $cm^3 \cdot s^{-1}$ were converted to $mol \cdot s^{-1}$ and to mole fractions using the densities of the pure materials estimated as follows. The density of CO_2 at 298.15 K at the experimental pressure was calculated by interpolation from the IUPAC Tables (34). The density of each of the hydrocarbons was evaluated by using the literature value at 298.15 K and atmospheric pressure and the isothermal compressibility literature value at 298.15 K (10-23).

RESULTS AND DISCUSSION

Three H_m^E versus mole fraction CO_2 curves located along an isobar are shown in Figure 2 for the (CO_2 + toluene) binary system. A critical locus curve for (CO_2 + toluene) in P-T space as determined by Ng and Robinson (33) is shown in Figure 3. Pressure-temperature coordinates at which the curves in Figure 2 were determined are indicated. The curves at 308.15 and 573.15 K (Figure 2) were obtained under conditions where the two components are completely miscible and are representative of curves for other systems studied in corresponding regions. The curve at 413.15 K is typical of those measured in the gas-liquid coexistence region. The straight line portion in the center of the curve indicates the existence of two immiscible phases, gas and liquid. The compositions of the two phases are given by the mole fractions at either end of the linear portion where the H_m^E curve begins to deviate from a straight line.

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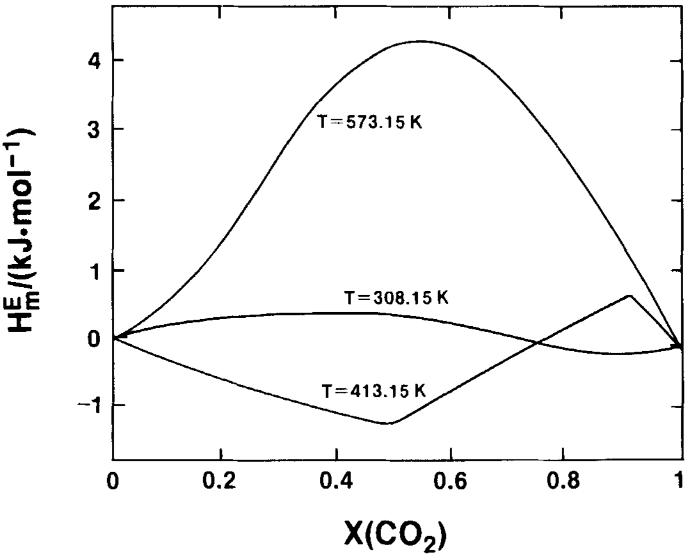

Figure 2. Plot of H_m^E against x at 12.67 MPa for [xCO_2 + (1−x)toluene] as a function of temperature.

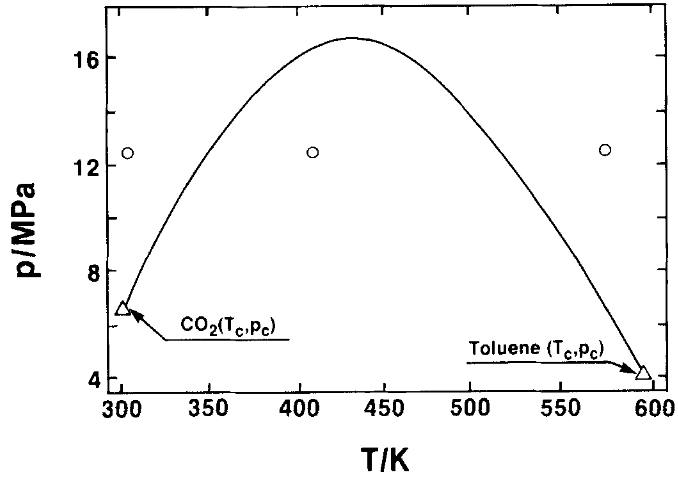

Figure 3. Plot of p against T for [xCO_2 + (1−x)toluene] showing critical points and critical locus. The p−T conditions for the plots in Figure 2 are indicated by o.

