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# Vapor-liquid equilibria of the system: tetrafluoromethane-trifluorochloromethane- trifluoromethane

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VAPOR-LIQUID EQUILIBRIA OF THE SYSTEM ;  
TETRAFLUOROMETHANE - TRIFLUOROCHLOROMETHANE - TRIFLUOROMETHANE

by  
Patricio C. Proust

A Thesis  
Presented in Partial Fulfillment  
of the Requirements for the Degree of  
Master of Science  
in  
Chemical Engineering.

Lehigh University

1970

## DEDICATION

To my wife Rosemarie and my children, whose love and sacrifices made this work possible.

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## ABSTRACT

Vapor-liquid equilibrium compositions of the ternary system : Tetrafluoromethane - Trifluorochloromethane - Trifluoromethane were determined at  $-100^{\circ}\text{F}$  and at total pressures of 50 and 100 p.s.i.a., covering the full range of compositions.

Data for the binary system : Tetrafluoromethane - Trifluorochloromethane were also taken at  $-100^{\circ}\text{F}$ .

Liquid-phase activity coefficients were calculated, a modified Redlich-Kwong equation of state being used to describe the vapor phase.

The experimental results can be satisfactorily correlated using data of the pure components and of the three binary systems. The correlation developed also permits the prediction of the phase equilibria of the ternary system at  $-100^{\circ}\text{F}$  and any intermediate pressure between 25 and 220 p.s.i.a.

## 1. INTRODUCTION

The importance of the halogenated hydrocarbons, commercially called "Freons", as refrigerants, solvents, aerosol propellants, etc. is well known.

The proper design of the equipment where these substances are used or processed requires knowledge of their volumetric behavior, heat capacity, phase equilibria, etc. Therefore, these thermodynamic properties have been investigated with some extension during the last few years.

As part of a continuing program directed toward these goals, the vapor-liquid equilibria of binary systems of the lighter fluorocarbons  $\text{CF}_4$  (Freon-14),  $\text{CClF}_3$  (Freon-13) and  $\text{CHF}_3$  (Freon-23) have been determined (10, 13, 14).

Thus, it was decided to study the corresponding ternary system, under isothermal and isobaric conditions, and to find out whether these experimental values agreed with the ones predicted using pure and binary data only.

The temperature selected was  $-100^\circ\text{F}$ , since two of the sets of binary data already available included this isotherm. Vapor-liquid equilibria of the other binary ( $\text{CF}_4 - \text{CClF}_3$ ) had been established at  $-120^\circ$  and  $-60^\circ\text{F}$ . Interpolation procedures used to generate data at  $-100^\circ\text{F}$  were not considered adequate, and therefore this binary system was also included in the present work.

At the temperature selected, the vapor pressures of  $\text{CF}_4$ ,  $\text{CClF}_3$  and  $\text{CHF}_3$  are 223.8, 22.3 and 23.7 p.s.i.a. respectively. Accordingly, pressure levels of 50 and 100 p.s.i.a. were chosen.

## 2. EXPERIMENTAL APPARATUS

Vapor-liquid equilibrium data were taken using an apparatus of the vapor-recirculation type, which has been described previously ( 10 ).

Essentially, its operation is as follows : the equilibrium glass cell is placed in a constant-temperature bath, and once a liquid level is established, the vapor phase is removed and continuously circulated, by means of a gas pump, to the bottom of the cell, thereby promoting the intimate contact of both phases which is needed to attain equilibrium conditions.

The equilibrium cell has an approximate volume of six cc. It is provided with a three-junction thermopile for temperature measurement, a liquid sampling probe, vapor dispersion devices and a liquid-entrainment suppressor.

After removal from the top of the cell, the vapor passes successively through a sampling coil, a reciprocal pump which is operated magnetically, a volume regulator, and a cooling coil placed in the constant-temperature bath, from which it is injected to the bottom of the cell.

The volume regulator is used to keep a constant pressure in the system while liquid samples are withdrawn.

The constant-temperature bath consists of a three-liter flask filled with an appropriate liquid and provided with a stirrer

in order to have a vigorous agitation.

Low temperatures are attained by circulating liquid nitrogen inside a finned heat exchanger placed inside the thermostatic bath. A Bayley proportional temperature controller, which operates an electrical heater, is used to keep the bath temperature at a constant level.

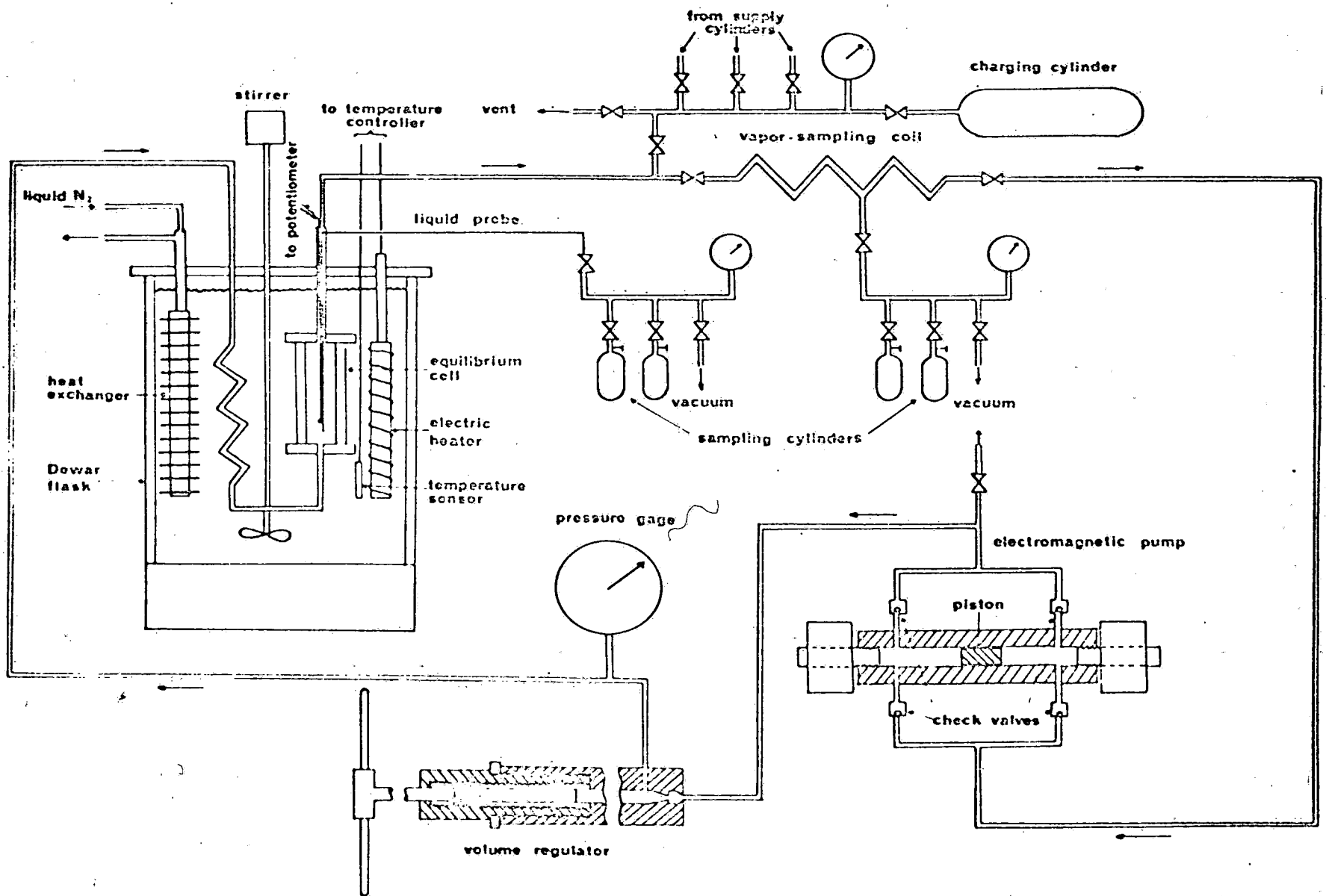
The liquid sampling probe and the vapor sampling coil are connected to corresponding manifolds, where samples are collected in small cylinders.

