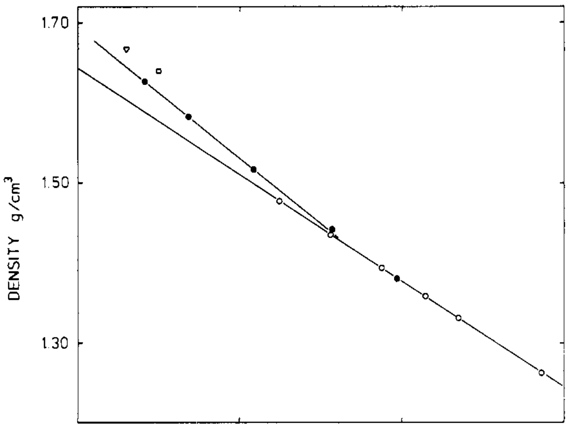

Figure 3. The density of the KCl-AlCl$_3$ system at X_{KCl} = 0.5000 vs. temperature: (●) this work; (○) values from ref 4; (▽) value from ref 6; (□) value from ref 10.

in Figure 2, it is recommended only to apply the equation for calculation of densities in the range $0.35 \leq X_{KCl} \leq 0.55$. It can be seen that the present values of $A(X)$ and $B(X)$ differ considerably from the values calculated from Morrey and Carter (*4*). The reason for this is rather clear. Apparently the density for some of the KCl-AlCl$_3$ compositions does not vary linearly with the temperatures over a large range and therefore the measurements cannot be extrapolated to, for example, 200 °C. This phenomenon is illustrated in Figure 3 for X_{KCl} = 0.5000. The same observation can be made in the equimolar KCl-FeCl$_3$ system, where a similar deviation from linearity is found at high tempertures (cf. Table I, footnote *a*).

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Gas-Liquid Phase Equilibria in the H_2-CF_4 (95-165 K) and H_2-$CClF_3$ (135-220 K) Systems at Pressures of 20-120 Atm

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A single-pass, continuous-flow type equilibrium apparatus has been used to determine gas- and liquid-phase equilibrium data for the CF_4-H_2 system at six constant temperatures from 95 to 165 K and for the $CClF_3$-H_2 system at seven constant temperatures from 135 to 220 K at six constant pressures from 20 to 120 atm. Values of the second virial interaction coefficient, B_{12}, have been extracted from these data as a function of temperature, as well as K_{12}, the correction parameter to the energy parameter of the Kihara intermolecular potential model. Gas-phase compositions computed from thermodynamic considerations, assuming various models for the gas phase (Lennard-Jones, Kihara, Benedict-Webb-Rubin), have been compared with the experimental data in terms of the enhancement factor. The Kihara model gave the best representation of the experimental gas-phase data for both systems (within about 10%).

Introduction

This work is a continuation of phase equilibrium studies made in this laboratory involving helium or hydrogen gases as one component of binary systems. The present work is concerned with gas-liquid phase equilibrium measurements (*1*) for the hydrogen-tetrafluoromethane system over the temperature range 95-165 K and the hydrogen-chlorotrifluoromethane system over the temperature range 135-220 K from 20 to 120 atm pressure. The analogous helium fluorocarbon systems have been studied by Yoon (*2-4*). Other hydrogen systems which have been studied by using techniques similar to those used in this work are H_2-CH_4 (*5*,*6*) and H_2-Ar (*7*,*8*).

The experimental gas-liquid phase equilibrium values have been compared with values computed from various models by appropriate thermodynamic relations.

Experimental Section

All phase equilibrium measurements have been made by using a single-pass flow-type apparatus described by Kirk (*5*) and Kirk and Ziegler (*6*). This apparatus consisted of a thermostated copper equilibrium cell in which the pure liquid condensable component (in this instance fluoromethane or chlorotrifluoromethane) was condensed, after which the pure hydrogen gas was bubbled through the liquid until the composition of the exit gas mixture became constant at which time the liquid phase was sampled to determine its composition. The detailed operating procedures used were similar to those described by Kirk and Ziegler (*6*).

The hydrogen gas used in this work was obtained from Airco, Inc., and has a quoted purity of 99.97%. The argon and helium gases used as carrier gases for the chromatographs had quoted purities of better than 99.99%. The tetrafluoromethane and chlorotrifluoromethane were obtained from E. I. DuPont de Nemours, Inc., and had a quoted purity of 99.9%. These materials were used without further purification. The chromatograms gave no evidence of impurities.

The composition analyses were made by using two separate gas chromatographs (Perkin-Elmer Model 154 vapor fractometers). Hydrogen was determined in the liquid samples by using a Linde molecular sieve (5A) column at 30 °C and argon as the carrier gas. Tetrafluoromethane was determined in the gas-

Table I. Experimental Values of Equilibrium Gas- and Liquid-Phase Compositions for the $CF_4(1)-H_2(2)$ System

T, K	P, atm	P_{01}, atm	gas phase $100y_1$, mol %	liquid phase $100x_2$, mol %	$\phi_1 = Py_1/P_{01}$
164.99	20.13	3.3599		1.644	
	40.30		12.20	3.545	1.463
	40.30[a]		12.12	3.511	1.453
	40.30[b]		12.16	3.517	1.458
	59.91		9.41	5.437	1.678
	80.19		8.566	7.115	2.644
	100.06		8.015	8.964	2.387
	100.04[a]		7.984	9.98	2.377
	119.99		7.668		2.738
149.98	20.05	1.3903	8.701	1.433	1.255
	40.30		5.335	2.923	1.546
	59.76		4.333	4.377	1.863
	80.04		3.943	5.886	2.270
	100.06		3.741	7.011	2.688
	120.06		3.695	8.446	3.191
135.01	20.19	0.4824	3.054	1.198	1.334
	40.30		1.982	2.355	1.728
	60.17		1.676	3.399	2.181
	80.11		1.559	4.475	2.701
	100.11		1.534	5.578	3.321
	120.05		1.559	6.287	4.048
119.94	20.06	0.11073	0.8078	0.8981	1.463
	40.01		0.5483	1.793	1.985
	60.38		0.4966	2.576	2.708
	79.91		0.4980	3.216	3.579
	100.08		0.5146	3.970	4.650
	119.98		0.5431	4.657	5.885
105.01	20.07	0.01664	0.1345	0.6356	1.622
	40.19		0.1096	1.201	2.646
	60.18		0.1095	1.704	3.959
	79.93		0.1193	2.179	5.729
	99.99		0.1284	2.629	7.714
	120.00		0.1463	3.048	10.55
94.94	20.14	0.00310	0.03324	0.4676	2.159
	20.21[a]		0.03430	0.4692	2.235
	20.09[b]		0.03278	0.4682	2.124
	40.37		0.02823	0.8833	3.675
	60.17		0.03155	1.262	6.123
	80.04		0.03079	1.572	9.575
	100.06		0.04466	1.846	14.39
	119.94		0.05432	2.136	21.01
	119.38		0.05333	2.114	20.53
	119.38		0.05336	2.123	20.55

[a] Flow rate was half the normal flow rate of 100 cm^3/h at P,T of cell. [b] Flow rate was twice the normal flow rate.