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Compositions found from H_m^E data are listed in Table 1 for the systems (CO_2 + toluene) (13,17), (CO_2 + pentane) (11,22), and (CO_2 + decane) (10,20) along with corresponding values interpolated from literature data obtained from non-calorimetric methods. Agreement between the values obtained from the two methods is excellent. Phase composition data determined calorimetrically are also listed for the (CO_2 + cyclohexane) (14,23) system.

TABLE 1
Comparison of Vapor and Liquid Equilibrium Phase Compositions Obtained from H_m^E Data and from Values Interpolated from Those in the Literature

$xCO_2 + (1-x)$toluene

T/K	p/MPa	x_l(H_m^E data)	x_l(literature)	x_g(H_m^E data)	x_g(literature)
308.15	7.60	0.970	--	0.995	0.996
358.15	7.60	0.425	0.422	0.955	0.975
	10.64	0.650	0.633	0.960	0.960
	12.67	0.810	--	0.955	--
390.15	14.91	0.725	0.708	0.925	0.900
413.15	7.60	0.290	0.295	0.930	0.923
	10.64	0.420	0.418	0.925	0.923
	12.67	0.495	0.505	0.915	0.913
	14.91	0.650	0.634	0.875	0.868
470.15	7.60	0.240	0.229	0.800	0.810
	10.64	0.350	0.333	0.810	0.814
	12.67	0.415	0.410	0.800	0.804
	14.91	0.485	0.544	0.740	0.750
508.15	10.64	0.330	--	0.610	--

$xCO_2 + (1-x)$n-pentane

T/K	p/MPa	x_l(H_m^E data)	x_l(literature)	x_g(H_m^E data)	x_g(literature)
308.15	7.58	0.960	--	0.995	--
323.15	7.58	0.810	0.90	0.945	0.96
348.15	7.58	0.565	0.71	0.860	0.89
373.15	7.58	0.475	0.60	0.815	0.83
413.15	7.58	0.410	0.49	0.570	0.67

Table 1. (continued)

			xCO_2 + (1-x)n-decane		
T/K	p/MPa	x_l(H_m^E data)	x_l(literature)	x_g(H_m^E data)	x_g(literature)
308.15	7.58	0.950	--	0.995	--
313.15	7.58	0.805	0.80	0.995	~1
323.15	7.58	0.660	0.67	0.995	~1
363.15	12.50	0.705	0.73	0.990	0.98
413.15	12.50	0.590	0.57	0.970	0.98
573.15	12.50	0.510	0.51	0.929	0.94
			xCO_2 + (1-x)cyclohexane		
308.15	7.50	0.965		0.999	
358.15	7.50	0.400		0.950	
	10.50	0.625		0.940	
	12.50	0.830		0.940	
390.15	14.39	0.745		0.875	
413.15	7.50	0.280		0.855	
	10.50	0.420		0.865	
	12.50	0.525		0.850	
	14.39	0.640		0.810	
470.15	7.50	0.260		0.670	
	10.50	0.325		0.690	
	12.50	0.390		0.640	

Using H_m^E data along several isobars for various locations within the two-phase region, the critical locus curve can be determined for a binary system. For each component, i, the ratio K_i at equilibrium of the mole fractions of component i in the gas and liquid phases, respectively is written

$$K_i = x_{g,i}/x_{l,i} \qquad (1)$$

When the compositions of the two phases become equal at the mixture critical point, K_i becomes unity. A plot of $\ln(K_i)$ versus $\ln(T)$ for several K_i values along an isobar can be extrapolated to obtain

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the corresponding temperature (T) for a K_i of one. Plots made for this study are shown in Figure 4 for the systems (CO_2 + toluene) (Figure 4a) and (CO_2 + cyclohexane) (Figure 4b). In Figure 5, critical loci taken from the literature (28,29) for these two systems are given [(CO_2 + toluene) (Figure 5a) and (CO_2 + cyclohexane) (Figure 5b)]. Mixture critical points located from the H_m^E data are shown for comparison. Agreement is good. Deviation from the literature critical locus curves is partially due to inaccuracy in the extrapolation described above. Unfortunately, data were not available near enough to the critical loci to eliminate this problem. Also, the literature curves were based upon only a few values which were themselves obtained by extrapolation. For example, the curve in Figure 5a for the (CO_2 + toluene) system is based on measured values taken at four temperatures (311.3, 352.6, 393.7, and 477.0 K).

