carbons are surrounded by π-bonding rather than s-bonding electrons which characterize saturated hydrocarbons.

Conclusion

The data presented here may be useful for engineering design where higher temperatures are increasingly encountered. Further, these data contribute toward the experimental information required to construct a successful theory of gas solubility.

Appendix I. Minimum Cell Volume Error Analysis

Since some high-boiling solvents are costly, it is desirable to use a small solubility cell. Therefore, it is important to determine how small the solubility cell can be made without a large increase in experimental error. Further, some gases of scientific and industrial interest, e.g., hydrogen sulfide, are extremely toxic making it advisable to use as small an amount as possible.

The error in Henry's constants was calculated as a function of liquid cell volume for a typical case and for the worst case with respect to pairs of gases and high-boiling solvents. The worst case is for a very slightly soluble gas, e.g., hydrogen, in a solvent with high vapor pressure, e.g., octamethylcyclotetrasiloxane. The typical case is for the squalane–ethane system. Results are presented in Figure A1. From these results it was decided that, for expensive solvents and/or toxic solutes, we may use a new, interchangeable solubility cell with a liquid volume of between 30 and 40 cm^3. The cell used in previous work has a volume of 300 cm^3.

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Received for review June 24, 1975. Accepted December 17, 1975. For financial support the authors are grateful to the American Petroleum Institute, the National Science Foundation, and the American Gas Association.

Vapor–Liquid Equilibria in the Freon 12–Freon 13 System

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Isothermal vapor–liquid equilibrium data were determined for the Freon 12–Freon 13 system at 255 and 290 K using a high-pressure vapor recirculation apparatus. The experimental vapor compositions are compared with those calculated from the *P–x* data on the basis of the Gibbs–Duhem equation. The two sets of vapor phase compositions are on the average found to be consistent within 0.01 mol fraction.

Analysis of thermodynamic irreversibility in refrigeration cycles shows that for optimal efficiency (and thus minimal use of energy), the temperature difference between the refrigerant and the process stream must be small. Cooling cycles with mixed refrigerants can be designed to meet this requirement (*5*), provided the physical and thermodynamic properties of the mixtures can be predicted accurately. Thus experimental information on mixtures of refrigerants is of increasing practical importance, and this work gives isothermal vapor–liquid equilibrium data for the Freon 12(CCl_2F_2)–Freon 13 ($CClF_3$) system at 255 K and 290 K. Vapor–liquid equilibrium data for this system have not been reported in the literature previously. Vapor-phase mole fractions (y) were calculated directly from the P–x data without making use of the experimental y's. The calculated and experimental y's compare satisfactorily, and thus the data are thermodynamically consistent.

Experimental Section

The Freons were obtained from Danfoss a/s and had a guaranteed purity of better than 99.8%. The impurities consisted mainly of partly halogenated methane. No further purification was performed. Published and experimental values of pure component physical properties are shown in Table I.

The experiments were carried out using a high-pressure vapor recirculation apparatus described in detail elsewhere (*3*). The cell contains a stationary liquid phase, and the vapor is circulated through the liquid using a diaphragm compressor. The cell volume is 50 cm^3 and the total vapor volume is roughly equal to that; about 3 μl of liquid is withdrawn per liquid sample, and roughly 2×10^{-4} mol is used for each vapor sample. The temperature is measured and maintained to

Table I. Pure-Component Parameters

Property	Freon 12	Freon 13
Vapor pressure at 255 K, atm		
Measured	1.602	11.902
Lit. (*2*)	1.601	11.920
Vapor pressure at 290 K, atm		
Measured	5.096	29.288
Lit. (*2*)	5.127	29.593
Critical temperature, K	301.93	385.15
Critical volume, cm^3/g mol	179.8	216.7
Critical pressure, atm	38.144	41.032
Acentric factor	0.1695	0.1803
Redlich–Kwong parameters[a]		
Ω_A	0.4216	0.4215
Ω_B	0.9361	0.08480
Deviation from geometric mean: $1 - k_{12} = T_{12}^C(T_1^C \cdot T_2^C)^{-0.5}$	$k_{12} = 0.03$	

[a] Redlich–Kwong equation of state: $P = [RT/(V - b)] - [(a/V)/\sqrt{T}(V + b)]$; $a = \Omega_A R^2 T_C^{2.5}/P_C$; $b = \Omega_B RT_C/P_C$.

within 0.01 K using a calibrated platinum resistance thermometer. The pressure is measured using a Ruska deadweight gauge. The composition measurements are carried out using a gas chromatograph equipped with a hot wire detector and a 10-ft column packed with 80–100 mesh Chromosorb P containing 20% di-*n*-butyl phtalate. The peak areas are carefully calibrated against gas mixtures of known compositions, and the calibrations were found to be constant with time. As described previously (*4*), the signal from the gas chromatograph has been coupled to an IBM-1800 computer, which performs an on-line intergration of the chromatogram peaks.

