Carbon Dioxide-Ethane Phase Equilibrium and Densities from Experimental Measurements and the B-W-R Equation

Liquid composition-total pressure and liquid composition-liquid density data for the carbon dioxide-ethane system were measured at −31.7°, −17.8°, −3.9°, and 10.0°C (−25°, 0°, 25°, and 50°F ±0.02°F), from 0 to 80 mole % CO_2 at 10°C and 0 to 100% CO_2 for the other isotherms. The Benedict-Webb-Rubin equation of state with a modified A_0 mixing rule was used to correlate the composition-pressure data, with deviations in predicted pressures of only 0.8% average and 2% maximum. Vapor-liquid equilibrium compositions and component K values y/x were then predicted for this minimum boiling azeotrope system from 10° down to −56.7°C (50° to −70°F).

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The objective of this study was to obtain sufficient experimental data on the behavior of the minimum boiling azeotrope system, carbon dioxide-ethane, to develop mathematical correlations which can be used for reliable predictions of vapor-liquid equilibrium compositions and vaporization equilibrium constants for designing the most efficient distillation towers for the cryogenic processing of natural gas. The importance of the carbon dioxide-ethane system results primarily from the fact that most natural gases contain sufficient carbon dioxide to warrant concern in processing plants, where solidified carbon dioxide can dangerously plug low-temperature equipment. Carbon dioxide also lowers the heating value of natural gas.

To remove the carbon dioxide, either absorption in amine solutions or adsorption by molecular sieves has commonly been used, but low temperature distillation offers both operating and economic advantages. The accurate phase equilibrium data required for design of the most efficient cryogenic distillation towers were not available from the literature, however.

Therefore, experimental measurements of total vapor pressure versus liquid composition were made as a basis for developing correlations for calculating the needed phase equilibrium data, and liquid density data were determined in the same runs for use in other design calculations.

A modified mixing rule with the Benedict-Webb-Rubin equation of state was then used to correlate the pressure-composition data. Finally, the resulting equations were employed to predict vapor-liquid compositions, and equilibrium constants for both components, over the temperature range of interest.

CONCLUSIONS AND SIGNIFICANCE

The experimental values obtained for total vapor pressure and liquid density as a function of saturated liquid phase composition at −31.7°, −17.8°, −3.9°, and 10.0°C (−25°, 0°, 25°, and 50°F) are presented in Table 1. The range of liquid compositions covered was 0 to 80 mole % CO_2 at 10°C and 0 to 100% at each of the other isotherms.

The Benedict-Webb Rubin equation of state with a modified A_0 mixing rule, presented in Table 2, very successfully correlated the experimental pressure-composition data, with an average deviation in predicted pressure of only 0.8% and a maximum deviation of 2%. These correlation curves are shown in Figures 4 and 5. The vapor-liquid equilibrium compositions, and the equilibrium constants for both components, which were then predicted with these equations over the temperature range from 10° down to −56.7°C (50° to −70°F) are shown in Figures 6 to 9. These results have considerable industrial significance in that they provide the needed information for designing the most efficient distillation towers for the cryogenic processing of natural gas.

It is also significant that it was demonstrated that the Benedict-Webb-Rubin equation when coupled with the modified A_0 mixing rule can so well correlate and predict the behavior of such a highly nonideal hydrocarbon-nonhydrocarbon system, including its minimum boiling azeotrope. It was found that the composition of the azeotrope shifts gradually toward a higher ethane content as the temperature and pressure are decreased. The binary interaction coefficient for the modified A_0 mixing rule was found to be inversely proportional to the temperature. It was also found that the original A_0 mixing rule was completely inadequate for describing the behavior of this system, not even predicting an azeotrope at all.

The importance of the carbon dioxide-ethane system results mainly from the low-temperature processing of natural gas. The majority of natural gases contain sufficient concentrations of carbon dioxide to require concern, and it must be removed to avoid plugging of the low-temperature equipment by solidified carbon dioxide. In addition to this operating problem, carbon dioxide has the undesirable effect of reducing the heating value of natural gas in direct proportion to its concentration. The common techniques for its removal are by amine absorption or by selective adsorption on molecular sieves. Another approach which was shown to have operating and economic advantages is fractional distillation. The design of this unit requires accurate phase equilibrium data for the carbon dioxide-ethane system in the cryogenic temperature region. These data were not available from the literature.