A plot of $\ln(K_i)$ versus $\ln(P)$ for K_i values along an isotherm can also be extrapolated to the critical pressure but this is more difficult due to the large change in slope as the critical pressure is approached. Data were not taken near enough to the critical locus curve to reliably use the second method in this study.

There are several advantages in using flow calorimetry to examine binary systems in their critical region. First, H_m^E data can be measured relatively easily for the wide range of temperatures and pressures often needed to completely span the critical locus region. The large H_m^E values near the critical locus and the large changes in these values with changes in pressure, temperature, and mole fraction (10-29) can be determined accurately. These H_m^E data provide an excellent test for equations of state used to model phenomena in the critical region. Second, the presence of two phases can be detected and the compositions of these phases can be determined quantitatively without removing samples or changing the pressure-temperature-composition conditions existing within the system. Third, excellent pressure and temperature control allow precise specification of the physical conditions of measurement. Appropriate adjustment of pressures and temperatures of measurement allow the determination of the critical locus curve for the binary system. The ability to obtain both enthalpy and phase equilibrium data simultaneously should be useful in designing separation schemes.

There are drawbacks to the methods described herein. A large amount of H_m^E data is needed in order to completely describe a binary system, with some trial and error involved initially to establish the limits of the two-phase region. As either the temperature or pressure approaches very near the mixture critical value, the linear section of the H_m^E curve becomes very short and the endpoints for this section become difficult to locate precisely due to rounding of the curve.

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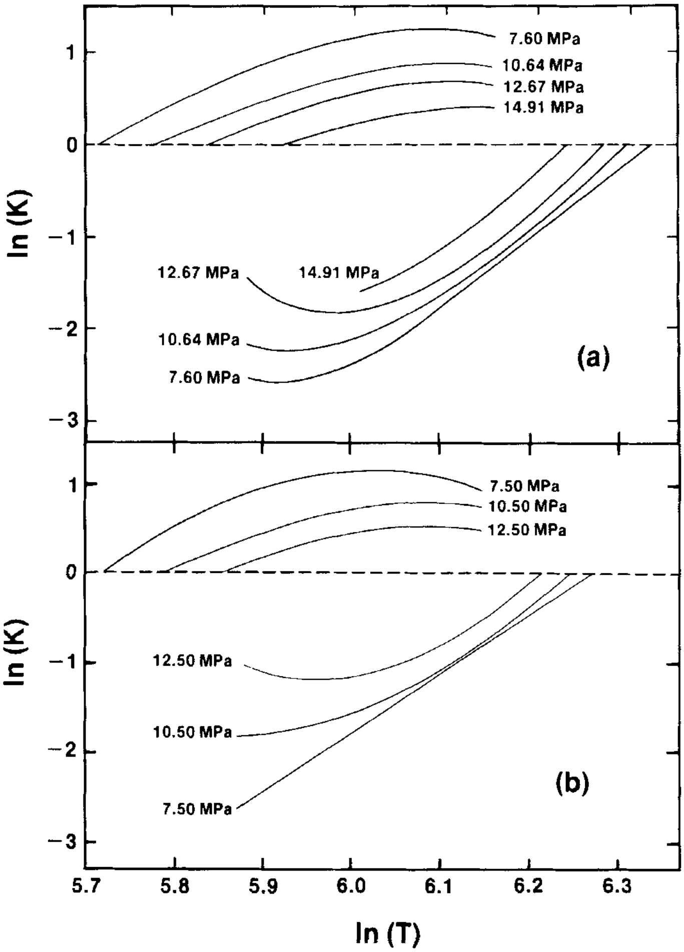

Figure 4. Plot of ln K against ln T for (a) [xCO_2 + (1-x)toluene] and (b) [xCO_2 + (1-x)cyclohexane].