A 165 cc cylinder was added to the inlet manifold, in order to facilitate the charging of gases into the apparatus by recording the manifold pressure before and after a given gas is admitted.

The total volume of the apparatus is approximately 270 cc.

A schematic of the system is shown in Fig. 1.

Fig. 1 Experimental Apparatus



### 3. EXPERIMENTAL PROCEDURE

#### 3.1 Temperature measurement.

The temperature was measured with a three-junction copper - constantan thermopile placed inside the equilibrium cell. The reference junction was immersed in a water - ice bath, and the voltages generated were determined with a Leeds & Northrup type K-3 potentiometer.

The thermopile had been previously calibrated against a platinum resistance thermometer, calibrated at the National Bureau of Standards. The maximum possible error in the reported temperature is  $\pm 0.1^{\circ}\text{F}$ .

Temperatures were controlled to within  $\pm 0.02^{\circ}\text{F}$  with the proportional controller.

#### 3.2 Pressure measurement.

Heise precision Bourdon-tube gauges were employed, and depending on the system conditions, a 0-100 p.s.i.a. gauge with 0.1 p.s.i.a. subdivisions, or a 0-500 p.s.i.a. gauge with 0.5 p.s.i.a. subdivisions, was selected.

These gauges had been calibrated with a dead-weight tester manufactured by Ruska Company. This calibration indicates that the accuracy of the gauges is as good as they can be read.

Pressures could be read to within  $\pm 0.01$  and  $\pm 0.1$  p.s.i.a.



respectively.

When working in the ternary system under isobaric conditions, pressures were kept constant to within  $\pm 0.1$  p.s.i.a.

### 3.3 Operation.

#### 3.3-1 General.

The whole apparatus was evacuated to approximately 100 microns of mercury, this vacuum being read with a McLeod gage. After purging twice with the first component to be added, the gas pump was started and liquid nitrogen was circulated to cool the bath liquid to a temperature slightly below  $-100^{\circ}\text{F}$ . Then the temperature controller was connected and its set point adjusted until the desired millivoltage from the cell thermopile was read in the potentiometer.

Liquid-nitrogen flow rate and the power output of the controller were manually adjusted so that the controller meter could be stabilized near the middle of its range. An adjustable transformer was used to supply the heating element, and final manipulations were made in order to have the output of the transformer at around 25% of the total output. This procedure allowed a low consumption of liquid nitrogen.

### 3.3-2 Binary System.

The first component, either  $\text{CF}_4$  or  $\text{CClF}_3$ , was slowly admitted to the apparatus through the gas-inlet manifold, which was connected to the supply cylinders of the pure gases, until a liquid level could be seen inside the cell. After a short time, gas bubbles rose through the liquid. The amplitude and frequency of the gas pump were then adjusted so as to have a steady stream of bubbles in the cell.

The system was left to run until a constant pressure could be recorded, which corresponded to the vapor pressure of the first component. The pump was stopped and this pressure was recorded.

The gas pump was then started again, and the second component, which had been previously charged in the evacuated gas-inlet manifold, was slowly admitted to the apparatus until the liquid level reached approximately one half of the cell height.

Pressure oscillations were observed which lasted for about 20 minutes. After the system pressure was at a steady-state value, at least 30 more minutes were allowed to elapse, to be sure that equilibrium conditions had been attained. During this period the liquid sampling probe was flushed twice.

The gas pump was then stopped and the pressure was recorded. A vapor sample was trapped in the vapor sampling coil, while simultaneously a liquid sample was obtained through the cell probe and sent to the evacuated sampling manifold, while the pressure was

kept unchanged by reducing the volume of the system with the volume regulator.

The vapor trapped in the sampling coil was sent to a sampling manifold, from where it was directed to a stainless-steel cylinder, with a capacity of 75 cc, which had been evacuated to about 50 microns. A similar procedure was followed with the liquid.

Except for a few samples with high  $\text{CClF}_4$  content, most samples were obtained at a total pressure of 30 p.s.i.g., which was found to provide enough material for analysis.

Since there remained some liquid in the cell after the sampling procedure, another run was possible by further addition of the second component. In this way, three or four runs were made during one day.

After some practice, it was possible to get equilibrium pressures which covered more or less evenly the full range of compositions.

### 3.3-3 Ternary Systems.

The experimental method differed somewhat in this case, for besides isothermal conditions, the total system pressure was also to be kept constant.