Table II. Experimental Values of Equilibrium Gas- and Liquid-Phase Compositions for the $CF_3Cl(1) - H_2(2)$ System

T, K	P, atm	P_{01}, atm	gas phase $100y_1$, mol %	liquid phase $100x_2$, mol %	$\phi_1 = Py_1/P_{01}$
219.99	20.20	3.656	21.67	1.630	1.197
	20.67[a]		21.50	1.620	1.192
	20.06[b]		21.89	1.616	1.202
	39.90		12.42	3.481	1.355
	59.90		9.801	5.340	1.606
	79.91		8.155	7.213	1.782
	99.98		7.354	8.984	2.011
	119.99[a]		6.761	10.487	2.219
	119.99		6.733	10.585	2.210
205.03	20.20	1.9312	11.28	1.544	1.180
	40.10		6.820	2.213	1.416
	59.90		5.139	4.773	1.594
	79.91		4.461	6.412	1.846
	100.15		4.102	7.869	2.127
	120.02		3.883	9.365	2.413
189.97	20.09	0.90822	5.551	1.407	1.229
	40.16		3.293	2.920	1.456
	59.76		2.540	4.201	1.671
	79.90		2.290	-	2.015
	80.25		2.276	5.480	2.011
	99.91		2.102	6.890	2.312
	119.98		2.024	8.200	2.674
175.02	20.06	0.37095	2.368	1.212	1.280
	40.37		1.378	2.448	1.499
	59.97		1.142	3.647	1.847
	79.70		1.028	4.673	2.209
	99.91		0.974	5.716	2.622
	119.88		0.9603	6.864	3.103
160.02	20.13	0.12416	0.7922	1.055	1.284
	40.17		0.5110	2.018	1.653
	59.77		0.4236	3.090	2.039
	79.63		0.3903	3.909	2.503
	100.05		0.3801	4.790	3.063
	119.99		0.3913	5.681	3.782
145.02	20.26	0.03180	0.2164	0.8783	1.379
	40.23		0.1417	1.667	1.793
	59.97		0.1300	2.446	2.451
	79.50		0.1254	3.182	3.135
	99.84		0.1296	3.889	4.069
	119.92		0.1363	4.553	5.140
134.97	20.09[a]	0.010462	0.0737	0.7477	1.416
	20.06		0.0749	0.7453	1.436
	20.06[b]		0.0748	0.7382	1.435
	40.17		0.0527	1.419	2.023
	59.83		0.0489	2.051	2.796
	79.63		0.0503	2.674	3.823
	99.84		0.05367	3.311	5.122
	119.91[b]		0.0592	3.894	6.782
	120.02[a]		0.0587	3.894	6.728

[a] Flow rate was half of the normal flow rate. [b] Flow rate was twice the normal flow rate.

phase samples by using a silica gel column at 50 °C with helium as the carrier gas. Chlorotrifluoromethane was determined in the gas-phase samples by using a silica gel column operating at 75 °C with helium as the carrier gas.

Calibration curves for the chromatographs were constructed prior to beginning the measurements on a peak-height basis from gas mixtures of known composition prepared by using a gas mixing buret described by Kirk (*5*). Corrections for gas imperfection were taken into account in computing the composition of these standards. The stability of the chromatographs was monitored during the course of the measurements by means of a set of standard gas mixtures which were analyzed from time to time as the work proceeded. The calibration of the chromatographs was checked at the end of the measurements. The details of these analyses are given by Shiau (*1*).

The experimental phase equilibrium measurements consisted of six or seven isotherms at six or more pressures from 20 to 120 atm. The experimental results for the CF_4-H_2 system are given in Table I and for the $CClF_3$-H_2 system in Table II. The temperature of the equilibrium cell could be controlled to ±0.03 K. All temperatures were measured with a capsule-type platinum resistance thermometer calibrated by the U.S. National Bureau of Standards on the International Practical Temperature Scale of 1948 (IPTS-48). All temperatures in Tables I and II are given on the International Practical Temperature Scale of 1968 (IPTS-68), the conversion of Barber (*9*) having been used to convert the IPTS-48 to IPTS-68.

The normal flow rate of hydrogen through the condensed liquid phase used in the present studies was 100 cm^3/h (measured at cell pressure and temperature). This flow rate had been determined to give equilibrium values in earlier studies made with the same apparatus for the CH_4-H_2 system by Kirk (*6*) and the Ar-H_2 system studied by Mullins (*7*). This was verified in the present studies by determining gas- and liquid-phase compositions in which the flow rate was made half or twice this normal rate at widely different pressures and temperatures. These comparisons are shown in Tables I and II. Varying the flow rate did not affect the composition of the gas and liquid phases by more than the estimated uncertainty of the composition measurements, and it was concluded that the results correspond to true phase equilibrium.