After constant pressure is obtained, which normally takes about 2 h, four separate liquid and gas samplings are carried out at each data point. The pressure is measured before and after the sampling and changed less than 0.3% during the sampling. The four consecutive composition measurements are found to agree to within 0.004 mol fraction.

The results are given in Table II.

Thermodynamic Analysis

When isothermal, binary vapor–liquid equilibrium data are reported as both liquid composition x and vapor composition y as a function of pressure P, then, according to the phase rule, the system is overspecified. In fact, y may be calculated from classical thermodynamics without making use of the experimental y's. As discussed by Van Ness et al. (*7*), comparison between y(calcd) and y(exptl) furnishes a reliable consistency test.

Application of the condition for phase equilibrium and the isothermal, nonisobaric Gibbs–Duhem equation to binary vapor–liquid equilibria results in the following equation (see Nomenclature):

$$P = y_1P + y_2P = x_1f_1{}^0\gamma_1/\varphi_1 + x_2f_2{}^0\gamma_2/\varphi_2$$

$$\begin{aligned} P = (x_1f_1{}^0/\varphi_1)\exp\{g + x_2(\mathrm{d}g/\mathrm{d}x_1)_\sigma - (x_2V^E/RT)(\mathrm{d}P/\mathrm{d}x_1)_\sigma\} \\ + (x_2f_2{}^0/\varphi_2)\exp\{g - x_1(\mathrm{d}g/\mathrm{d}x_1)_\sigma \\ + (x_1V^E/RT)(\mathrm{d}P/\mathrm{d}x_1)_\sigma\} \quad (1) \end{aligned}$$

When the standard state is the pure components at the temperature and pressure of the system

$$f_i{}^0 = P_i{}^{\mathrm{sat}}\varphi_i{}^{\mathrm{sat}} \exp \int_{P_i^{\mathrm{sat}}}^{P} \frac{V_i{}^0}{RT}\,\mathrm{d}P$$

$$V^E = V - x_1V_1{}^0 - x_2V_2{}^0\cdot$$

In this work, the liquid-phase molar volumes, $V_i{}^0$, and vapor-phase fugacity coefficients, φ_i, are calculated following the methods of Prausnitz and Chueh (*6*). Liquid-phase molar volumes at saturation are calculated using the Lyckman–Eckert–Chueh correlation. Vapor-phase fugacity coefficients for pure components as well as mixtures are calculated from the Redlich–Kwong equation of state. The parameters necessary for these calculations are given in Table I.

Equation 1 is a differential equation in $g(x_1)$, and it may be solved using the numerical method of orthogonal collocation as shown by Christiansen and Fredenslund (*1*). The dependent variable g is approximated using nth order Legendre polynomials in $x_1, L_n(x_1)$:

$$g = x_1(1 - x_1) \sum_{k=1}^{n} A_kL_k(x_1) \qquad (2)$$

The Legendre polynomials $L_k(x_1)$, $k = 1, 2, \ldots, n$, are functions which are shown in most textbooks of numerical analysis. The coefficients A_k are evaluated in the n collocation points, that is, for n specific values of x_1. The collocation points are the zeroes of the nth order Legendre polynomial, and they are in general different from the experimental points.

Thermodynamic Consistency Test

Equation 1 is solved for g as a function of x_1 using eq 2 as a test function. The calculations proceed as follows.

(1) An analytical expression for the P–x data is obtained. This is convenient (a) to allow the calculation of (dP/dx) and (b) because eq 1 is solved at the collocation points.

(2) V^E, $f_i{}^0$, and φ_i are calculated from the Redlich–Kwong

Table II. Vapor Liquid Equilibrium Data for the Freon 12–Freon 13 System

Mole fraction Freon 13 in liquid	Pressure (atm)	Mole fraction Freon 13 in vapor		Activity coefficients	
		Exptl	Calcd	Freon 13	Freon 12
		T = 255 K			
0.0	1.601	0.0	0.0	1.533	1.000
0.0360	2.117	0.2301	0.2500	1.480	1.001
0.0791	2.685	0.3985	0.4227	1.427	1.003
0.1535	3.520	0.5653	0.5885	1.337	1.011
0.2392	4.432	0.6862	0.6947	1.255	1.027
0.3461	5.539	0.7793	0.7757	1.175	1.055
0.4602	6.656	0.8401	0.8339	1.111	1.096
0.5841	7.756	0.8877	0.8815	1.061	1.152
0.7817	9.596	0.9460	0.9420	1.015	1.266
0.9123	10.907	0.9794	0.9772	1.002	1.358
1.0	11.920	1.0	1.0	1.000	1.426
		$\overline{\Delta y}$ = 0.0100			
		T = 290 K			
0.0	5.127	0.0	0.0	1.707	1.000
0.0079	5.343	0.0380	0.0493	1.687	1.000
0.0569	6.843	0.2376	0.2665	1.578	1.002
0.1890	10.249	0.5220	0.5358	1.356	1.023
0.3382	13.673	0.6817	0.6759	1.195	1.070
0.5486	18.120	0.8090	0.7978	1.069	1.165
0.7388	22.196	0.8919	0.8863	1.018	1.267
0.9004	26.215	0.9566	0.9571	1.002	1.352
0.9494	27.468	0.9774	0.9781	1.001	1.375
1.0	29.593	1.0	1.0	1.000	1.400
		$\overline{\Delta y}$ = 0.0097			