At  $-100^\circ\text{F}$  the binary  $\text{CHF}_3 - \text{CClF}_3$  encompasses a pressure range of 22.3 to 31.3 p.s.i.a. ( 14 ), while the observed vapor

pressure of  $CF_4$  was 221.5 p.s.i.a. Therefore, the procedure adopted was the same as if the mentioned binary system was to be determined, i.e. getting equilibrium pressures necessary to cover the whole composition range, as described in Section 3.3-2. Once equilibrium conditions were reached, the light component  $CF_4$  was added very carefully until the desired pressure was attained. Final adjustments were made by slightly venting the apparatus if the pressure had been exceeded, or adding more  $CF_4$ , and by manipulating the volume regulator, which provided a very convenient way to get the exact pressure desired.

As in the case of the binary system, at least 30 minutes, and usually one hour of steady-state operation were allowed before beginning the sampling procedure, which was the same as in the binary case.

Obviously, it was necessary to begin each ternary run with the apparatus completely evacuated, then add the two heavy components in succession, and finally admit the light component as already described.

The total time required for a given ternary run was approximately 2.5 hours.

## 3.3-4 Remarks.

a) Bath fluid : Trichlorofluoromethane ( Freon-11 ) was initially used in the cryostat. However, it was observed that the moisture from the air which condensed over the cold liquid and melting frost that drained into it from other parts of the apparatus formed a suspension with the organic compound, thus limiting, and eventually forbidding, visual observation of the equilibrium cell.

Acetone was then successfully used as a constant-temperature medium. Some safety precautions were taken, such as blowing air over the liquid surface, to avoid acetone accumulation in the vapor space above the surface that would cause an explosion hazard in the electric motor of the stirrer. This precaution was required only during the start-up period, because at  $-100^{\circ}\text{F}$  the vapor pressure of acetone is so low as to make its evaporation negligible.

b) Gas pump : It was necessary to externally cool the pump with ice in order to have an adequate vapor flow in the apparatus. It was later verified that this procedure could be avoided by a proper choice of the pump piston diameter, since if the gap between the piston and the cylinder wall is very close, the heat generated by friction expands the piston tightly against the wall, and prevents the gas from being displaced inside the pump.

c) Low-pressure samples : When the system pressure was low, on the order of 30 p.s.i.a., the samples collected were small enough to cause difficulties in the analytical procedure. In these cases the sample cylinders were externally chilled with ice, and in this way the mass that flowed into the cylinders was increased.

#### 3.4 Analytical technique.

Samples were analyzed chromatographically, using a Beckman Instruments, Inc. model GC-2A gas chromatograph. The adsorbent column consisted of 18 feet of di-n-butyl maleate coated onto C-22 firebrick. Helium was the carrier gas, and it was injected to the chromatograph at a pressure of 10 p.s.i.g., which proved to give a good separation of the three fluorocarbons. The operating temperature was 40°C and the filament current of the thermal conductivity detector was 100 mA. Each run lasted approximately 15 minutes.

Peak areas were measured automatically with an electronic integrator consisting of a Hewlett-Packard model 8875A differential amplifier, a Dymec model 2210 voltage-to-frequency converter and an Anadex model CF-200R digital counter. A strip-chart recorder was also used as a visual aid.

Unknown compositions were determined by comparison with peak areas of samples of known composition, both being fed to the chromatograph in succession. These peak areas were expressed as

counts per mm Hg of sample, so as to consider different sample pressures that were introduced to the instrument. Sample inlet pressures were measured with a Ruska Company model XR-38 pressure counter, consisting of a very precise Bourdon tube made of fused quartz, which had been calibrated by the manufacturer against a dead-weight tester. Sample pressures ranged from 300 to 700 mm Hg.

All the runs with samples of known composition were duplicated, and a maximum departure of 0.3% from the arithmetic average was permitted. The occasional sample that resulted in a greater departure was rejected.

If the mole fraction of the minor component of an unknown sample was less than 0.10, this sample was run twice, allowing the 0.3% departure. Then this mole fraction was assumed true and was left unchanged, and the other two mole fractions were then normalized to a total of 1.00. Otherwise, all three mole fractions were normalized.

Most of the unknown samples analyzed gave an unnormalized total mole fraction ranging from 0.98 to 1.02.

Reference samples, or high-pressure standards, had been prepared several weeks prior to their use in a gas mixing apparatus, at a total pressure of 400 p.s.i.a. Their composition had been, in turn, determined chromatographically by comparison with low-pressure standards of approximately the same composition.

The compositions of the low-pressure standards were

obtained by means of partial pressure measurements made with the pressure counter already mentioned. Since this is a very sensitive instrument, capable of reflecting even ambient temperature fluctuations, sufficient time was allowed before a pressure reading was made, while room temperature was continuously monitored with a mercury thermometer. When a constant value of the pressure was reached, both this pressure and the room temperature were recorded. The second component of the mixture was then added and a similar procedure was followed. If the second temperature was not the same, one of the pressure readings was corrected through the ideal gas law.

Once the compositions of the binary standard were calculated by means of the partial pressures recorded, they were corrected slightly for non-ideal behavior of the gas mixture, using the virial equation of state truncated after the second virial coefficient term.

Second virial coefficients for the pure components were calculated from the Martin-Hou equation of state ( 9 ) :

$$B_{ii} = \frac{A_{2i} + B_{2i} T + C_{2i} \exp(-k_i T r_i)}{RT} + b_i \quad ( 3.4-1 )$$

Values of the individual coefficients and critical temperatures of  $CF_4$  and  $CClF_3$  were taken respectively from ( 2 ) and ( 3 ).



For  $\text{CHF}_3$ , Martin-Hou constants were taken from ( 4 ) and the critical temperature from ( 5 ).

Second virial cross coefficients,  $B_{ij}$ , were computed from the generalized Pitzer-Curl correlation ( 11 ), using the mixing rules proposed by Prausnitz et al. ( 12 ).

Low- and high-pressure standards consisted only of binary systems of  $\text{CF}_4 - \text{CHF}_3$  and  $\text{CClF}_3 - \text{CHF}_3$ , because it was verified that peak areas for a given component were not affected by the presence of the other components nor by their identity. Therefore, each unknown composition was determined in the way described by comparison with standards of approximately the same composition. Most of the time three standards were needed to analyze one single unknown sample.