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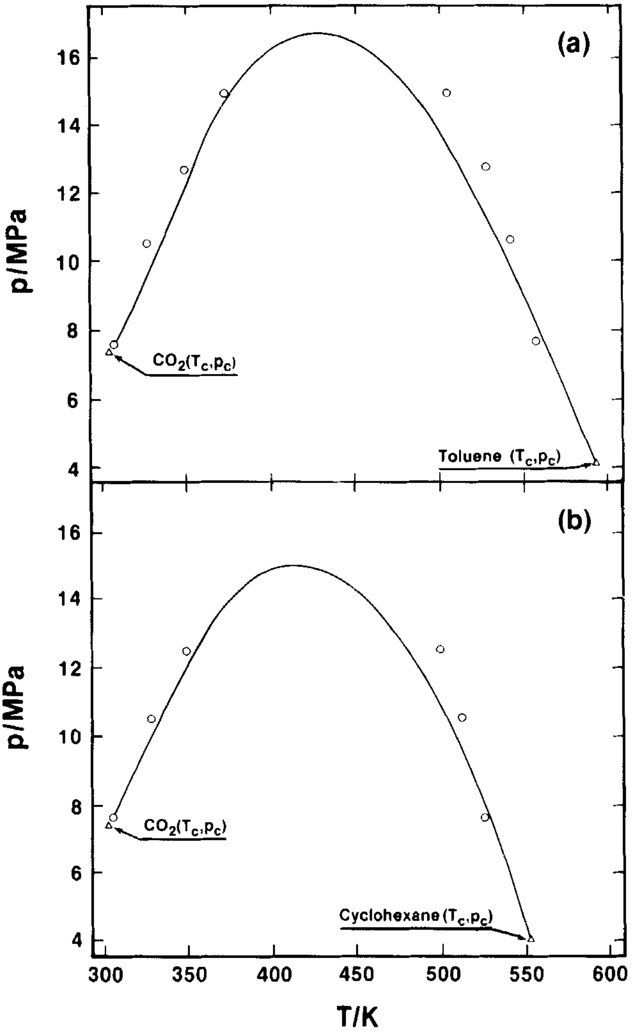

Figure 5. Plot of p against T showing critical points and critical locus curve for (a) [xCO_2 + (1-x)toluene] and (b) [xCO_2 + (1-x)cyclohexane]. Points calculated from H_m^E data are indicated by o.

This study has dealt only with the simplest of phase phenomena. Schneider (3) and Rowlinson and Swinton (9) have described a great variety of phase diagrams for binary systems alone. Also, in addition to the gas-liquid equilibria studied thus far, there are gas-gas and liquid-liquid equilibria which can be explored through flow calorimetry.