To remedy this problem a two-step approach was taken. The first was an experimental determination of total vapor pressure versus liquid composition and liquid density versus liquid composition for saturated liquid mixtures of ethane and carbon dioxide. The investigation was carried out at four isotherms: −31.7°, −17.8°, −3.9°, and 10.0°C (−25°, 0°, 25°, and 50°F). An equilibration cell was charged with a known amount of ethane and then pressurized with carbon dioxide to the desired level. After the mixture reached equilibrium, a liquid sample was isolated, weighed for density determination, and analyzed on a gas chromatograph. The second step was the correlation of these data by the Benedict-Webb-Rubin equation of state to provide accurate extrapolations and interpolations to any desired design conditions. While the density data are useful in the design calculations, only the x-T-P data were correlated in this study.

EXPERIMENT

Apparatus

A rocking equilibration cell assembly designed as a modification of that of Buell and Eldridge (1962) was constructed as shown in Figure 1. The interface, liquid, and expansion chambers were all of carbon steel and were hydrostatically tested to 136 atm. Their approximate volumes were 100, 60, and 110 cm,^{3} respectively. The 1.9 cm (¾-in.) ball valve and the 3.2 mm (⅛-in.) needle valves were all rated for 136 atm, and the 6.35 mm (¼-in.) pressure relief valve was adjusted to open at 68 atm. The relief valve was not suitable for −31.7°C operation so was replaced for that isotherm with a rupture disk rated for 75 atm at room temperature.

The entire cell assembly on its saddle was totally immersed in a large low temperature bath controllable to ±0.01°C, in which it could be rocked via the arm connected to a motor mounted on top of the lid above. The 3.2 mm (⅛-in.) semi-flexible copper coil from the interface chamber was connected to the charging system and pressure gauge as shown in Figure 2. Both the carbon dioxide and ethane were 99.99% purity grade, and the cylinders were equipped with special high pressure regulators capable of delivery pressures up to about 68 atm for carbon dioxide and 27 atm for ethane. The system equilibrium pressures were measured with a Heise Pressure Gauge featuring a thermal compensator that would take temperature differences into account down to −35°C. It had a 68 atm dial with ½ lb./sq. in. (3.45 kN/m^2) graduations and a double revolution pointer, and was rated at better than 1 lb./sq. in. (6.9 kN/m^2) accuracy, 0.1 lb./sq.in. (0.69 kN/m^2) sensitivity, and 0.2 lb./sq.in. (1.4 kN/m^2) reproducibility.

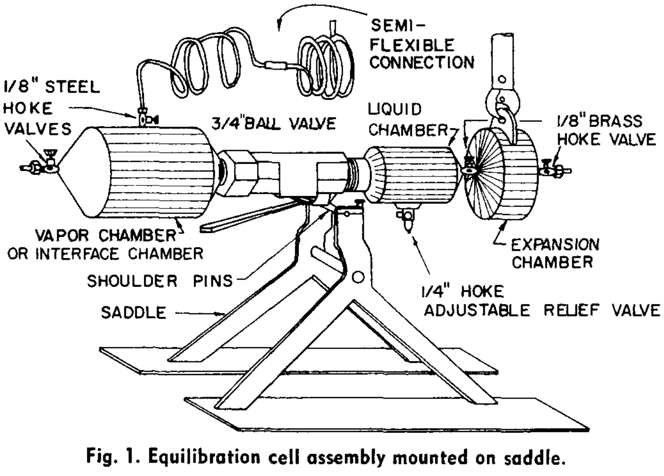

Fig. 1. Equilibration cell assembly mounted on saddle.

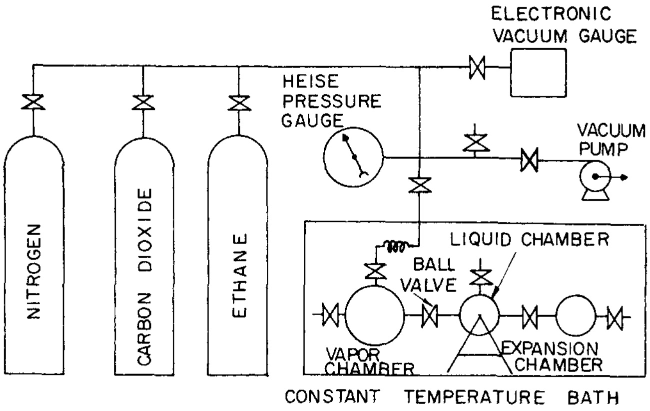

Fig. 2. Experimental system as assembled for a run.