The maximum possible error in the reported lesser mole fraction is estimated to be  $\pm 0.3\%$ .

### 3.5 Materials.

The three fluorocarbons used were made by E.I. du Pont de Nemours & Co. The manufacturer indicated the following purities:

$\text{CF}_4$	99.7%
$\text{CClF}_3$	99.96%
$\text{CHF}_3$	99.98%

Chromatographic analysis of  $\text{CF}_4$  and  $\text{CHF}_3$  confirmed these figures. However, the  $\text{CClF}_3$  supplied had a purity of 99.9% , the remaining 0.1% being  $\text{CF}_4$ .

#### 4. EXPERIMENTAL RESULTS

Experimental equilibrium compositions and pressures for the binary system  $\text{CF}_4$  -  $\text{CClF}_3$  at  $-100^\circ\text{F}$  are given in Table 1.

Equilibrium compositions for the ternary system  $\text{CF}_4$  -  $\text{CClF}_3$  -  $\text{CHF}_3$  at  $-100^\circ\text{F}$  and 50 p.s.i.a., and at  $-100^\circ\text{F}$  and 100 p.s.i.a. are given in Tables 2 and 3, respectively.

These experimental results are also shown in graphical form in Figures 2, 3 and 4.

##### Discussion.

The pressure-composition diagram of the binary system, Fig. 2, shows that the liquid phase has a nearly ideal behavior, the saturated liquid line going slightly above and below the straight line drawn between the pure-component vapor pressures. This fact is also reflected in the activity coefficients determined in the next section, where the values for  $\text{CClF}_3$  have a positive and negative deviation from unity.

The binary system  $\text{CClF}_3$  -  $\text{CHF}_3$  forms a maximum-pressure azeotrope at  $-100^\circ\text{F}$  ( 14 ). No such behavior was observed by the addition of a third and lighter component  $\text{CF}_4$ , as would happen if the vapor and liquid envelopes on Figures 3 and 4 touched each other.

However, at the lower pressure of 50 p.s.i.a., two "partial azeotropes" are formed in the ternary system, whereby the composition of one of the two heavy components is the same in the liquid and vapor phases. This occurs for a  $\text{CClF}_3$  mole fraction of about 0.15, and for a  $\text{CHF}_3$  mole fraction of about 0.23. For mole fractions smaller than these values, the vapor phase is richer than the liquid in the corresponding heavy component.

This peculiar behavior was not observed in the ternary system at 100 p.s.i.a. total pressure. In this case all the tie-lines had a positive slope.

TABLE 1

Experimental data for the binary system :

 $\text{CF}_4$  -  $\text{CClF}_3$  at  $-100^\circ\text{F}$ .

Pressure ( p.s.i.a. )	Mole Fraction $\text{CF}_4$		Mole Fraction $\text{CClF}_3$	
	<u>Liquid</u>	<u>Vapor</u>	<u>Liquid</u>	<u>Vapor</u>
22.4	0.0	0.0	1.0	1.0
29.2	0.0277	0.2278	0.9723	0.7722
35.5	0.0540	0.3805	0.9460	0.6195
50.0	0.1192	0.5811	0.8808	0.4189
52.2	0.1248	0.6017	0.8752	0.3983
77.2	0.2422	0.7534	0.7578	0.2466
100.0	0.3617	0.8283	0.6383	0.1717
123.1	0.4942	0.8772	0.5058	0.1228
150.1	0.6489	0.9165	0.3511	0.0835
174.5	0.7783	0.9479	0.2217	0.0521
199.5	0.8949	0.9737	0.1051	0.0263
221.5	1.0	1.0	0.0	0.0

TABLE 2

Experimental data for the ternary system :  
 $\text{CF}_4 - \text{CClF}_3 - \text{CHF}_3$  at  $-100^\circ\text{F}$  and 50 p.s.i.a.

Liquid Mole Fraction			Vapor Mole Fraction		
$\text{CF}_4$	$\text{CClF}_3$	$\text{CHF}_3$	$\text{CF}_4$	$\text{CClF}_3$	$\text{CHF}_3$
0.0445	0.0	0.9555	0.5205	0.0	0.4795
0.0446	0.0341	0.9213	0.4901	0.0450	0.4649
0.0452	0.0692	0.8856	0.4656	0.0843	0.4501
0.0466	0.1096	0.8438	0.4448	0.1211	0.4341
0.0490	0.1525	0.7985	0.4290	0.1490	0.4220
0.0486	0.1716	0.7798	0.4223	0.1666	0.4111
0.0510	0.2218	0.7272	0.4104	0.1952	0.3944
0.0525	0.2542	0.6933	0.4043	0.2114	0.3843
0.0556	0.3019	0.6425	0.4001	0.2293	0.3706
0.0608	0.4163	0.5229	0.3898	0.2743	0.3359
0.0634	0.4554	0.4812	0.3909	0.2859	0.3232
0.0668	0.5055	0.4277	0.3945	0.3004	0.3051
0.0691	0.5290	0.4019	0.3974	0.3061	0.2965
0.0740	0.6074	0.3186	0.4073	0.3272	0.2655
0.0754	0.6292	0.2954	0.4103	0.3311	0.2586
0.0814	0.6978	0.2208	0.4284	0.3495	0.2221

TABLE 2 ( cont. )

Liquid Mole Fraction			Vapor Mole Fraction		
<u>CF<sub>4</sub></u>	<u>CClF<sub>3</sub></u>	<u>CHF<sub>3</sub></u>	<u>CF<sub>4</sub></u>	<u>CClF<sub>3</sub></u>	<u>CHF<sub>3</sub></u>
0.0886	0.7470	0.1644	0.4490	0.3642	0.1868
0.1010	0.8183	0.0807	0.4978	0.3932	0.1090
0.1100	0.8536	0.0364	0.5384	0.4074	0.0542
0.1192	0.8808	0.0	0.5811	0.4189	0.0

TABLE 3

Experimental data for the ternary system :  
 $\text{CF}_4 - \text{CClF}_3 - \text{CHF}_3$  at  $-100^\circ\text{F}$  and 100 p.s.i.a.

