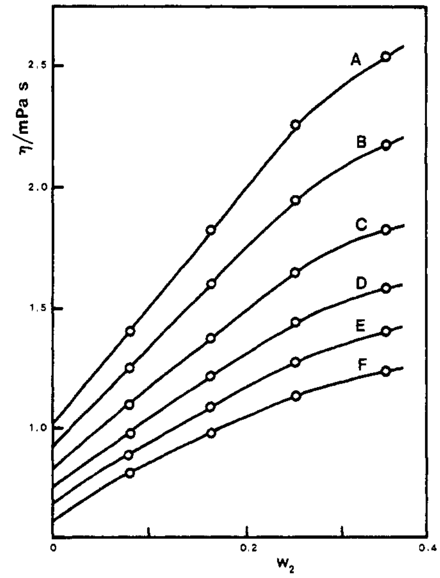

Figure 4. Shear viscosity of a 4.76% sucrose solution in water + ethanol as a function of ethanol mass fraction w_2: A, 25 °C; B, 30 °C; C, 35 °C; D, 40 °C; E, 45 °C; F, 50 °C.

anomaly reduces sharply as the temperature increases (Figure 4). Preliminary work on mixtures richer in ethanol suggests that the position of the maximum viscosity on the w_2 axis is insensitive to the amount of sucrose.

Acknowledgment

We thank Mr. E. Bell for technical assistance and John Harvey and Sons Ltd. for some financial support.

Glossary

p	pressure
T, t	temperature
V	molar volume
w_i	mass fraction of component i
α_p	isobaric thermal expansion coefficient
η	shear viscosity coefficient
ρ	density

Literature Cited

(1) Pemberton, R. C., Mash, C. J., *J. Chem. Thermodyn.*, **10**, 867 (1978).
(2) Larkin, J. A., *J. Chem. Thermodyn.*, **7**, 137 (1975).
(3) Osborn, N. S., *Bur. Stand.* (*U.S.*), *Bull.*, **9**, 405 (1913).
(4) Kikuchi, M., Oikawa, E., *Nippon Kagaku Zasshi*, **88**, 1259 (1967).
(5) Hosking, *Philos. Mag.*, **49**, 274 (1900).
(6) Ben-Naim, A., Baer, S., *Trans. Faraday Soc.*, **60**, 1736 (1964).
(7) Kumaran, M. K., McGlashan, M. L., *J. Chem. Thermodyn.*, **9**, 259 (1977).
(8) Orwoll, R. A., Flory, P. J., *J. Am. Chem. Soc.*, **89**, 6814 (1967).
(9) Ubbelohde, A. R., *J. Inst. Pet., London*, **23**, 427 (1973).
(10) Martinus, N., Vincent, C. A., *J. Chem. Soc., Faraday Trans. 1*, **72**, 2505 (1976).
(11) Garrod, J. E., Herrington, T. M., *J. Phys. Chem.*, **74**, 363 (1970).

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Densities of Molten $FeCl_3$, KCl–$FeCl_3$, and KCl–$AlCl_3$

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Liquid densities of $FeCl_3$, KCl–$FeCl_3$, and KCl–$AlCl_3$ mixtures were measured by using the automated float method. The compositions measured for the KCl–$FeCl_3$ (and $FeCl_3$) system were in mole fractions of potassium chloride, X_{KCl}: 0.0000, 0.4000, 0.4500, 0.5000, 0.5250. The compositions measured for the KCl–$AlCl_3$ system were at X_{KCl} 0.4000 and 0.5000. The obtained densities were at each composition fitted to an equation of the form $\rho = A(X) + B(X)(t - 300)$ and $A(X)$ and $B(X)$ again fitted by polynomials of X_{KCl} in the whole mole fraction range. Furthermore, for each of the systems KCl–$FeCl_3$ and KCl–$AlCl_3$, all the measured data were fitted to an equation of form $\rho = \sum_0^n A_n X^n + (\sum_0^m B_m X^m)(t - 300)$. Interesting enough the change in molar volumes of the KCl–$FeCl_3$ mixtures was an almost linear function of the composition. Maximum deviations of only −3.5% were obtained in contrast to the deviations of up to −26% at 300 °C which can be calculated for the analogous KCl–$AlCl_3$ system. The difference between these two systems is probably due to the formation of ionic species in the molten ferric chloride in contrast to the existence of only molecular Al_2Cl_6 in liquid aluminum chloride.