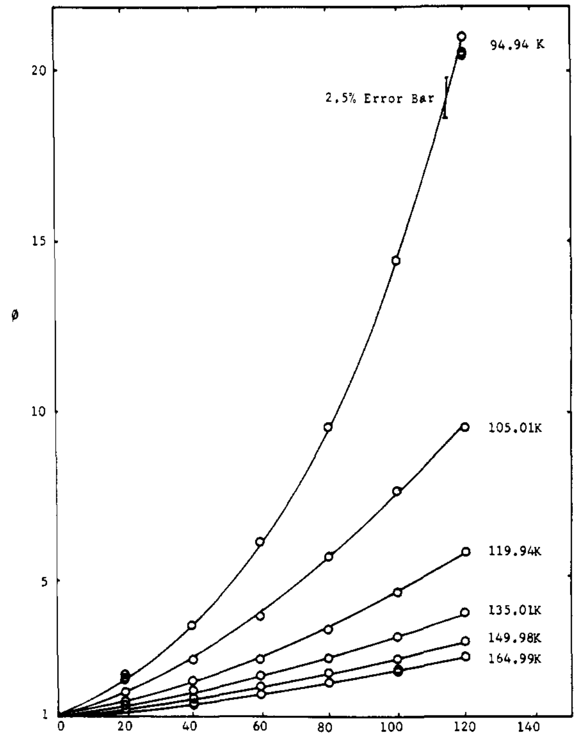

Figure 1. Experimental enhancement factors of carbon tetrafluoride in hydrogen at 94.94, 105.01, 119.94, 135.01, 149.98, and 164.99 K.

Experimental Results

Gas and liquid phase equilibrium compositions were determined in the CF_4–H_2 system along isotherms at 94.94, 105.01, 119.94, 135.01, 149.98, and 164.99 K. For the $CClF_3$–H_2 system the same range of pressures was used along isotherms at 134.97, 145.02, 160.02, 175.02, 189.97, 205.03, and 219.99 K. Six pressure points from 20 to 120 atm at intervals of approximately 20 atm were measured along each isotherm. The uncertainty of the gas-phase analyses is estimated to be ±2.5% of the values given for the fluorocarbon in the CF_4–H_2 system and ±3.0% for the $CClF_3$–H_2 system. The analyses for the liquid phase are estimated to have an uncertainty of ±2.0% of the values given for hydrogen. These estimates of uncertainties are based on the uncertainties in the temperature (±0.03 K) and the pressure (±0.5%) measurements and the uncertainty in the chromatograph calibration curves.

Discussion of Experimental Results

The experimental phase equilibrium compositions are presented in Tables I and II. No previous measurements for these systems could be found in the published literature. The gas-phase composition is also expressed in terms of the enhancement factor, ϕ_1, defined by the relation

$$\phi_1 = Py_1/P_{01} = y_1/y_1{}^{\circ} \qquad (1)$$

where y_1 is the composition (mole fraction) of the condensable component in the gas phase at the equilibrium P and T, and P_{01} is the vapor pressure of the pure condensable component at T. If one assumes the gas phase at P and T to be an ideal gas mixture, then $y_1{}^{\circ}$ is the mole fraction which one would expect if the partial pressure of the condensable component in the gas phase were P_{01}. The vapor pressure of CF_4 was computed from the equation

$$\log P(\text{torr}) = 6.8368405 - 5.1169474/(T - 15.7744)$$

of Simon et al. (*10*) where T is in kelvins. This equation represents the experimental vapor pressure data of Simon et al. (*10*) and Chari (*11*) to within 0.5% up to 5 atm.

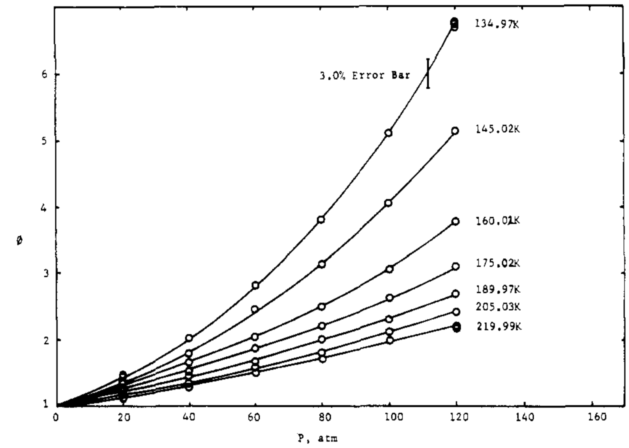

Figure 2. Experimental enhancement factors of chlorotrifluoromethane in hydrogen at 134.97, 145.02, 160.02, 175.02, 189.97, 205.03, and 219.99 K.

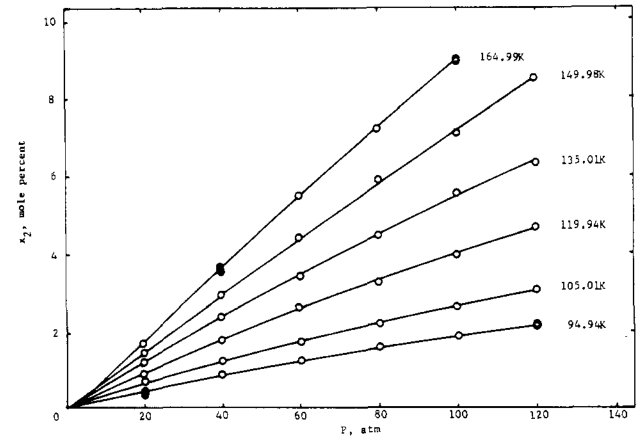

Figure 3. Experimental solubility of hydrogen in liquid carbon tetrafluoride.

For the vapor pressure of $CClF_3$ the vapor pressure relation of Albright and Martin (*12*) has been used to compute P_{01}. This equation represents their experimental vapor pressure data to within 0.06%.

Figures 1 and 2 show the gas-phase compositions of the two systems expressed in terms of the experimental enhancement factors. The experimental solubility of hydrogen in the condensed liquid phases is shown in Figures 3 and 4.

The experimental phase equilibrium data of the CF_4–H_2 and $CClF_3$–H_2 systems given in Tables I and II have been used to obtain a smooth set of values of ϕ_1 and x_2 (mole fraction of hydrogen) by means of a least-squares fitting procedure. The experimental data of each isotherm, expressed in terms of ϕ_1 or x_2, were fitted to polynomials of order 1 up to order 4, and the best fit polynomial was chosen to represent the data. The polynomials chosen always fitted the experimental data to within 2% (the estimated uncertainty in the experimental values of y_1 or x_2). Smoothed values of ϕ_1 and x_2 are computed from these polynomials at 20, 40, 60, 80, 100, and 120 atm as shown in Tables III and IV. The smoothed values of ϕ_1 were used to construct the isobars shown in Figures 5 and 6.