Analyses were made with a gas chromatograph, using the thermal conductivity detector and a column packed with Porapak Q (Analabs, Inc.). Liquid densities were measured by determining the net weight of the samples isolated in the volume-calibrated liquid chamber, using a 1,500 g. pulp balance with ±0.005 g. accuracy.

Procedure

After thoroughly cleaning and drying the equilibrium cell assembly it was first evacuated, outside the bath, with the ball valve half open to ensure that the space between the ball and its housing would also be emptied. The valve between the liquid chamber and the expansion chamber was then closed, isolating the latter under vacuum. The ball valve was next fully opened and to remove any residual air the cell (except for the closed expansion chamber) was flushed with ethane and re-evacuated.

The cell was then cooled in dry ice so that the desired amount of ethane could be charged and condensed. The weight of liquid ethane which would result in approximately 100 cm^3 of final liquid solution after equilibration was estimated in advance, and the cell was charged until that weight had condensed in it. The final total liquid phase volume of 100 cm^3 or so would ensure both enough vapor space to provide ample interface during rocking for good equilibration and enough liquid so that the interface was well above the ball valve during isolation of the sample.

The cell assembly containing the ethane was then mounted on its saddle, submerged in the bath, and connected to the rocker arm and to the charging system as shown in Figure 2. After evacuating all connecting lines, the cell was charged with carbon dioxide while rocking for about 15 min. with the high pressure regulator set at the desired total pressure for that run. Upon equilibration for an additional hour or more after the carbon dioxide cylinder valve had been closed, the then constant total system pressure was read on the precision gauge.

The cell assembly was then rotated to a vertical position while still totally submerged, with the interface chamber at the top, and the completely liquid sample was isolated in the liquid chamber by closing the ball valve. When the cell assembly was lifted from the bath, the valve to the expansion chamber was immediately opened to avoid excessive pressure developing in the liquid chamber as it warmed to room temperature.

After venting and then removing the interface chamber from the cell assembly, the remainder of the assembly containing the sample was thoroughly cleaned and dried externally and then weighed (to ±0.005 g) for the density determination. The volume in which the sample had been isolated was precisely known from calibration to within one part per thousand as a function of pressure at each isotherm, using liquids of known density (water at 10°C and 99.99% pure propane for all other isotherms) in a modification of the same procedure as described above, since composition equilibration was not involved.

TABLE 1. EXPERIMENTAL VALUES OF TOTAL VAPOR PRESSURE AND DENSITY OF SATURATED LIQUID SYSTEM OF ETHANE AND CARBON DIOXIDE

−31.7°C (−25°F)			−17.8°C (0°F)			−3.9°C (25°F)			10°C (50°F)		
Mole % CO_2	Pressure, atm	Density g/cm^3	Mole % CO_2	Pressure, atm	Density g/cm^3	Mole % CO_2	Pressure, atm	Density g/cm^3	Mole % CO_2	Pressure, atm	Density g/cm^3
0	9.96	0.4614	0	14.83	0.4352	0	21.37	0.4149	0	29.72	0.3731
8.32	11.89	0.4895	12.09	18.81	0.4800	16.56	27.51	0.4552	13.98	36.73	0.3953
17.11	13.45	0.5192	24.36	21.17	0.5103	31.88	31.35	0.4956	22.81	36.69	0.4140
30.47	14.98	0.5729	34.78	22.64	0.5528	42.29	33.20	0.5322	25.98	41.25	0.4200
45.94	15.89	0.6414	46.51	23.72	0.6115	51.25	34.27	0.5674	38.13	45.15	0.4457
56.04	16.17	0.7007	57.85	24.27	0.6631	57.62	34.75	0.5982	50.92	47.58	0.4881
63.30	16.24	0.7443	59.27	24.34	0.6699	62.11	35.02	0.6259	55.39	48.23	0.5015
71.45	16.15	0.8017	60.64	24.31	0.6814	62.84	35.05	0.6325	57.30	48.46	0.5112
79.96	15.89	0.8759	62.37	24.37	0.6913	67.13	35.18	0.6528	60.62	48.60	0.5206
90.98	14.96	0.9841	63.84	24.37	0.7011	71.83	35.19	0.6858	62.49	48.87	0.5434
100.00	13.23	1.0807	65.54	24.37	0.7122	76.92	34.99	0.7240	67.49	49.23	0.5750
			70.53	24.37	0.7450	84.07	34.50	0.7819	71.19	49.24	0.5966
			70.91	24.31	0.7474	86.11	34.23	0.7997	77.12	49.00	0.6309
			73.66	24.22	0.7635	93.66	32.84	0.8684	80.12	48.84	0.6682
			82.35	23.76	0.8350	100.00	31.05	0.9524			
			92.72	22.40	0.9371						
			100.00	20.72	1.0213						