In connection with a potentiometric and spectrophotometric investigation of the molten KCl–$FeCl_3$ system (*1*), the densities for this system were measured at a few compositions around a mole fraction of potassium chloride of $X_{KCl} = 0.5$ and at different temperatures. In the present paper we have supplemented these measurements to cover the mole fraction range of $0 \leq X_{KCl} \leq 0.5250$. For comparison of these densities with the densities of the KCl–$AlCl_3$ system, a few measurements have also been performed on this system. The method employed is the previously described "automated float method" for determination of densities of molten salts (*2*). This method is very well suited for the present systems, especially the KCl–$FeCl_3$ system which at compositions rich in ferric chloride has a high vapor pressure. The melt is furthermore dark colored which makes visual observations of the floats impossible. Visual observations of floats have successfully been used by other authors in connection with aluminum chloride containing systems (*3-5*), which also have high vapor pressures for mixtures rich in aluminum chloride.

Densities of the KCl–$FeCl_3$ system in a rather limited range where the vapor pressure is low and only at one temperature have been measured by the Archimedian method by Juvet, Shaw, and Khan (*6*).

Experimental Section

The densities were measured by the automated float method (*2*). This method is based on magnetic detection of quartz floats with iron cores as they pass a differential transformer. The idea is that the temperature of the melt (placed in a long tube together

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Table I. Experimental Densities and Temperatures of the Molten KCl-$FeCl_3$ System

densities of floats, g cm^{-3}		measd temps at the given mole fractions, °C					
at 20 °C	at measd temp	$X_{KCl} = 0.0000$	$X_{KCl} = 0.2000$	$X_{KCl} = 0.4000$	$X_{KCl} = 0.4500$	$X_{KCl} = 0.5000$	$X_{KCl} = 0.5250$
1.6010	1.5994					626.5 (6)[a]	
1.6730	1.6716					524.0 (11)	529.0 (11)
1.6752	1.6741	402.0 (8)					
1.7101	1.7089		443.7 (8)				
1.7101	1.7091	371.1 (5)[b]					
1.7210	1.7198		432.2 (7)				
1.7210	1.7200	363.3 (7)					
1.7480	1.7468			429.3 (11)	433.8 (11)	436.0 (9)	438.5 (8)
1.7610	1.7601	331.0 (7)					
1.7673	1.7662		385.4 (7)				
1.7673	1.7664	326.5 (6)					
1.7945	1.7935			373.5 (8)	378.5 (10)	381.5 (8)	383.3 (6)
1.8061	1.8051		344.3 (6)				
1.8157	1.8147			350.8 (8)	355.0 (9)		
1.8600	1.8592			297.5 (12)	303.5 (16)	308.0 (8)	308.3 (12)
1.8971	1.8964			258.0 (7)	263.5 (8)		

[a] I.e., 626.5 ± 0.6; this point is not included in the calculations of the density polynomials. [b] Measured in two different tubes to 370.7 and 371.5 °C (with float in different position in the density tubes).

with the floats) is increased or decreased gradually. In this way the density of the melt is either decreased or increased gradually. The density of the quartz floats does not change much with temperature, and if the difference in density between floats and melt originally is small, the floats will consequently either sink or float at a given temperature. Floats of different densities were made by sealing small weights of iron (50-300 mg) into small pieces of quartz tubes (outside diameter 6 mm and length 2-3 cm). The densities at 20 °C of these floats were obtained by the buoyancy method (or Archimedian method) by weighing the floats in air and in water.