Comparison of Experimental Results with Theoretical Models

The prediction of gas–liquid phase equilibria such as those determined in this work from thermodynamic considerations has been discussed by numerous investigators. Kirk et al. (*5*, *6*, *13*) have discussed such calculations for the CH_4 (1)–H_2 (2) system under conditions where the condensed phase may be considered to be a pure solid or pure liquid. Mullins and Ziegler (*8*) have discussed such calculations for the Ar–H_2 system,

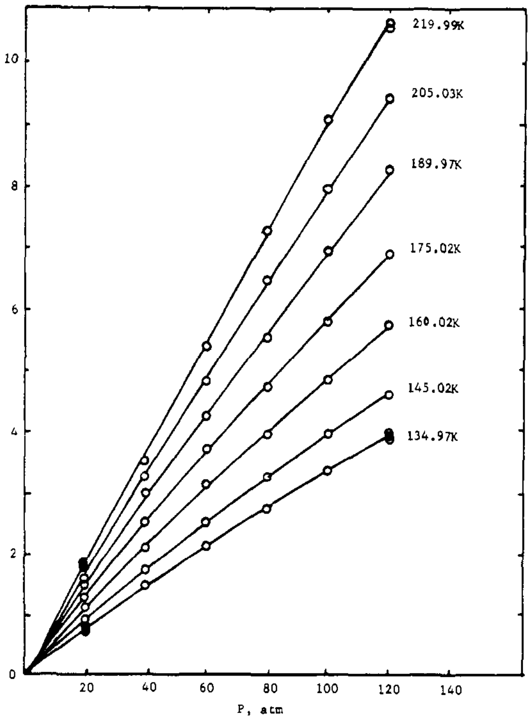

Figure 4. Experimental solubility of hydrogen in liquid chlorotrifluoromethane.

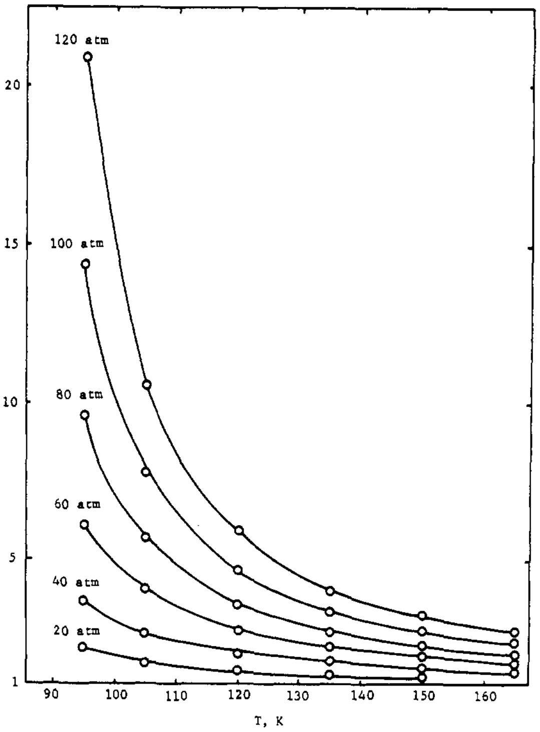

Figure 5. Experimental enhancement factors of carbon tetrafluoride in hydrogen along isobars.

assuming the liquid phase to be an ideal solution. These discussions have made use of the enhancement factor, ϕ_1, defined in eq 1. Both forms of ϕ_1 given in eq 1 have been used to describe such binary gas-phase equilibria (see, for instance, Dokoupil et al. (*14*) and Rowlinson and Richardson (*15*)). The quantity ϕ_1 is called the enhancement factor because it is almost always greater than unity in binary systems of this type. Thermodynamic expressions for ϕ_1 can be developed from the thermodynamic requirement that the chemical potential (or alternately, the fugacity) of a component must be equal in both the gas and the condensed phase at equilibrium.

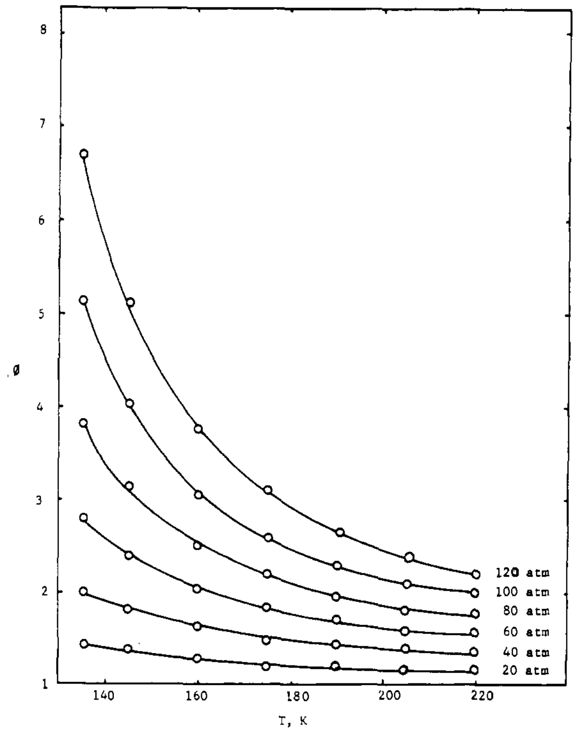

Figure 6. Experimental enhancement factors of chlorotrifluoromethane in hydrogen along isobars.

The condition of equality of chemical potential (or fugacity) for the condensable component (here designated as component 1) in the two phases leads to the following exact thermodynamic expression for ϕ_1 (*6*, *13*, *14*, *16*)

$$\ln \phi_1 = \ln \frac{PV_m}{P_{01}V_{01}} + \frac{1}{RT}\int_{P_{01}}^{P} v_1^c \, dP + \frac{1}{RT}\int_{V_{01}}^{\infty}\left[\left(\frac{\partial P_1}{\partial n_1}\right)_{V,T} - \frac{RT}{V_1}\right] dV_1 - \frac{1}{RT}\int_{V_m}^{\infty}\left[\left(\frac{\partial P}{\partial n_1}\right)_{V_m,T,n_2} - \frac{RT}{V_m}\right] dV_m + \ln \gamma_1 x_1 \quad (2)$$

The calculation of ϕ_1 from eq 2 requires that the properties (vapor pressure and equation of state for the pure liquid and gas of component 1) be known, that an equation of state for the gas-phase mixture be known in order to calculate the last integral, and finally that the mole fraction x_1 and activity coefficient γ_1 of component 1 in the condensed phase be known or that some reasonable assumption be made concerning the condensed-phase solution.