TABLE 2. *B-W-R* EQUATION OF STATE

B-W-R Equation

$$P = RTD + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^3}{T}[(1 + \gamma d^2)e^{-\gamma d^2}]$$

Original *B-W-R* Mixing Rules

$$A_0 = \sum_i \sum_j x_i x_j A_{0i}^{1/2} A_{0j}^{1/2} \qquad a = [\sum_i (x_i a_i^{1/3})]^3$$

$$B_0 = \sum_i x_i B_{0i} \qquad c = [\sum_i (x_i c_i^{1/3})]^3$$

$$C_0 = [\sum_i (x_i C_{0i}^{1/2})]^2 \qquad \alpha = [\sum_i (x_i \alpha_i^{1/3})]^3$$

$$b = [\sum_i (x_i b_i^{1/3})]^3 \qquad \gamma = [\sum_i (x_i \gamma_i^{1/2})]^2$$

Modified *B-W-R* Mixing Rule

$$A_0 = \sum_i \sum_j x_i x_j A_{0i}^{1/2} A_{0j}^{1/2} (1 - k_{ij})$$

where x is the mole fraction in the liquid or vapor phase

Finally, the total sample was completely vaporized and transferred out of the cell system by expansion into a gas bag, from which, after thorough mixing to ensure homogeneity, samples were taken through the gas sampling valve on the gas chromatograph for analysis for ethane and carbon dioxide.

THERMODYNAMIC FRAMEWORK

The Benedict-Webb-Rubin equation of state shown in Table 2, from Benedict et al. (1940), was developed to predict thermodynamic properties and phase equilibrium data for light hydrocarbons and their mixtures at moderate and high reduced temperatures. Each pure component is defined by eight coefficients. Mixing rules are then used to combine the pure-component B-W-R coefficients for the prediction of mixture properties. The ability of this equation of state to handle both the vapor and liquid phases is one of its significant advantages and provides for internally consistent predictions between the phases.

Benedict et al. (1942) demonstrated the ability of their equation to successfully predict phase equilibrium data for the methane-butane system at high temperatures. Nine years later, the same group extended the equation to low temperature predictions of pure-component vapor pressures by defining the pure-component C_0 coefficient as a function of temperature.

Stotler and Benedict (1953) further extended the B-W-R equation to predict hydrocarbon-nonhydrocarbon systems. They discovered that even though pure component vapor pressures were accurately predicted, the calculated phase equilibrium for mixtures of the same pure components showed significant errors. The inaccuracies were said to lie in the inability of the mixing rules to describe system nonidealities. The solution to this problem was to make the A_0 mixing rule a function of the binary nonidealities. Their modification of this mixing rule consisted of introducing a binary interaction coefficient k_{ij}, which was back calculated from experimental phase equilibrium data into the A_0 mixing rule. Using this modification, phase equilibrium data for the nitrogen-methane system were accurately predicted. Barner and Adler (1968), while working with natural gas systems, found that though predictions for wide-boiling hydrocarbon-hydrocarbon mixtures could be accurately made at moderate and high temperatures, errors appeared at low temperatures. Their conclusion was that the mixing rules were the cause of these errors. Thus even for the prediction of a relatively close-boiling system, methane-propane, at low temperatures the original mixing rules were inadequate.

Orye (1969) successfully predicted phase equilibrium data for several wide-boiling hydrocarbon-hydrocarbon and hydrocarbon-nonhydrocarbon (CO_2, H_2S, etc.) systems, by the modified A_0 mixing rule of Stotler and Benedict (1953). Included in these systems were the methane, propane, and butane-carbon dioxide binaries. Accurate data for the ethane-carbon dioxide system were not available for testing at the time.