Liquid Mole Fraction			Vapor Mole Fraction		
$\text{CF}_4$	$\text{CClF}_3$	$\text{CHF}_3$	$\text{CF}_4$	$\text{CClF}_3$	$\text{CHF}_3$
0.1488	0.0	0.8512	0.7666	0.0	0.2334
0.1656	0.0428	0.7916	0.7546	0.0264	0.2190
0.1842	0.0871	0.7287	0.7519	0.0415	0.2066
0.2174	0.1758	0.6068	0.7382	0.0752	0.1866
0.2490	0.2649	0.4861	0.7373	0.0947	0.1680
0.2698	0.3410	0.3892	0.7371	0.1099	0.1530
0.2933	0.4418	0.2649	0.7405	0.1349	0.1246
0.3069	0.4876	0.2055	0.7484	0.1431	0.1085
0.3152	0.5146	0.1702	0.7556	0.1492	0.0952
0.3197	0.5242	0.1561	0.7598	0.1488	0.0914
0.3234	0.5524	0.1242	0.7688	0.1531	0.0781
0.3355	0.5906	0.0739	0.7874	0.1589	0.0537
0.3454	0.6186	0.0360	0.8087	0.1642	0.0271
0.3523	0.6256	0.0221	0.8143	0.1672	0.0185
0.3617	0.6383	0.0	0.8283	0.1717	0.0

## 5. CORRELATION OF THE DATA

## 5.1 General.

The fundamental equilibrium equation is

$$f_i^{-v} = f_i^{-l} \quad (\text{constant } T, P) \quad (5-1)$$

This equation is more conveniently written as

$$\phi_i y_i P = \gamma_i x_i f_i^{\circ l} \quad (5-2)$$

If an equation of state is assumed to describe the behavior of the vapor phase, then the fugacity coefficient,  $\phi_i$ , can be calculated from the equation chosen by means of exact thermodynamic relationships ( 12 ).

The liquid-phase standard state or reference fugacity,  $f_i^{\circ l}$ , can also be readily determined, since only data of the pure components is required.

Therefore, experimental phase-equilibria compositions can be reduced to liquid-phase activity coefficients through the application of Eq. 5-2.

Once the activity coefficients are calculated, they can be correlated in terms of the liquid mole fractions according to semi-empirical equations.



This completes the information needed to correlate and predict the equilibrium conditions within the range experimentally investigated.

### 5.2 Vapor-phase fugacity coefficients.

A modified Redlich-Kwong equation of state ( 1 ) was used :

$$P = \frac{RT}{V - b} - \frac{a}{T^{0.5} V (V + b)} \quad ( 5-3 )$$

The two constants of the equation are given by

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \quad ( 5-4 )$$

$$b = \frac{\Omega_b RT_c}{P_c} \quad ( 5-5 )$$

The modification introduced to the original equation consisted of the determination of the dimensionless parameters  $\Omega_a$  and  $\Omega_b$  by fitting the equation to the volumetric data of the saturated vapor.

Chueh and Prausnitz ( 1 ) have presented such results for 19 components. During the course of the present work it was verified that those two parameters could be well correlated with the

acentric factor. Accordingly, the parameters for the three fluorocarbons were determined in this way.

Numerical values of  $\Omega_a$  and  $\Omega_b$ , together with pure-component constants and physical properties, are given in Table 4.

In order to apply the equation of state to a mixture, some combining rules are needed to compute constants for the mixture from the pure-component constants. Such rules have also been established in the reference mentioned.

For any given binary system, only one interaction constant,  $k_{ij}$ , is required. No ternary or higher interaction constants are needed to calculate the constants of the equation of state for a multicomponent system. The interaction term is usually determined from volumetric data of the binary mixture.

The following values of  $k_{ij}$  were used :

$\text{CF}_4 - \text{CHF}_3$	0.1055	( 8 )
$\text{CClF}_3 - \text{CHF}_3$	0.0640	( 14 )
$\text{CF}_4 - \text{CClF}_3$	0.0	

No volumetric data were available for the last binary.

Since the interaction term can be, in some way, related to a different molecular size of the two species, and, since  $\text{CF}_4$  and  $\text{CClF}_3$  have a similar size, it was assumed that  $k_{ij}$  was zero for this system.

Once the mixture constants are known, the fugacity coefficient is given by the expression ( 1 )

$$\ln \phi_i = \ln \frac{V}{V-b} + \frac{b_i}{V-b} - \frac{2 \sum_{j=1}^N y_j a_{ij}}{RT^{1.5}b} \ln \frac{V+b}{V} + \quad (5.6)$$

$$\frac{ab_i}{RT^{1.5}b^2} \left( \ln \frac{V+b}{V} - \frac{b}{V+b} \right) - \ln \frac{PV}{RT}$$

where

$$a = \sum_i^N \sum_j^N y_i y_j a_{ij} \quad (5.7)$$

$$b = \sum_i^N y_i b_i \quad (5.8)$$

The molar volume of the vapor was calculated from Eq. ( 5-3 ) using a Newton-Raphson iterative technique.

The fugacity coefficients of the binary system  $\text{CF}_4 - \text{CHF}_3$  had been previously calculated ( 10 ) through the use of the Martin-Hou equation of state ( 9 ). For the sake of consistency, values of  $\phi_i$  needed to get activity coefficients, which in turn were used in the correlation of ternary data, were recalculated with the modified Redlich-Kwong equation applied to the experimental vapor compositions of this binary.

TABLE 4

Constants of the pure components.

	CF <sub>4</sub>	CClF <sub>3</sub>	CHF <sub>3</sub>
T <sub>c</sub> °R	409.5	543.6	538.3
P <sub>c</sub> p.s.i.a.	543.2	561.3	701.4
V <sub>c</sub> ft <sup>3</sup> /lb mole	2.2531	2.8961	2.1356
ω	0.1777	0.1703	0.2654
Ω <sub>a</sub>	0.4408	0.4400	0.4532
Ω <sub>b</sub>	0.0896	0.0894	0.0923
P <sup>s</sup> at -100°F p.s.i.a.	223.8	22.28	23.72
V <sup>l</sup> at -100°F ft <sup>3</sup> /lb mole	1.1200	1.1232	0.7958

### 5.3 Liquid-phase standard-state fugacity.

At the temperature of  $-100^{\circ}\text{F}$ , the three fluorocarbons are subcritical, that is to say, they can exist as a pure liquid.