In the evaluation of ϕ_1 from eq 2 the first integral, called the Poynting term, is often evaluated by assuming that the volume of the pure liquid, v_1^c, is independent of pressure and equal to the volume of the saturated liquid at T. In the present work v_1^c has been expressed by a relation due to Chueh and Prausnitz (*17*) having the form

$$v_1^c = v_{01}^c[1 + n\beta^s(P - P_{01})]^{-1/n} \quad (3)$$

where v_{01} and P_{01} are the saturated liquid molar volume and vapor pressure of the pure liquid at T. β^s is the isothermal compressibility of the saturated liquid, and n is an empirical constant.

The isothermal compressibility of the saturated liquid β^s is given by the generalized relation

$$\beta^s = \frac{v_{01}^c}{R(T_c)_1}(1.0 - 0.89w^{1/2})[\exp(6.9447 - 76.2853T_{R_1} + 191.3060T_{R_1}^2 - 203.5472T_{R_1}^3 + 82.7361T_{R_1}^4)] \quad (4)$$

Table III. Smoothed Experimental and Theoretical Enhancement Factors of Carbon Tetrafluoride in Hydrogen and the Smoothed Experimental Solubility of Hydrogen in Liquid Carbon Tetrafluoride

P, atm	ϕ exp	ϕ LJCL	ϕ KIH	ϕ KIHCK12	ϕ BWR[a]	ϕ BWR[b]	$100x_2$, mol %
94.94 K							
20	2.165	1.878	1.870	1.863	1.938	1.911	0.4653
40	3.640	3.447	3.382	3.360	3.603	3.503	0.8768
60	6.092	6.141	3.869	5.813	6.372	6.112	1.257
80	9.581	10.571	9.739	9.617	10.679	10.111	1.574
100	14.36	17.543	15.456	15.220	16.959	15.860	1.844
120	20.86	28.053	23.521	23.102	25.568	23.631	2.132
105.01 K							
20	1.652	1.634	1.626	1.622	1.630	1.610	0.6334
40	2.606	2.614	2.571	2.559	2.577	2.512	1.197
60	4.002	4.084	3.947	3.919	3.946	3.799	1.708
80	5.679	6.221	5.875	5.819	5.843	5.559	2.182
100	7.743	9.235	8.482	8.385	8.367	7.867	2.628
120	10.54	13.370	11.911	11.750	11.600	10.784	3.048
119.94 K							
20	1.462	1.429	1.426	1.423	1.411	1.395	0.8935
40	1.982	2.006	1.989	1.982	1.937	1.894	1.760
60	2.693	2.769	2.725	2.710	2.614	2.527	2.534
80	3.583	3.761	3.665	3.640	3.466	3.312	3.252
100	4.646	5.025	4.844	4.803	4.514	4.265	3.949
120	5.886	6.608	6.299	6.236	5.777	5.396	4.662
135.01 K							
20	1.330	1.318	1.322	1.321	1.319	1.306	1.182
40	1.723	1.704	1.709	1.704	1.677	1.642	2.345
60	2.175	2.181	2.186	2.177	2.112	2.045	3.379
80	2.700	2.755	2.762	2.747	2.631	2.519	4.480
100	3.316	3.443	3.456	3.433	3.249	3.073	5.567
120	4.046	4.277	4.307	4.272	3.992	3.729	6.287
149.98 K							
20	1.255	1.256	1.270	1.269	1.291	1.280	1.436
40	1.537	1.544	1.569	1.566	1.579	1.548	2.871
60	1.876	1.877	1.921	1.915	1.915	1.856	4.450
80	2.260	2.267	2.343	2.332	2.319	2.218	5.832
100	2.691	2.722	2.852	2.835	2.807	2.646	7.034
120	3.189	3.235	3.453	3.428	3.389	3.141	8.435
164.99 K							
20		1.218	1.242	1.241	1.292	1.282	1.627
40	1.452	1.451	1.499	1.497	1.585	1.535	3.496
60	1.698	1.709	1.797	1.792	1.885	1.824	5.445
80	2.022	2.005	2.159	2.150	2.289	2.175	7.100
100	2.386	2.330	2.591	2.577	2.815	2.609	8.966
120	2.736	2.692	3.137	3.113	3.609	3.187	10.80[c]

[a] LORENTZ. [b] LINEAR. [c] Extrapolated value.

where w is the Pitzer acentric factor and $T_{R_1} = T/T_{c_1}$; T_{c_1} is the critical temperature of component 1.

Chueh and Prausnitz (*17*) have suggested the use of a value of $n = 9$ in eq 4 for normal liquids. This value has been used in the present work. Equation 4 provides a useful correlation of isothermal compressibility over the reduced temperature range $0.4 \leq T_R \leq 0.98$ which covers the range of temperatures of the present work. Using eq 3 with $n = 9$ in the first integral of (2) and integrating gave

$$\frac{1}{RT}\int_{P_{01}}^{P} v_1^c \, dP = \frac{v_{01}^c}{8\beta^s RT}[\{1 + 9\beta^s(P - P_{01})\}^{8/9} - 1] \quad (5)$$

If the virial equation of state in the form

$$\frac{PV_m}{RT} = 1 + \frac{B_m}{V_m} + \frac{C_m}{V_m^2} \quad (6)$$

with

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (7)$$

$$C_m = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222} \quad (8)$$

is used to represent the gas phase and the pure condensable vapor, then eq 2 for ϕ_1 can be written in the form

$$\ln \phi_1 = \frac{1}{RT}\int_{P_{01}}^{P} v_1^c \, dP + 2\frac{B_{11}}{V_{01}} + \frac{3}{2}\frac{C_{111}}{V_{01}^2} - \ln \frac{P_{01}V_{01}}{RT} - \frac{2}{V_m}(y_1 B_{11} + y_2 B_{12}) - \frac{3}{2V_m^2}(y_1^2 C_{111} + 2y_1 C_{112} + y_2^2 C_{122}) + \ln \frac{PV_m}{RT} + \ln \gamma_1 x_1 \quad (9)$$

where V_m is the molar volume of the gas-phase mixture at the equilibrium P and T as computed from eq 6, v_1^c is the molar volume of the pure condensed component, and V_{01} represents the molar volume of pure saturated condensable vapor at T and P_{01} as computed from eq 6. When the condensed phase is a solid, the assumption is often made that the equilibrium condensed phase is a pure solid phase (*13, 16*). In this case the term $\ln \gamma_1 x_1$ is zero. When the condensed phase is a liquid and the solubility of component 2 is expected to be small, the assumption that the liquid phase may be treated as a pure liquid phase (*6*) or an ideal solution (*8*) may be made in order to permit predictive calculation of ϕ_1 to be made from eq 2 or 9.