CARBON DIOXIDE-ETHANE SYSTEM

The experimental data obtained in this investigation are presented in Table 1. The reproducibility and uncertainty in the liquid density measurements were ±0.001 g/cm³. The precision of the chromatographic analyses when expressed as mole % of the mixture is inherently a function of operating point in the composition range, being poorest at the mid-point. The reproducibility and uncertainty of these liquid composition measurements were ± 0.4 mole % at 50 mole % and ± 0.3 mole % at the azeotropic point.

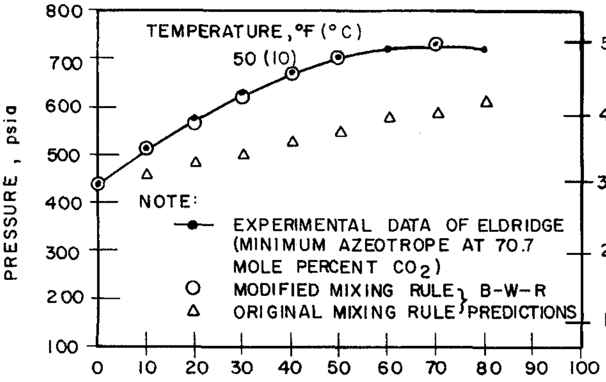

Fig. 3. Pressure-liquid composition curve for carbon dioxide-ethane at 10°C: predictions vs. data.

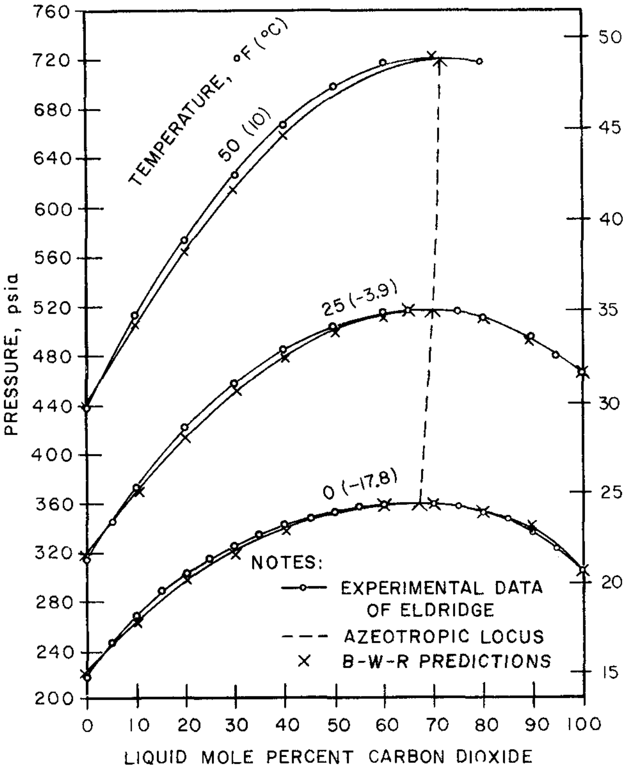

Fig. 4. Pressure-liquid composition curve for carbon dioxide-ethane from −17.8° to 10°C: predictions vs. data.

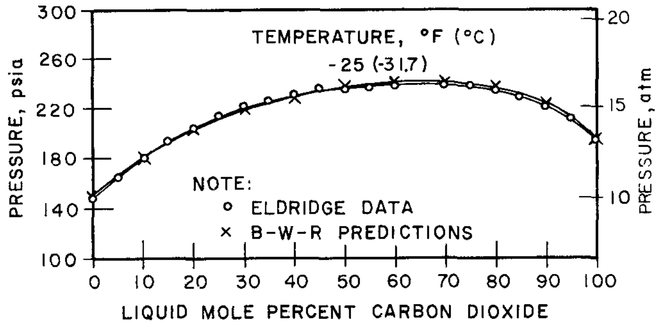

Fig. 5. Pressure-liquid composition curve for carbon dioxide-ethane at −31.7°C: predictions vs. data.