The furnace and its regulation have been described in detail previously in connection with the introduction of the "automated float method" (*2*). The chromel-alumel thermocouples (from Pyrotenax) were calibrated at the freezing points of pure tin, lead, and zinc to within ±0.5 °C. The measured temperatures are probably correct to within ±0.7 °C (the regulation of the furnace is approximately ±0.1 °C). KCl (analytical reagent from Riedel-de Haën) was purified by first passing HCl gas over the solid and then through the melt, flushing with pure N_2, and finally filtering the melt. $FeCl_3$ was made from iron (99.999%) and chlorine (Fluka >99.9%) and further purified by distillation in chlorine gas. $AlCl_3$ was made from the pure metal (99.999%) and HCl gas (made by reaction between hydrochloric acid and H_2SO_4). Handling of the solid salts was performed as described earlier (*1*). In order to avoid decomposition of ferric chloride we sealed the density tubes under a chlorine pressure of 0.5 atm.

Results

The experimental densities and temperatures of the KCl-$FeCl_3$ system are given in Table I. The densities of the used floats are calculated on the basis of eight determinations at room temperature and corrected for the thermal expansion of quartz at the measured temperature. The maximum mole fraction of KCl employed in this investigation is 0.5250. Due to limitations in our present experimental setup, it is not possible to obtain density values for melts having mole fractions of KCl larger than this value over a temperature range large enough to check the linearity of the density against temperature.

In Table II the results for the KCl-$AlCl_3$ system are given in a similar way. The standard deviation on the measured temperatures are calculated in accordance with the procedure described previously (*2*).

In Tables III and IV the obtained densities for the respective systems KCl-$FeCl_3$ and KCl-$AlCl_3$ are given for each composition by $A(X)$ and $B(X)$ ($\rho = A(X) + B(X)(t - 300)$), where ρ is the density in g cm^{-3}, $A(X)$ is the density at the composition X_{KCl} at 300 °C, $B(X)$ is the density change per degree for the melt at the composition X_{KCl}, and t is the temperature in °C. Since most of the experiments were performed around 300 °C the

Table II. Experimental Densities and Temperatures of the Molten KCl-$AlCl_3$ System

densities of floats, g cm^{-3}		measd temps at the given mole fractions	
at 20 °C	at measd temp	$X_{KCl} =$ 0.4000	$X_{KCl} =$ 0.5000
1.3823	1.3810		594.2 (13)
1.4429	1.4417		514.7 (12)
1.5180	1.5170		417.0 (8)
1.5180	1.5172	357.6 (7)	
1.5836	1.5828		337.0 (7)
1.5836	1.5829	280.0 (6)	
1.6010	1.6004	258.9 (6)	
1.6271	1.6264		283.8 (6)

Table III. Linear Density Equations and Molar Volumes of the Molten KCl-$FeCl_3$ System[a]

mole fraction KCl	$A(X)$,[b] g cm^{-3}	$10^3 B(X)$,[b] g cm^{-3} deg^{-1}	std dev, g cm^{-3}	molar volume at 300 °C, cm^3 mol^{-1}
0.0000	1.7981 (15)	−1.231 (22)	0.0014	90.21
0.2000	1.8485 (8)	−0.972 (7)	0.0006	78.27
0.4000	1.8585 (8)	−0.871 (11)	0.0014	68.41
0.4500	1.8632 (7)	−0.877 (9)	0.0012	65.89
0.5000	1.8652 (10)	−0.867 (7)	0.0011	63.47
0.5250	1.8652 (11)	−0.849 (8)	0.0013	62.29
1.0000[c]	1.8027 (18)	−0.584 (3)	0.0005	41.36[d]

[a] For the measured temperature ranges, see Table I. [b] $\rho = A(X) + B(X)(t - 300)$. [c] Values calculated from ref 7. [d] Extrapolated value.