The standard-state fugacity can then be chosen as that of the pure liquid at the system temperature and some specified pressure. This fugacity is more easily determined from the equilibrium equation applied to the pure component ( 12 ) :

$$f_i^l = f_i^v \quad (\text{constant } T, P) \quad (5-9)$$

where, by definition of the fugacity coefficient,

$$f_i^v = \phi_i^s P_i^s \quad (5-10)$$

The fugacity coefficient of the pure component in the vapor phase was calculated from the modified Redlich-Kwong equation of state, as explained in the preceding section.

For convenience, the reference pressure was selected as zero p.s.i.a. Therefore,

$$\left( f_i^l \right)_{P=0} = \phi_i^s P_i^s \exp \left( \int_{P_i^s}^0 \frac{V_i^l}{RT} dP \right) \quad (5-11)$$

In performing the integration, it was assumed that the molar volume of the pure liquid was independent of the pressure.

This assumption is very nearly true if the system is remote from its critical conditions, as in this case.

Values of saturation pressures and liquid volumes for  $\text{CF}_4$ ,  $\text{CClF}_3$  and  $\text{CHF}_3$  were taken from ( 6 ) , ( 3 ) and ( 4 ) respectively.

#### 5.4 Liquid-phase activity coefficients.

Isothermal activity coefficients were correlated using integrated forms of the Gibbs-Duhem equation

$$\sum_i x_i d \ln \gamma_i = 0 \quad (\text{Constant } T, P) \quad (5-12)$$

However, the starting, fundamental equilibrium relationship, equation ( 5-1 ), considers the system pressure, which for an isothermal binary system varies with the composition. This system pressure was also used in determining the fugacity coefficients  $\phi_i$ .

Therefore, it was desired to calculate all activity coefficients at a constant reference pressure, namely zero p.s.i.a.

For the ternary system, the pressure was held constant, as required by the Gibbs-Duhem equation. In the correlating procedure adopted, ternary activity coefficients are expressed in terms of binary coefficients. Since a comparison is desirable between experimental and predicted ( correlated ) activity coefficients, the same pressure correction was applied to the ternary

system :

$$\left( \bar{f}_i^l \right)_{P=P} = \left( \bar{f}_i^l \right)_{P=0} \exp \left( \int_0^P \frac{\bar{V}_i^l}{RT} dP \right) \quad (5-13)$$

where

$$\left( \bar{f}_i^l \right)_{P=0} = x_i \left( \gamma_i \bar{f}_i^{ol} \right)_{P=0} \quad (5-14)$$

Again, because all systems were remote from their critical conditions, it was assumed that the partial molar volumes could be replaced by the molar volumes of the pure liquids, and that these were pressure-independent.

The final expression for the activity coefficients is

$$\left( \gamma_i \right)_{P=0} = \frac{\phi_i y_i^P}{x_i \phi_i^{sP} \exp \left\{ \bar{V}_i^l (P - P_i^s) / RT \right\}} \quad (5-15)$$

For the binary  $\text{CF}_4 - \text{CHF}_3$ , Piacentini (10) did not use the molar volume of pure  $\text{CF}_4$ , but rather the partial molar volume at infinite dilution. At  $-100^\circ\text{F}$  the two values differ by approximately 10%. (The difference was much greater at the higher temperatures also investigated by Piacentini).

Consequently, this slight modification was introduced to this binary by the use of the molar volume.

Calculated fugacity and activity coefficients for the binary systems  $\text{CF}_4 - \text{CClF}_3$  and  $\text{CF}_4 - \text{CHF}_3$  are given in Tables 5 and 6, respectively. In the latter, a comparison with Piacentini's values is given. The  $\gamma$ 's for both systems are shown in Figures 5 and 6.

Similar results for the ternary system at 50 and 100 p.s.i.a are given in Tables 7 and 8, respectively.

#### 5.5 Thermodynamic consistency.

The Redlich-Kister area test was used to check the thermodynamic consistency of the binary data. This well known method requires that

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad (5-16)$$

for a consistent set of binary equilibrium data.

The experimental values of  $\log (\gamma_1 / \gamma_2)$  were fitted with a third-order polynomial in  $x_1$  and an analytical integration was performed.

The results are shown in Table 9, where a comparison is again presented for the  $\text{CF}_4 - \text{CHF}_3$  system between Piacentini's values and the ones obtained in this work.



TABLE 5

Calculated Fugacity and Activity Coefficients of the System

 $\text{CF}_4$  ( 1 ) -  $\text{CClF}_3$  ( 2 ) at  $-100^\circ\text{F}$ .

$x_1$	$\phi_1$	$\phi_2$	$\gamma_1$	$\gamma_2$
0.0277	0.9759	0.9433	1.3953	1.0245
0.0540	0.9694	0.9316	1.4411	1.0126
0.1192	0.9552	0.9056	1.3779	1.0026
0.1248	0.9531	0.9017	1.4186	0.9967
0.2422	0.9295	0.8581	1.3105	0.9957
0.3617	0.9083	0.8192	1.2132	1.0111
0.4942	0.8869	0.7803	1.1228	1.0629
0.6489	0.8621	0.7355	1.0506	1.1872
0.7783	0.8396	0.6957	1.0185	1.2810
0.8949	0.8166	0.6553	1.0045	1.4582

TABLE 6

Calculated Fugacity and Activity Coefficients of the System

 $\text{CF}_4$  ( 1 ) -  $\text{CHF}_3$  ( 2 ) at  $-100^\circ\text{F}$ .