The experimental pressure-composition data were correlated by the B-W-R equation of state using the modified A_0 mixing rule of Stotler and Benedict (1953); see Table 2. A bubble-point program was written to satisfy the following binary conditions:

$$P(d^V, y_1) = P(d^L, x_1) \quad (1)$$

$$f_1(d^V, y_1) = f_1(d^L, x_1) \quad (2)$$

$$f_2(d^V, y_1) = f_2(d^L, x_1) \quad (3)$$

at a specified temperature and liquid composition. These equations yield the desired equilibrium constants

$$K_i(\text{calc.}) = \frac{f_i^L/x_i}{f_i^V/y_i} = \frac{y_i}{x_i}$$

Figure 3 fully documents the limitations of the original A_0 mixing rule in predicting the carbon dioxide-ethane system. In this case the minimum boiling azeotrope was completely missed.

The eight pure-component B-W-R coefficients for carbon dioxide and ethane were obtained from Orye (1969) with the exception of the C_0 coefficients which were developed by the M. W. Kellogg Company as a function of temperature. Excellent vapor pressure predictions over the complete temperature range were obtained using these coefficients. The binary interaction coefficient k_{ij} for this modified A_0 mixing rule was found to be inversely proportional to temperature. The values of C_0 and k_{ij} are given below over the temperature range for which equilibrium data correlations are presented. The metric units used are atm, °K and g-mole/l; the English units are lb./sq.in.abs., °R, and lb-mole/ft³.

Temperature		$C_0^{1/2}$, Ethane		$C_0^{1/2}$, Carbon Dioxide		
°C	°F	Metric	English	Metric	English	k_{ij}
10.00	50	423.675	46831.24	374.542	41400.23	0.130
4.44	40	423.642	46827.64	374.542	41400.23	0.134
−6.67	20	423.575	46820.20	374.542	41400.23	0.142
−17.78	0	423.454	46806.81	374.542	41400.23	0.150
−28.89	−20	423.218	46780.74	372.546	41179.71	0.158
−40.00	−40	422.807	46735.27	372.087	41128.93	0.166
−51.11	−60	422.159	46663.67	371.203	41031.18	0.174
−56.67	−70	421.727	46615.96	370.486	40951.95	0.178

Predictions of the experimental *x-T-P-* data using this modified A_0 mixing rule are presented in Figures 4 and 5. The average deviation of the predicted pressures is 0.8% with a maximum of 2% for all the experimental isotherms. These are excellent predictions for a system which is complicated by a minimum boiling azeotrope. The B-W-R equation is used to extrapolate the experimental results from −37.7° to −56.7°C (−25° to −70°F). Predicted data for *x-y-T-P* are presented in Figures 6 and 7 and the corresponding equilibrium constants in Figures 8 and 9.

Phase equilibrium data for the carbon dioxide-ethane system were published previously by Khazanova et al. (1967) and Kuenen (1897). Kuenen's data covered a composition range of 57 to 85% carbon dioxide for temperatures of 10° to 23.3°C. The data of Khazanova et al. were measured over a 100% composition range for temperatures from 10° to 20°C. Both sets of data were measured very close to the true critical point of the mixture composition in question. All the data are at reduced temperatures above 0.93. The accuracy of these two sets of measurements is in question because of the high susceptibility to error of experimental measurements in the critical region. Furthermore, data in this critical region are far removed from the areas of industrial use. More recently, Kurata-Swift (1971) obtained new data on this system for NGPA. Their data cover a much wider and lower temperature range than earlier data, extending from 15.5° to −51.1°C (60° to −60°F) within a concentration range of 13 to 78% carbon dioxide.

The data of Khazanova et al. at 10°C, and Kurata-Swift at −6.7°, −28.9°, and −51.1°C are also included in Fig-