Table IV. Linear Density Equations and Molar Volumes of the Molten KCl-$AlCl_3$ System[a]

mole fraction KCl	$A(X)$,[b] g cm^{-3}	$10^3 B(X)$,[b] g cm^{-3} deg^{-1}	std dev, g cm^{-3}	molar volume at 300 °C, cm^3 mol^{-1}
0.0000[c]	1.033 (10)	−2.34 (11)	0.0025	129.08
0.4000	1.5658 (1)	−0.844 (3)	0.0002	70.13
0.5000	1.6126 (12)	−0.801 (9)	0.0016	64.46
1.0000[d]	1.8027 (18)	−0.584 (3)	0.0005	41.36[e]

[a] For the measured temperature ranges, see Table II. [b] $\rho = A(X) + B(X)(t - 300)$. [c] Values calculated from ref 3. [d] Values calculated from ref 7. [e] Extrapolated value.

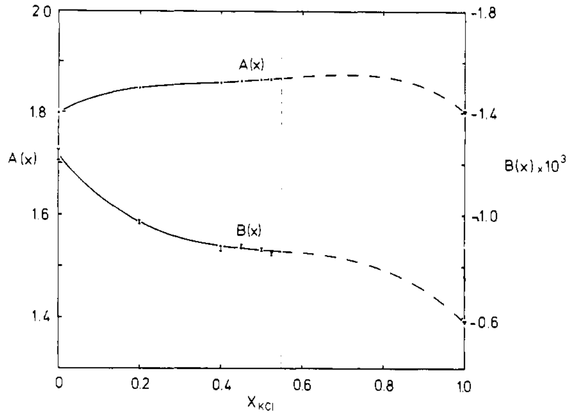

Figure 1. Variations of the parameters $A(X)$ and $B(X)$ vs. mole fraction X_{KCl} in the KCl-FeCl$_3$ system: curved lines, $A(X) = 1.7981 + 0.4729X - 1.5204X^2 + 2.3099X^3 - 1.2578X^4$, $B(X) = -1.232 \times 10^{-3} + (1.895 \times 10^{-3})X - (3.385 \times 10^{-3})X^2 + (2.138 \times 10^{-3})X^3$; (I) (●) this work; (▼) values calculated from ref 7.

given equation was found more satisfactory than the normal way of presenting density measurements, namely, by $\rho = A(X) + B(X)t$. The uncertainty in $A(X)$ is much smaller in the former equation than in latter equation. This is of course of importance when $A(X)$ is given as a function of X_{KCl}.

The $A(X)$ and $B(X)$ values for molten KCl are taken from the work by Van Artsdalen and Yaffe (*7*). Since KCl melts at 772 °C, we are using extrapolated values below this temperature. The measurements on the pure FeCl$_3$ done by us were performed in the temperature range 326-402 °C.

In Tables III and IV are also listed the molar volumes of the mixtures of different compositions. It is interesting here to note that for the KCl-FeCl$_3$ system the deviation from linearity is at the most -3.5%; whereas for the KCl-AlCl$_3$ system, which in many respects has similar properties as the KCl-FeCl$_3$ system, deviations from linearity as high as -26% are observed. An explanation for this can be found in the difference of the structure of liquid aluminum chloride and liquid ferric chloride. It is well-known that in the gas phase at moderate temperatures, Fe$_2$Cl$_6$ and Al$_2$Cl$_6$ are the main gas species. The molar conductivity of molten AlCl$_3$ is approximately 6 × 10^{-4} cm^2 Ω^{-1} mol^{-1} at 210 °C (*8*) and the molar conductivity of molten FeCl$_3$ is approximately 4 cm^2 Ω^{-1} mol^{-1} at 300 °C (*9*) (which is not far from the range of normal ionic melts). On the basis of these results it is obvious that molten ferric chloride cannot, in contrast to molten aluminum chloride, exist only as Fe$_2$Cl$_6$ molecules. We will in this connection suggest that molten ferric chloride is partly dissociated into FeCl$_2^+$ and FeCl$_4^-$. Another interesting phenomenon pointing in the same direction is that the molar volumes for equimolar mixtures of KCl-FeCl$_3$ and KCl-AlCl$_3$ are almost identical, indicating that AlCl$_4^-$ and FeCl$_4^-$ have the same size, whereas the molar volumes of molten ferric chloride and molten aluminum chloride are very different.