Table IV. Smoothed Experimental and Theoretical Enhancement Factors of Chlorotrifluoromethane in Hydrogen and the Smoothed Experimental Solubility of Hydrogen in Liquid Chlorotrifluoromethane

P, atm	ϕ exp	ϕ LJCL	ϕ KIH	ϕ KIHCK12	$100x_2$, mol %
			134.97 K		
20	1.428	1.500	1.461	1.418	0.7404
40	2.013	2.197	2.089	1.970	1.413
60	2.811	3.144	2.923	2.682	2.058
80	3.842	4.400	4.003	3.581	2.694
100	5.137	6.027	5.374	4.691	3.317
120	6.729	8.091	7.082	6.043	3.896
			145.02 K		
20	1.373	1.403	1.376	1.342	0.8682
40	1.800	1.930	1.859	1.769	1.658
60	2.426	2.600	2.467	2.295	2.447
80	3.181	3.443	3.222	2.933	3.021
100	4.064	4.482	4.144	3.695	3.904
120	5.147	5.745	5.256	4.595	4.556
			160.02 K		
20	1.282	1.306	1.292	1.267	1.046
40	1.647	1.673	1.641	1.578	2.030
60	2.049	2.113	2.056	1.941	3.060
80	2.507	2.634	2.550	2.363	3.965
100	3.064	3.245	3.131	2.855	4.768
120	3.782	3.944	3.802	3.409	5.686
			175.02 K		
20	1.271	1.246	1.243	1.223	1.207
40	1.496	1.519	1.511	1.464	2.432
60	1.841	1.832	1.820	1.736	3.629
80	2.221	2.188	2.178	2.046	4.703
100	2.621	2.589	2.587	2.395	5.714
120	3.107	3.030	3.047	2.778	6.874
			189.97 K		
20	1.225	1.210	1.215	1.200	1.396
40	1.449	1.423	1.433	1.396	2.923
60	1.706	1.663	1.682	1.617	4.190
80	1.966	1.924	1.962	1.860	5.490
100	2.320	2.206	2.274	2.126	6.883
120	2.677	2.511	2.623	2.420	8.204
			205.03 K		
20	1.177	1.191	1.203	1.191	1.532
40	1.416	1.369	1.394	1.363	3.186
60	1.594	1.557	1.604	1.549	4.819
80	1.824	1.759	1.838	1.654	6.382
100	2.124	1.975	2.101	1.979	7.877
120	2.413	2.202	2.394	2.225	9.360
			219.99 K		
20	1.195	1.182	1.199	1.190	1.606
40	1.378	1.338	1.378	1.352	3.487
60	1.583	1.496	1.570	1.523	5.356
80	1.799	1.659	1.782	1.708	7.215
100	2.014	1.829	2.020	1.911	8.989
120	2.217	2.010	2.300	2.141	10.54

Table V. Intermolecular Potential Parameters

parameters	H_2	CF_4	$CClF_3$
	LJCL (6-12)		
ref	this work	24	2
ϵ/k, K	31.68	151.5	185.8
b_0, cm³/g-mol	32.73	134.7	220.2
σ, Å	2.96	4.74	5.59
	KIH		
ref	21	24	2
U_0/k, K	46.00	289.7	404.4
ρ_0, Å	2.808	3.232	3.367
M_0, Å	2.33	9.048	10.21
S_0, Å²	0.00	6.514	8.302
V_0, Å³	0.00	1.564	2.250
M, g/g-mol	2.01594	88.005	104.47

Enhancement factors for the CF_4 (1)–H_2 (2) system have been calculated for five different theoretical models for the gas phase and are compared with the experimental values in Table III. In all cases the liquid phase has been assumed to be an ideal solution ($\gamma_1 = 1$) and x_1 has been used from the experimental data ($0.892 < x_1 < 1$). These five models are the Lennard-Jones (6-12) classical (LJCL), the Kihara core model (KIH), the Kihara core model with modified rule for combining the energy parameters (U_0) of the pure species (KIHCK12) with the interaction parameter K_{12} being computed from a relation proposed by Hiza and Duncan (*18*), the Benedict-Webb-Rubin (BWR) equation of state for the gas mixture with the mixture parameter $(B_0)_{12}$ calculated by using a linear average (BWRLINEAR), and the BWR equation of state using the Lorentz average for $(B_0)_{12}$ (BWRLORENTZ). Only three models, LJCL, KIH, and KIHCK12, were calculated for the $CClF_3$ (1)–H_2 (2) system, since the BWR constants were not available for $CClF_3$. The various models are described in greater detail below.

The molar volume, v_{01}^c, of saturated liquid tetrafluoromethane was obtained from an equation developed by Terry et al. (*19*) fitted to experimental data for v_{01}^c over the entire temperature range of our measurements. For chlorotrifluoromethane a density-temperature relation developed by Albright and Martin (*12*) was used to compute the saturated molar volume.

Lennard-Jones (6-12) Model (LJCL)

This model made use of eq 9 to compute ϕ_1. The virial coefficients B_{11}, B_{12}, B_{22}, C_{111}, C_{112}, C_{122}, and C_{222} were evaluated at each temperature by using the classical Lennard-Jones (6-12) parameters for hydrogen (component 2) and the fluorocarbons given in Table V and the methods described by Hirschfelder et al. (*20*). The usual geometric combination rules were used for (ϵ/k) and the Lorentz rule for b_0.