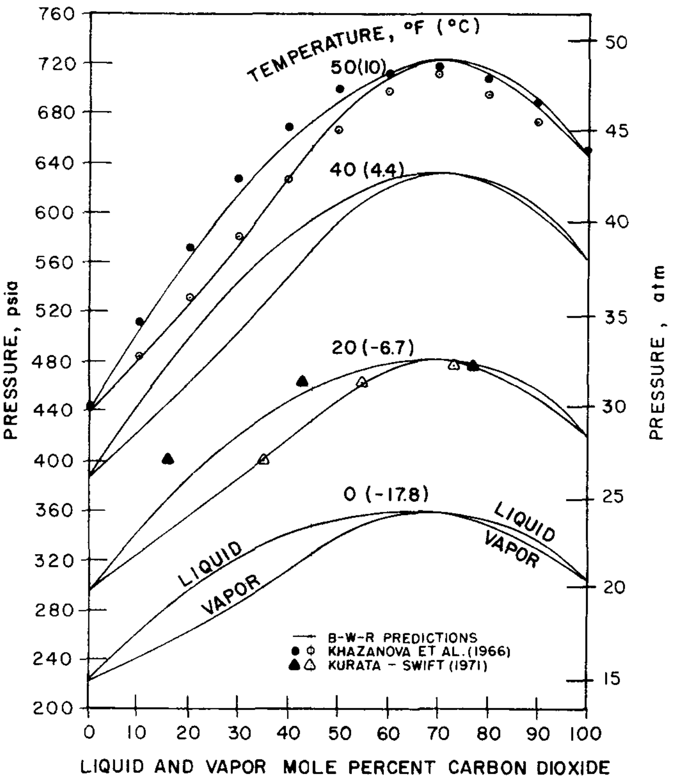

Fig. 6. B-W-R predictions of the bubble-dew points for carbon dioxide-ethane system from −17.8° to 10°C.

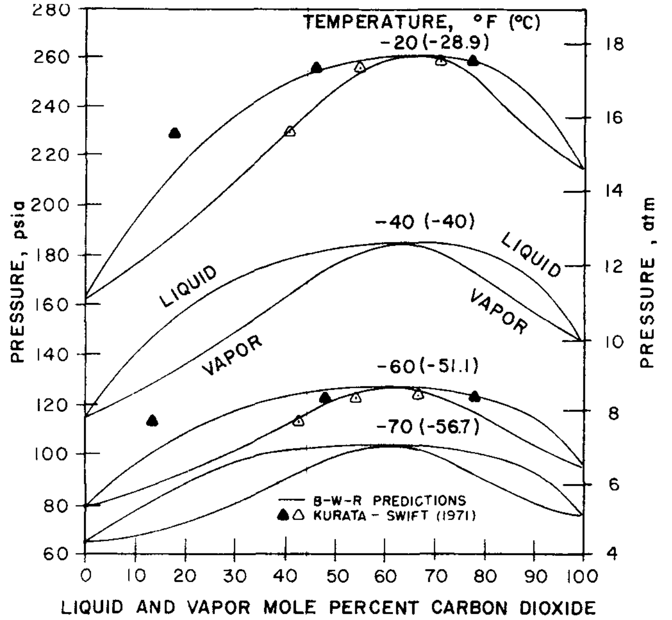

Fig. 7. B-W-R predictions of the bubble-dew points for carbon dioxide-ethane system from −56.7° to −28.9°C.

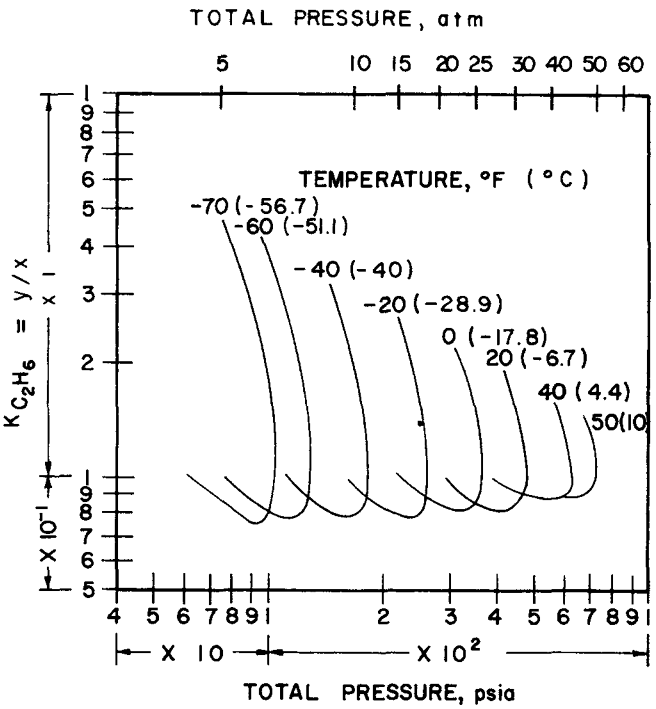

Fig. 8. B-W-R predictions of the equilibrium constants of ethane in carbon dioxide from −56.7° to 10°C.