In Figures 1 and 2, $A(X)$ and $B(X)$ are shown as functions of the composition of the systems KCl-FeCl$_3$ and KCl-AlCl$_3$, respectively. The curved lines show the best polynomials of third degree fitted (by the least-squares method) to the data (except for $A(X)$ in Figure 1, where a polynomial of fourth degree must be employed to fit the data satisfactory). The parameters used are given in the figure captions.

Another way to treat the data, which is especially useful in connection with computer programs is to combine all the data obtained at different temperatures and different compositions into one empirical equation of the form $\rho = \sum_0^n A_n X^n + (\sum_0^m B_m X^m)(t - 300)$. For the KCl-FeCl$_3$ system this equation has been examined for two mole fraction ranges of X_{KCl} 0.4000-0.5250 and 0.0000-0.5250. The results of this examination are given in Table V. If this equation (based on the range 0.4000-0.5250) is used on the composition range and the temperature 290 °C in which the density has been measured by Juvet et al. (*6*) (i.e., X_{KCl} 0.500-0.521) a density of 1.874 (1) is found for this range. This result agrees reasonable well with densities of 1.890-1.888 obtained by Juvet et al. (*6*) by the Archimedian method. For the KCl-AlCl$_3$ system an analogous equation is calculated on the basis of data from the complete composition range $0 \leq X_{KCl} \leq 1$. This equation is shown in Table VI. However, as indicated by the dashed curves

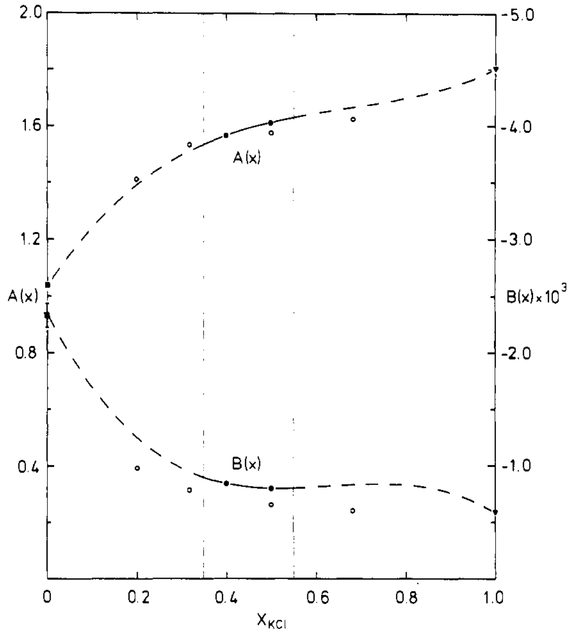

Figure 2. Variations of the parameters $A(X)$ and $B(X)$ vs. mole fraction X_{KCl} in the KCl-AlCl$_3$ system: curved lines, $A(X) = 1.0331 + 2.3396X - 3.1524X^2 + 1.5824X^3$, $B(X) = -2.336 \times 10^{-3} + (7.691 \times 10^{-3})X - (12.544 \times 10^{-3})X^2 + (6.605 \times 10^{-3})X^3$; (●) this work; (▼) values calculated from ref 7; (O) values calculated from ref 4; (■) values calculated from ref 3.