The necessary third virial coefficients were computed from the corresponding reduced virial coefficients computed by using the methods given by Hirschfelder et al. (*20*), the appropriate interaction distance and energy parameters being computed from the pure component parameters by the relations

$$(b_0)_{ijk} = \frac{1}{27}[(b_0)_i^{1/3} + (b_0)_j^{1/3} + (b_0)_k^{1/3}]^3 \qquad (10)$$

$$(\epsilon/k)_{ijk} = (\epsilon/k)_i^{1/3}(\epsilon/k)_j^{1/3}(\epsilon/k)_k^{1/3} \qquad (11)$$

Kihara Core Model (KIH)

In this model which also made use of eq 9 the second virial coefficients B_{11}, B_{22}, and B_{12} were computed by using the Kihara intermolecular potential function as discussed by Prausnitz and Myers (*21*). The Kihara potential function assumes that each molecule has an impenetrable core described by the three parameters M_0, S_0, and V_0 and involves a distance parameter ρ_0 and an energy parameter U_0. The method of calculation used is that given in Prausnitz and Myers (*21*). The parameters used in the present calculations are given in Table V.

The interaction parameters $(U_0)_{12}$ and $(\rho_0)_{12}$ used to compute B_{12} were computed from the relations

$$(U_0)_{12} = (U_{01})^{1/2}(U_{02})^{1/2} \qquad (12)$$

$$(\rho_0)_{12} = [(\rho_0)_1 + (\rho_0)_2]/2 \qquad (13)$$

For pure gases of small molecular weight such as hydrogen, it is necessary to consider quantum corrections to the second virial coefficient (*21*, *22*). Prausnitz and Myers (*21*) have suggested that for interaction between a quantum gas such as hydrogen and a gas of relatively larger molecular weight such as CF_4 which we shall refer to as a nonquantum gas, it is necessary to include quantum effects in computing B_{ij}. This was done for the two hydrogen systems discussed in the present paper by using the procedures given in Prausnitz and Myers (*21*).

For the KIH model calculations, the third virial and third virial interaction coefficients in eq 6 and 9 have been calculated by using an empirical corresponding states correlation developed by Chueh and Prausnitz (*23*) for the third virial coefficient C of pure gases. This correlation is

$$C/V_c^2 = [0.232T_R^{-0.25} + 0.468T_R^{-5}][1 - \exp(1 - 1.89T_R^2)] + d\exp(-2.49 + 2.30T_R - 2.70T_R^2) \quad (14)$$

where

$$T_R = T/T_c \quad (15)$$

and V_c is the critical volume and T_c is the critical temperature of the substance.

Chueh and Prausnitz (*23*) recommend the use of this correlation for $T_R \geq 0.8$. The parameter d must be estimated for the particular substance for which the calculation is to be made. Yoon (*2*, *3*) has used experimental third virial coefficient data to obtain values of $d = 0.8$ and 0.6 for CF_4 and $CClF_3$, respectively. These values of d have been used in the present calculations for the pure substance. For the cross virial calculations d_{12} was taken to be the linear average of the pure gas values.

For a quantum gas such as hydrogen a modification of the strict corresponding state behavior is required. Chueh and Prausnitz (*23*) have presented a method for obtaining *effective* critical constants T_c and V_c which were used in our calculation. The effective critical temperature T_c and the critical volume V_c used in eq 9 and 10 were

$$T_c = \frac{T_c^\circ}{1 + 21.8/MT} \quad (16)$$

$$V_c = \frac{V_c^\circ}{1 + 9.9/MT} \quad (17)$$

For hydrogen we used $T_c^\circ = 43.6$ K and $V_c^\circ = 51.5$ cm^3/g-mol (*23*) with $M = 2.016$ as the molecular weight of hydrogen. Shiau (*1*) found that using these values of T_c and V_c in eq 14 and $d = 0$, eq 14 fitted experimental third virial coefficient data for hydrogen reasonably well.

To calculate C_{112} and C_{122}, the third virial interaction coefficients, in the various KIH models, we made use of the suggestion of Chueh and Prausnitz (*23*) regarding the use of eq 14.

Kihara Core Model with K_{12} (designated KIHCK12)

In this model the geometric mixing rule for the energy parameter $(U_0)_{12}$ given in eq 12 has been modified by the factor $(1 - K_{12})$. Thus eq 12 becomes

$$(U_0)_{12} = (1 - K_{12})(U_{01})^{1/2}(U_{02})^{1/2} \quad (18)$$

Chueh and Prausnitz (*23*) have shown that such a modification of the geometric combination rule for the energy parameters permits one to obtain a better fit of experimental high-pressure phase equilibrium data for binary systems involving helium and hydrogen gases. Hiza and Duncan (*18*) and Hiza (*27*) have determined values of K_{12} in eq 18 by a least-squares fit of experimental second virial interaction (B_{12}) data obtained from experimental phase equilibrium data for hydrogen and helium binaries together with the Kihara model. Hiza and Duncan (*18*) have also developed a semitheoretical relation for estimating the K_{12} parameter which has the form

$$K_{12} = 0.17(I_v - I_c)^{1/2} \ln I_v/I_c \quad (19)$$

where I_v (in electron volts) is the first ionization potential of the more volatile component, say, hydrogen, and I_c is the first ionization potential of the condensable component (say CF_4).

Table VI. Values of K_{12} for the CF_4-H_2 and $CClF_3$-H_2 Systems

substance	ionization potential I, eV	K_{12} calcd from eq 19	K_{12} this work exptl
H_3	15.426 (26)[a]		
CF_4	15.00 (25)	0.003	0.0
$CClF_3$	12.91 (26)	0.048	0.0

[a] Source of ionization potential.

Table VII. BWR Equation of State Parameters (L atm K g-mol)

ref	H_2 (31)	CF_4 (32)
A_0	1.551 633 6 (−1)[a]	1.860 000
B_0	2.084 654 1 (−2)	5.520 00 (−2)
C_0	1.841 523 9 (+2)	1.545 00 (+5)
a	1.632 198 5 (−3)	3.985 30 (−1)
b	b	1.211 47 (−2)
c	7.271 450 7	2.433 00 (+4)
α	1.165 598 8 (−4)	2.500 00 (−4)
γ	3.507 369 2 (−3)	1.250 00 (−2)

[a] Number in parentheses indicates power of 10. [b] $b = 3.3834422 \times 10^{-4} + 2 \times 1.6321985 \times 10^{-3}/(RT)$.