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REFERENCES

1. N. Basta, High Technology, June 1984, 75.

2. M.E. Paulaitis, V.J. Krukonis, R.T. Kurnik, and R.C. Reid, Rev. Chem. Eng. 1, 179 (1983).

3. G.M. Schneider, Agnew. Chem. Int. Ed. Engl. 17, 716 (1978).

4. M.E. Paulaitis, R.G. Kander, and J.R. DiAndreth, Ber. Bunsenges. Phys. Chem., 88, 869 (1984).

5. E. Stahl, K.W. Quirin, A. Glatz, D. Gerard, and G. Rau, Ber. Bunsenges. Phys. Chem., 88, 900 (1984).

6. J.J. Christensen and R.M. Izatt, Thermochim. Acta., 73, 117, (1984).

7. J.J. Christensen, R.M. Izatt, D.J. Eatough, and L.D. Hansen, J. Chem. Thermodyn., 10, 25 (1978).

8. T.A. McFall, M.E. Post, S.G. Collins, J.J. Christensen, and R.M. Izatt, J. Chem. Thermodyn., 13, 41 (1981).

9. J.S. Rowlinson and F.L. Swinton, "Liquids and Liquid Mixtures," 3rd ed.; Butterworth: Boston, MA, 1982.

10. C. Pando, J.A.R. Renuncio, T.A. McFall, R.M. Izatt, and J.J. Christensen, J. Chem. Thermodyn., 15, 173 (1983).

11. C. Pando, J.A.R. Renuncio, R.M. Izatt, and J.J. Christensen, J. Chem. Thermodyn., 15, 259 (1983).

12. C. Pando, J.A.R. Renuncio, R.M. Izatt, and J.J. Christensen, J. Chem. Thermodyn., 15, 231 (1983).

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13. C. Pando, J.A.R. Renuncio, R.S. Schofield, R.M. Izatt, and J.J. Christensen, J. Chem. Thermodyn., 15, 747 (1983).

14. J.J. Christensen, S.P. Christensen, R.S. Schofield, P.W. Faux, P.R. Harding, and R.M. Izatt, J. Chem. Thermodyn., 15, 1151 (1983).

15. J.J. Christensen, S.P. Christensen, R.S. Schofield, P.W. Faux, P.R. Harding, and R.M. Izatt, J. Chem. Thermodyn., 16, 249 (1984).

16. J.J. Christensen, T.A.C. Walker, R.S. Schofield, P.W. Faux, P.R. Harding, and R.M. Izatt, J. Chem. Thermodyn., 16, 445 (1984).

17. J.J. Christensen, D.M. Zebolsky, and R.M. Izatt, J. Chem. Thermodyn., 17, 1 (1985).

18. J.J. Christensen, D.M. Zebolsky, and R.M. Izatt, J. Chem. Thermodyn., 17, 183 (1985).

19. J.J. Christensen, D.M. Zebolsky, and R.M. Izatt, J. Chem. Thermodyn., 17, 785 (1985).

20. J.J. Christensen, D.R. Cordray, and R.M. Izatt, J. Chem. Thermodyn., 18, 53 (1986).

21. J.J. Christensen, D.R. Cordray, and R.M. Izatt, J. Chem. Thermodyn., in press, M-1917.

22. J.J. Christensen, P.W. Faux, R.M. Izatt, and D.R. Cordray, J. Chem. Thermodyn., in press, M-1953.

23. J.J. Christensen, T.A.C. Walker, R.M. Izatt, and D.R. Cordray, J. Chem. Thermodyn., in press, M-1962.

24. J.J. Christensen, M.E. Post, T.A. McFall, and R.M. Izatt, Thermochim. Acta., 50, 73 (1981).

25. R.S. Schofield, M.E. Post, T.A. McFall, R.M. Izatt, and J.J. Christensen, J. Chem. Thermodyn., 15, 217 (1983).

26. J.J. Christensen, S.P. Christensen, R.S. Schofield, P.W. Faux, P.R. Harding, and R.M. Izatt, Thermochim. Acta, 67, 315 (1983).

27. R.M. Izatt, R.S. Schofield, P.W. Faux, P.R. Harding, S.P. Christensen, and J.J. Christensen, Thermochim. Acta, 68, 223 (1983).

28. J.J. Christensen, D.M. Zebolsky, R.S. Schofield, D.R. Cordray, and R.M. Izatt, J. Chem. Thermodyn., 16, 905 (1984).

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29. J.J. Christensen, D.R. Cordray, D.M. Zebolsky, and R.M. Izatt, J. Chem. Thermodyn., 17, 335 (1985).

30. F.H. Poettmann and D.L. Katz, Ind. Eng. Chem. 37, 847 (1945).

31. H.H. Reamer and B.H. Sage, J. Chem. Eng. Data 8, 508 (1963); H.H. Reamer and B.H. Sage, J. Chem. Eng. Data 10, 49 (1965).

32. I.R. Krichevskii and G.A. Sorina, Russ. J. Phys. Chem. 34, 679 (1960).

33. H.J. Ng and D.B. Robinson, J. Chem. Eng. Data 23, 325 (1978).

34. Carbon Dioxide. IUPAC Thermodynamic Tables of the Fluid State. Pergamon Press: Oxford. 1976.

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