$x_1$	$\phi_1$		$\phi_2$		$\gamma_1$		$\gamma_2$	
	a	b	a	b	a	b	a	b
0.0032	0.9878	0.9896	0.9582	0.9354	5.2012	5.2589	1.0075	0.9989
0.0070	0.9842	0.9858	0.9545	0.9294	4.5865	4.6372	1.0080	0.9969
0.0127	0.9805	0.9819	0.9510	0.9237	3.8816	3.9240	0.9977	0.9843
0.0203	0.9747	0.9759	0.9442	0.9129	3.7130	3.7533	1.0242	1.0057
0.0362	0.9640	0.9644	0.9329	0.8939	3.5419	3.5782	1.0318	1.0042
0.0557	0.9531	0.9527	0.9218	0.8756	3.3191	3.3511	1.0288	0.9925
0.0924	0.9357	0.9341	0.9036	0.8458	2.9909	3.0171	1.0397	0.9884
0.1350	0.9171	0.9143	0.8844	0.8146	2.7728	2.7945	1.0428	0.9756
0.2424	0.8857	0.8810	0.8521	0.7631	2.1979	2.2120	1.0932	0.9945
0.3956	0.8582	0.8514	0.8229	0.7164	1.6648	1.6723	1.3019	1.1511

a This work , b Reference ( 10 )

TABLE 6 ( cont. )

$x_1$	$\phi_1$		$\phi_2$		$\gamma_1$		$\gamma_2$	
	a	b	a	b	a	b	a	b
0.5103	0.8438	0.8362	0.8091	0.6948	1.4208	1.4261	1.4775	1.2887
0.5721	0.8371	0.8291	0.8024	0.6844	1.3185	1.3230	1.6398	1.4206
0.5794	0.8372	0.8292	0.8024	0.6845	1.3009	1.3053	1.6718	1.4485
0.7462	0.8215	0.8119	0.7897	0.6635	1.1123	1.1140	2.2454	1.9163
0.8194	0.8132	0.8030	0.7837	0.6541	1.0633	1.0642	2.6609	2.2557
0.9068	0.8041	0.7931	0.7796	0.6473	1.0193	1.0193	3.4036	2.8704
0.9190	0.8034	0.7924	0.7788	0.6461	1.0084	1.0084	3.9173	3.3009
0.9484	0.7989	0.7875	0.7778	0.6443	1.0085	1.0080	4.0232	3.3850

a This work , b Reference ( 10 )

TABLE 7

Calculated Fugacity and Activity Coefficients of the System  
 $\text{CF}_4$  ( 1 ) -  $\text{CClF}_3$  ( 2 ) -  $\text{CHF}_3$  ( 3 ) at  $-100^\circ\text{F}$  and 50 p.s.i.a.

$x_1$	$x_2$	$x_3$	$\phi_1$	$\phi_2$	$\phi_3$	$\gamma_1$	$\gamma_2$	$\gamma_3$
0.0446	0.0341	0.9213	0.9603	0.9111	0.9298	3.1224	2.7988	1.0217
0.0452	0.0692	0.8856	0.9602	0.9105	0.9301	2.9265	2.5819	1.0292
0.0466	0.1096	0.8438	0.9600	0.9099	0.9303	2.7114	2.3403	1.0421
0.0490	0.1525	0.7985	0.9599	0.9095	0.9306	2.4867	2.0685	1.0708
0.0486	0.1716	0.7798	0.9598	0.9091	0.9308	2.4677	2.0547	1.0685
0.0510	0.2218	0.7272	0.9596	0.9087	0.9312	2.2849	1.8616	1.0997
0.0525	0.2542	0.6933	0.9595	0.9084	0.9315	2.1863	1.7586	1.1242
0.0556	0.3019	0.6425	0.9593	0.9081	0.9319	2.0426	1.6056	1.1703
0.0608	0.4163	0.5229	0.9589	0.9074	0.9328	1.8190	1.3918	1.3048
0.0634	0.4554	0.4812	0.9587	0.9072	0.9333	1.7490	1.3258	1.3648

TABLE 7 ( cont. )

$x_1$	$x_2$	$x_3$	$\phi_1$	$\phi_2$	$\phi_3$	$\gamma_1$	$\gamma_2$	$\gamma_3$
0.0668	0.5055	0.4277	0.9584	0.9069	0.9338	1.6748	1.2545	1.4505
0.0691	0.5290	0.4019	0.9583	0.9068	0.9341	1.6307	1.2214	1.5006
0.0740	0.6074	0.3186	0.9578	0.9064	0.9352	1.5600	1.1366	1.6970
0.0754	0.6292	0.2954	0.9577	0.9063	0.9355	1.5421	1.1102	1.7831
0.0814	0.6978	0.2208	0.9572	0.9059	0.9369	1.4906	1.0563	2.0519
0.0886	0.7470	0.1644	0.9568	0.9057	0.9383	1.4347	1.0279	2.3213
0.1010	0.8183	0.0807	0.9560	0.9054	0.9416	1.3941	1.0127	2.7693
0.1100	0.8536	0.0364	0.9555	0.9054	0.9442	1.3839	1.0059	3.0613

TABLE 8

Calculated Fugacity and Activity Coefficients of the System  
 $\text{CF}_4$  ( 1 ) -  $\text{CClF}_3$  ( 2 ) -  $\text{CHF}_3$  ( 3 ) at  $-100^\circ\text{F}$  and 100 p.s.i.a.

$x_1$	$x_2$	$x_3$	$\phi_1$	$\phi_2$	$\phi_3$	$\gamma_1$	$\gamma_2$	$\gamma_3$
0.1656	0.0428	0.7916	0.9106	0.8215	0.8788	2.4202	2.3252	1.0479
0.1842	0.0871	0.7287	0.9104	0.8211	0.8796	2.1675	1.7951	1.0749
0.2174	0.1758	0.6068	0.9102	0.8201	0.8807	1.8026	1.6097	1.1674
0.2490	0.2649	0.4861	0.9099	0.8196	0.8821	1.5715	1.3444	1.3140
0.2698	0.3410	0.3892	0.9097	0.8192	0.8832	1.4496	1.2114	1.4965
0.2933	0.4418	0.2649	0.9094	0.8186	0.8855	1.3392	1.1469	1.7952
0.3069	0.4876	0.2055	0.9092	0.8185	0.8869	1.2932	1.1022	2.0183
0.3152	0.5146	0.1702	0.9090	0.8184	0.8881	1.2710	1.0888	2.1411
0.3197	0.5242	0.1561	0.9090	0.8185	0.8885	1.2600	1.0661	2.2423
0.3234	0.5524	0.1242	0.9088	0.8185	0.8898	1.2601	1.0409	2.4116
0.3355	0.5906	0.0739	0.9086	0.8187	0.8922	1.2437	1.0107	2.7945
0.3454	0.6186	0.0360	0.9084	0.8189	0.8950	1.2405	0.9974	2.9039
0.3523	0.6256	0.0221	0.9083	0.8190	0.8959	1.2246	1.0043	3.2323

TABLE 9

Thermodynamic Consistency of the Binary Data at  $-100^{\circ}\text{F}$ .