equation of state. Since y_i enters into the calculation of φ_i, an initial estimate of φ_i must be made, here $\varphi_i = 1$.

(3) Solve eq 1 for g. Knowing g and g' gives the activity coefficients, and y_i(calcd) follows from $y_i = f_i^0 x_i \gamma_i / P\varphi_i$.

(4) Calculate new values of φ_i using y_i(calcd) from step 3. Repeat 2–4 until successive values of y_i(calcd) agree to within 10^{-6}. The end result is a set of values γ_i and y_i(calcd), which are thermodynamically consistent with the P–x data. Interpolation among $g(x_1)$ gives readily y_i(calcd) corresponding to the P–x data points. If y_i(exptl) agrees satisfactorily with y_i(calcd), the data are thermodynamically consistent.

Discussion

Equation 1 was solved using two internal collocation points. Using higher-order approximations does not alter the results significantly. The calculated activity coefficients and vapor phase mole fractions are given in Table II. The overall agreement between y_i(calcd) and y_i(exptl) is within 0.010 mol fraction. Considering the amount of impurities in the Freons and the uncertainties in the composition measurements and calculation of fugacity coefficients, the data set is thermodynamically consistent. The data may thus be included in the basis for correlating the thermodynamic properties of mixed refrigerants.

Acknowledgment

The authors are grateful to Statens teknisk-videnskabelige Forskningsrad for financial support and to Mr. Bent Johnsen for assistance with the experiments.

Nomenclature

A = coefficient in Legendre polynomial
f = fugacity
g = reduced excess Gibbs free energy, G^E/RT
L = Legendre polynomial
P = pressure
R = the gas constant
T = temperature
V = liquid molar volume
x = liquid-phase mole fraction
y = vapor-phase mole fraction
γ = activity coefficient
φ = fugacity coefficient

Superscripts

0 = standard state
sat = at saturation
E = excess property

Subscripts

1, 2, i = components
k = order of Legendre polynomial
n = maximum degree of Legendre polynomial
σ = along saturation line

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Received for review July 15, 1975. Accepted December 11, 1975.

A copy of the computer program used and printout of the intermediate results can be obtained from the authors for a fee of $10.

Vapor–Liquid Equilibrium Data for the Systems $C_2H_4 + C_2H_6$ and $CO_2 + C_2H_4 + C_2H_6$

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Earlier work from this laboratory resulted in isothermal vapor–liquid equilibrium (VLE) data for the systems $CO_2 + C_2H_4$ and $CO_2 + C_2H_6$. We now report isothermal VLE data for the $C_2H_4 + C_2H_6$ system and isothermal-isobaric VLE data for the ternary system $CO_2 + C_2H_4 + C_2H_6$ at 263.15 and 293.15 K. The pressures range from 20 to 60 atm.

Carbon dioxide, ethylene, and ethane are important compounds in the gas processing industry, and knowledge of the properties of the pure components and their mixtures is of practical importance for designing process equipment. The vapor–liquid equilibria among these compounds is complex; the mixtures are nonideal with $CO_2 + C_2H_6$ and $CO_2 + C_2H_4$ forming minimum boiling azeotropes. In this work, we provide VLE data for the $C_2H_4 + C_2H_6$ system and for the $CO_2 + C_2H_4 + C_2H_6$ system at two temperatures: 263.15 K, where all components are condensable, and 293.15 K, where CO_2 and C_2H_6 are condensable and C_2H_4 is noncondensable. Earlier work in this laboratory (*4, 14*) produced VLE data for the systems $CO_2 + C_2H_4$ and $CO_2 + C_2H_6$. This paper then completes a reliable and self-consistent description of mixtures of these compounds.

Other laboratories have studied the component binaries. References 7, 10, 11, 15, and 18 report VLE data for $CO_2 + C_2H_4$, while ref 3, 6, 7, 12, 13, 15, and 16 investigated $CO_2 + C_2H_6$. Reference 9 provides data for $C_2H_4 + C_2H_6$, and ref 2 predicts the low pressure behavior of the ternary. These data do not form a complete description, which led to the current study.

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