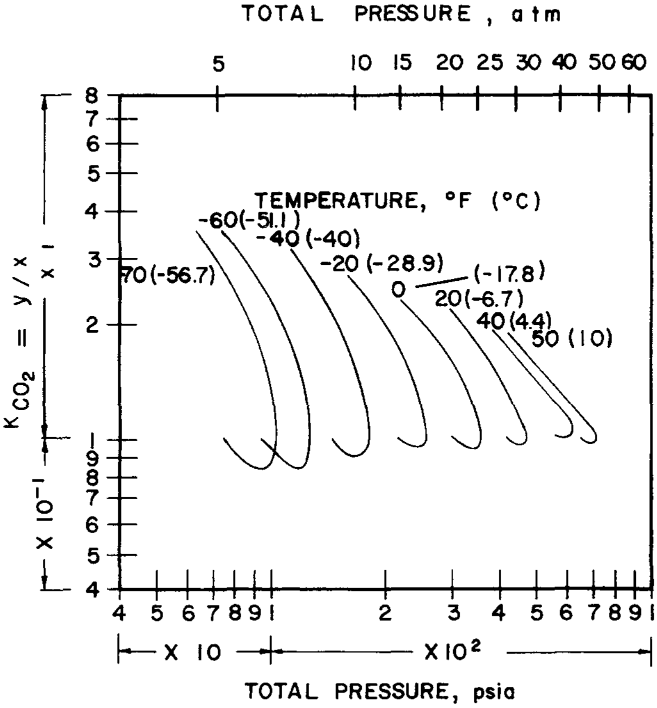

Fig. 9. B-W-R predictions of the equilibrium constants of carbon dioxide in ethane from −56.7° to 10°C.

ures 6 and 7 for comparison with the B-W-R predicted data. Considering that Khazanova et al. attach ± 0.5 atm uncertainty to their reported pressures, there seems to be a reasonable agreement at 10°C. At lower temperatures there is excellent agreement between dew-point pressures measured by Kurata-Swift and those predicted by B-W-R, and reasonable agreement in bubble-point pressures at carbon dioxide concentrations of 40% or more. However, at conditions corresponding to 10 to 20% carbon dioxide in the liquid, bubble-point pressures reported by Kurata-Swift are 1 to 2 atm higher than those measured and correlated in the work presented herein. Consequently, at these conditions the relative volatility of carbon dioxide to ethane implied by the data of Kurata-Swift is about 50% higher than that predicted by B-W-R.

NOTATION

$B_0, A_0, C_0, b, a, c, \alpha, \gamma$ = pure-component B-W-R coefficients
d = molal density
f = component fugacity
k_{ij} = binary interaction coefficient
K = component equilibrium constant
P = absolute pressure
R = universal gas constant
T = absolute temperature
x = mole fraction of the component in liquid phase
y = mole fraction of the component in vapor phase
Σ = summation term

Subscripts and Superscripts

i, j = total number of components
L = liquid phase
V = vapor phase

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Concentration Profiles in Free-Flow Electrophoresis

An analysis is presented which enables detailed description of solute concentration profiles for free-flow electrophoresis in planar slit flows. This analysis is suitable for either batch or continuous operation with arbitrary variation of solute input rate, and it requires no seriously restrictive assumptions other than constancy of equilibrium and transport properties. It permits for the first time a systematic investigation of the effects of governing parameters and can be used to optimize operating conditions. The most significant finding is that Taylor dispersion, ignored in previous analyses, markedly reduces separability.

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Electrophoresis has become an important analytical tool in protein chemistry because of its excellent resolving power, but it has not proven as successful on a preparative scale. Much developmental effort has been expended to scale up electrophoretic separations, and the reasons for their relative lack of success are not entirely clear. However, the lack of realistic quantitative descriptions of solute distributions has certainly been a major stumbling block. We are attempting to provide improved models as part of an overall design effort, and this paper presents our initial results.

To date the most reliable method for predicting solute separability appears to be the first-order approximation of Philpot (1940) for adiabatic separations in rectangular slit-flow apparatus. Philpot's model predicts that separability depends only upon carrier solvent temperature rise and is completely independent of apparatus shape. It is a quantitative expression of an earlier suggestion by Thomson (1884), and it is useful for orientation purposes. It is, however, a very primitive model which ignores both the nonuniform velocity profiles actually observed as well as spatial variations in fluid density and viscosity.