The model designated as KIHCK12 in Tables III and IV makes use of eq 19 to compute K_{12} for each system. The values of K_{12} obtained are shown in Table VI. The values of K_{12} provided a means for the calculation of B_{12} and hence the enhancement factor. Thus the calculations for this model differ from those of the KIH model only in the fact that eq 18 replaces eq 12 in the calculations.

Benedict-Webb-Rubin Model (BWR (Lorentz) and BWR (linear))

These calculations of the enhancement factor made use of eq 2 together with the assumption that the gas-phase mixture followed the BWR equation of state for mixtures in which the mixture parameters were computed by using the combination rules originally proposed by Benedict et al. (*28*) except that the parameter $(B_0)_{12}$ was computed by using both a Lorentz average and a linear average. The calculations from these models are designated as BWR (Lorentz) and as BWR (linear), respectively, in Table III. The values of the BWR parameters for hydrogen and tetrafluoromethane used are given in Table VII. No such calculations were made for the H_2-$CClF_3$ system because no BWR parameters for $CClF_3$ could be found.

Discussion

Examination of Tables III and IV shows that for both the CF_4 (1)-H_2 (2) and $CClF_3$ (1)-H_2 (2) systems the values of ϕ_1 (hence y_1) computed by using the KIH model give values of ϕ_1 which agree with the experimental values better than the LHCL model. The KIHCK12 model gives values of ϕ_1 only slightly different than the KIH model as is to be expected since the values of K_{12} are close to zero. For the CF_4-H_2 system the BWR (linear) model predicts values of ϕ_1 which agree with experimental somewhat better than the BWR (Lorentz) model.

Extraction of the Second Interaction Coefficient B_{12} from Gas-Liquid and Gas-Solid Phase Equilibrium Data

Reuss and Beenakker (*29*), Rowlinson and Richardson (*15*), Mullins (*7*), and Chui and Canfield (*30*) among others have discussed the calculation of the second virial interaction coefficient B_{12} from experimental gas-liquid and gas-solid phase equilibrium data.

If the virial equation of state in the Leiden form (eq 6) through the third coefficient is used to describe the gas-phase mixture

Table VIII. Smoothed Values of B_{12} Extracted from Experimental Phase Equilibrium Data

T, K	B_{12}, cm³/g-mol	T, K	B_{12}, cm³/g-mol
	CF_4-H_2 System		
94.94	−118.0 ± 4.0	135.01	−49.4 ± 4.0
105.01	−88.3 ± 4.0	149.98	−34.9 ± 4.0
119.94	−64.8 ± 4.0	164.99	−26.7 ± 4.0
	$CClF_3$-H_2 System		
134.97	−69.9 ± 3.0	189.97	−32.5 ± 3.0
145.02	−60.2 ± 3.0	205.03	−22.7 ± 3.0
160.02	−50.7 ± 3.0	219.99	−16.8 ± 3.0
175.02	−42.2 ± 3.0		

of a gas-liquid equilibrium, then eq 9 may be rearranged and solved for B_{12} to give

$$B_{12} = \frac{V_m}{2y_2}\left[2\frac{B_{11}}{V_{01}} + \frac{3}{2}\frac{C_{111}}{V_{01}^2} - \ln\frac{P_{01}V_{01}}{RT} - \frac{3}{2V_m^2}(y_1C_{111} + 2y_1y_2C_{112} + y_2^2C_{122}) + \frac{1}{RT}\int_{P_{01}}^{P} V_1^c\,dP - \frac{2y_1B_{11}}{V_m} + \ln\frac{PV_m}{RT} + \ln x_1 - \ln\phi_1\right] \quad (20)$$

Along a given experimental isotherm eq 20 is solved for B_{12} for each pressure by making use of experimental values for y_i, x_i, and v_i^c from eq 5 and P_{01} for the saturated phase and B_{11} and B_{22}, and by assuming a model from which the third interaction coefficients C_{112} and C_{122} as well as C_{111} and C_{222} may be estimated. The volume V_m is also calculated by using these third virial coefficients together with an estimated value of B_{12}. The values of B_{12} so found from eq 20 are then plotted vs. the quantity $(P - P_{01})$ and the curve extrapolated to $(P - P_{01}) = 0$ to obtain the values of B_{12} shown in Table VIII. The values of B_{12} so obtained are only slightly dependent upon the model used to estimate the third virial coefficients and V_m. The uncertainty listed for each value is based primarily upon the effects on B_{12} of the uncertainty in the experimental values of y_1 and x_1 on the calculation of B_{12} from eq 20.

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Gas-Liquid Equilibrium in Mixtures of Carbon Dioxide + Toluene and Carbon Dioxide + *m*-Xylene

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Gas-liquid equilibrium data are determined for mixtures of CO_2 + toluene at five temperatures from 120 to 270 °C and for mixtures of CO_2 + *m*-xylene at four temperatures from 190 to 310 °C. The pressures were up to 50 atm for both systems.

Introduction

The phase behavior of carbon dioxide mixtures is of technological interest because of the occurrence of carbon dioxide in natural gas, crude oil, and numerous chemical processes. A number of phase equilibrium studies have been made on mixtures of carbon dioxide and hydrocarbons, mostly paraffins. In this work we report the phase behavior of carbon dioxide in mixtures with two aromatic hydrocarbons.

Battino and co-workers reported solubility data of CO_2 in toluene (*2*) and in *m*-xylene (*1*) in the temperature range 10-40 °C. The vapor-phase solubility of toluene in compressed CO_2 was studied by Prausnitz and Benson (*5*) at 50-75 °C in the pressure range of 20-90 atm. Recently Ng and Robinson (*4*) presented the experimental results for CO_2 + toluene mixtures at temperatures from 38 to 204 °C and pressures up to 150 atm. We report in this study vapor-liquid equilibrium data for mixtures of carbon dioxide + toluene up to 270 °C and for carbon dioxide + *m*-xylene to 310 °C. The pressure range studied is 10-50 atm.

Experimental Section

The experimental apparatus and procedure used in this work are essentially the same as those described by Simnick and co-workers (*6*). Carbon dioxide was supplied by Matheson with a minimum purity of 99.99%. *m*-Xylene was purchased from Aldrich Chemical Co. with a claimed purity of 99+%. Toluene obtained from Mallinckrodt Co. is analytical reagent grade. The

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