Table V. Values of Coefficients for Empirical Polynomial[a] for Densities of the KCl-FeCl$_3$ System in Different Composition Ranges

	$0.4000 \leq X_{KCl} \leq 0.5250$[b] ($n = 2$, $m = 2$)[a]	$0.0000 \leq X_{KCl} \leq 0.5250$[c] ($n = 4$, $m = 3$)[a]
A_0	1.72089	1.79817
A_1	0.56531	0.57088
A_2	−0.55307	−2.47802
A_3		5.06570
A_4		−3.71475
B_0	0.09769 × 10^{-3}	−1.23355 × 10^{-3}
B_1	−4.38176 × 10^{-3}	2.06480 × 10^{-3}
B_2	4.90832 × 10^{-3}	−4.23868 × 10^{-3}
B_3		3.19491 × 10^{-3}

[a] $\rho = \Sigma_0^n A_n X^n + (\Sigma_0^m B_m X^m)(t - 300)$. [b] Standard error 0.0012 g cm^{-3}. [c] Standard error 0.0013 g cm^{-3}.

Table VI. Values of Coefficients for the Empirical Polynomial[a] for Densities of the KCl-AlCl$_3$ System

$0.3500 \leq X_{KCl} \leq 0.5500$[b] ($n = 4$, $m = 3$)[a]

A_0	1.03324	B_0	−2.33466 × 10^{-3}
A_1	2.22164	B_1	6.97573 × 10^{-3}
A_2	−2.19425	B_2	−9.89241 × 10^{-3}
A_3	−0.66001	B_3	4.66684 × 10^{-3}
A_4	1.40205		

[a] $\rho = \Sigma_0^n A_n X^n + (\Sigma_0^m B_m X^m)(t - 300)$. [b] Standard error (calculated for the composition range $0.0000 \leq X_{KCl} \leq 1.0000$) 0.0044 g cm^{-3}.

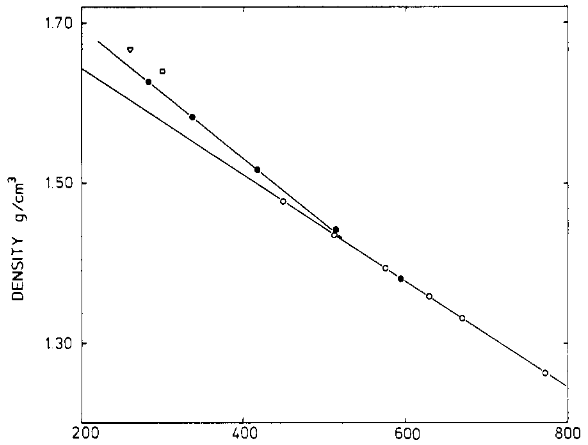

Figure 3. The density of the KCl-AlCl$_3$ system at X_{KCl} = 0.5000 vs. temperature: (●) this work; (○) values from ref 4; (▽) value from ref 6; (□) value from ref 10.

in Figure 2, it is recommended only to apply the equation for calculation of densities in the range 0.35 ≤ X_{KCl} ≤ 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*).

Literature Cited

(1) Andreasen, H. A., Bjerrum, N. J., *Inorg. Chem.*, **14**, 1807 (1975).
(2) Andreasen, H. A., Bjerrum, N. J., Foverskov, C. E., *Rev. Sci. Instrum.*, **48**, 1340 (1977).
(3) Boston, C. R., *J. Chem. Eng. Data*, **11**, 262 (1966).
(4) Morrey, J. R., Carter, D. G., *J. Chem. Eng. Data*, **13**, 94 (1968).
(5) Boston, C. R., *J. Chem. Eng. Data*, **13**, 117 (1968).
(6) Juvet, R. S., Jr., Shaw, V. R., Khan, M. A., *J. Am. Chem. Soc.*, **91**, 3788 (1969).
(7) Van Artsdalen, E. R., Yaffe, I. S., *J. Phys. Chem.*, **59**, 118 (1955).
(8) Semenenko, K. N., Naumova, T. N., *Zh. Neorg. Khim.*, **9**, 1316 (1964).
(9) Unpublished results.
(10) Øye, H. A., Gruen, D. M., *Inorg. Chem.* **4**, 1173 (1965).

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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-

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