	Positive Area	Negative Area	$\frac{\text{Pos.Area} - \text{Neg.Area}}{\text{Pos.Area} + \text{Neg.Area}}$
$\text{CF}_4 - \text{CClF}_3$	0.0487	0.0474	+0.014
$\text{CF}_4 - \text{CHF}_3^{\text{a}}$	0.1420	0.1615	-0.064
$\text{CF}_4 - \text{CHF}_3^{\text{b}}$	0.1587	0.1425	+0.053
$\text{CHF}_3 - \text{CClF}_3^{\text{c}}$			+0.001

<sup>a</sup> This work

<sup>b</sup> Reference ( 10 )

<sup>c</sup> Reference ( 14 )

### 5.6 Correlation of activity coefficients.

With activity coefficients already determined at constant temperature and reference pressure, it is necessary to express their dependence with liquid-phase composition.

The molar excess Gibbs energy,  $G^E$ , can be determined from

$$G^E = \frac{\sum_{i=1}^N x_i \ln \gamma_i}{RT} \quad (5-17)$$

From this, the following expression can be derived

$$\ln \gamma_i = \frac{1}{RT} \frac{\partial (n G^E)}{\partial n_i} \quad (\text{constant } T, P, n_j) \quad (5-18)$$

If an analytical equation relating  $G^E$  to  $x_i$  is assumed, then equation (5-18) can be used to find the composition dependence of the activity coefficients.

These analytical expressions are of an empirical or semi-empirical nature. They must also satisfy the Gibbs-Duhem equation, which is now written as

$$\sum_{i=1}^N x_i (d \ln \gamma_i)_{P=P^R} = 0 \quad (\text{constant } T) \quad (5-19)$$

with boundary conditions, for subcritical components,



$$\gamma_i = 1.0 \quad (x_i = 1.0) \quad (5-20)$$

In this work the Wilson equation ( 15 ) was adopted :

$$G^E = -RT \sum_{i=1}^N x_i \ln \left( \sum_{j=1}^N \Lambda_{ij} x_j \right) \quad (5-21)$$

The application of equation ( 5-18 ) to equation ( 5-21 ) yields

$$\ln \gamma_i = 1 - \ln \left( \sum_{j=1}^N x_j \Lambda_{ij} \right) - \sum_{k=1}^N \left[ \frac{x_k \Lambda_{ik}}{\sum_{j=1}^N x_j \Lambda_{jk}} \right] \quad (5-22)$$

where

$$\Lambda_{ii} = 1 \quad (5-23)$$

Equation ( 5-22 ) has the convenient feature of requiring only binary parameters  $\Lambda_{ij}$  in order to predict multicomponent activity coefficients. But its main advantage over other equations is its ability to give a better prediction of vapor-liquid equilibria at low and intermediate pressures ( 7 , 12 ).

The adjustable Wilson parameters were calculated by fitting equation ( 5-22 ) to experimental activity coefficients of the respective binary systems.

The procedure used was as follows :

A series of values of  $\Lambda_{12}$  and  $\Lambda_{21}$  were assumed and the corresponding  $\gamma_1$  and  $\gamma_2$  were calculated from equation ( 5-22 ). This was done for all experimental points.

The following terms were then calculated :

$$\left[ \frac{(\gamma_i)_{\text{exper.}} - (\gamma_i)_{\text{calc.}}}{(\gamma_i)_{\text{exper.}}} \right]^2 \quad (i=1,2) \quad (5-24)$$

The pair of parameters giving the smallest summation of all such terms were selected as the optimum.

The optimum values of the Wilson parameters for the three binaries are listed in Table 10, where the root-mean-square differences resulting from ( 5-24 ) is also given.

Activity coefficients obtained from these Wilson parameters have been plotted together with the experimental values in Figures 5 and 6 for the systems :  $\text{CF}_4 - \text{CClF}_3$  and  $\text{CF}_4 - \text{CHF}_3$  , respectively.

Once the six binary Wilson parameters were available, ternary activity coefficients were calculated from equation ( 5-22 ) in order to test the prediction ability of the Wilson equation.

For the ternary system at 50 p.s.i.a., an average deviation of 2.22% and a maximum deviation of 9.05% were found. For the ternary system at 100 p.s.i.a. the values found were 2.66% and 9.78%, respectively.

TABLE 10

Optimum Parameters for the Wilson Equation.

	$\Lambda_{12}$	$\Lambda_{21}$	Root-mean square percentage difference from ( 5-24 )
$\text{CF}_4$ (1) - $\text{CClF}_3$ (2)	0.995	0.609	1.78
$\text{CF}_4$ (1) - $\text{CHF}_3$ (2)	0.469	0.345	3.57
$\text{CHF}_3$ (1) - $\text{CClF}_3$ (2) <sup>a</sup>	0.494	0.504	1.40

<sup>a</sup> Reference ( 14 )

### 5.7 Correlation of the experimental data.

Once the activity coefficients were expressed in terms of liquid compositions through the application of the Wilson equation, it was possible to develop the following final correlating schemes :

#### 5.7-1 Binary system $\text{CF}_4$ - $\text{CClF}_3$ .

The saturation dew- and bubble-point pressures were determined by an iterative method ( 12 ). Two conditions must be specified; they were the system temperature and the liquid mole fraction. Vapor composition and equilibrium pressure were then calculated. The modified Redlich-Kwong equation of state was again used to compute vapor-phase fugacity coefficients and pure-component liquid reference fugacities, as explained in Sections 5.2 and 5.3.

The results are shown in Figure 2.

#### 5.7-2 Ternary system $\text{CF}_4$ - $\text{CClF}_3$ - $\text{CHF}_3$ .

Only pure-component and binary data were used in the correlation.

For a ternary system, three conditions must be stated which correspond to the input of the correlating method. These conditions were chosen as the system temperature and pressure, and one of the liquid mole fractions. By a procedure similar to

the one used in the binary system, the other two liquid mole fractions and the vapor composition were determined.

Such results are presented in Figures 3 and 4.

It is believed that this correlating method can adequately predict the equilibrium conditions of the ternary system at a temperature of  $-100^{\circ}\text{F}$  and any pressure within the range of the pure-component vapor pressures.

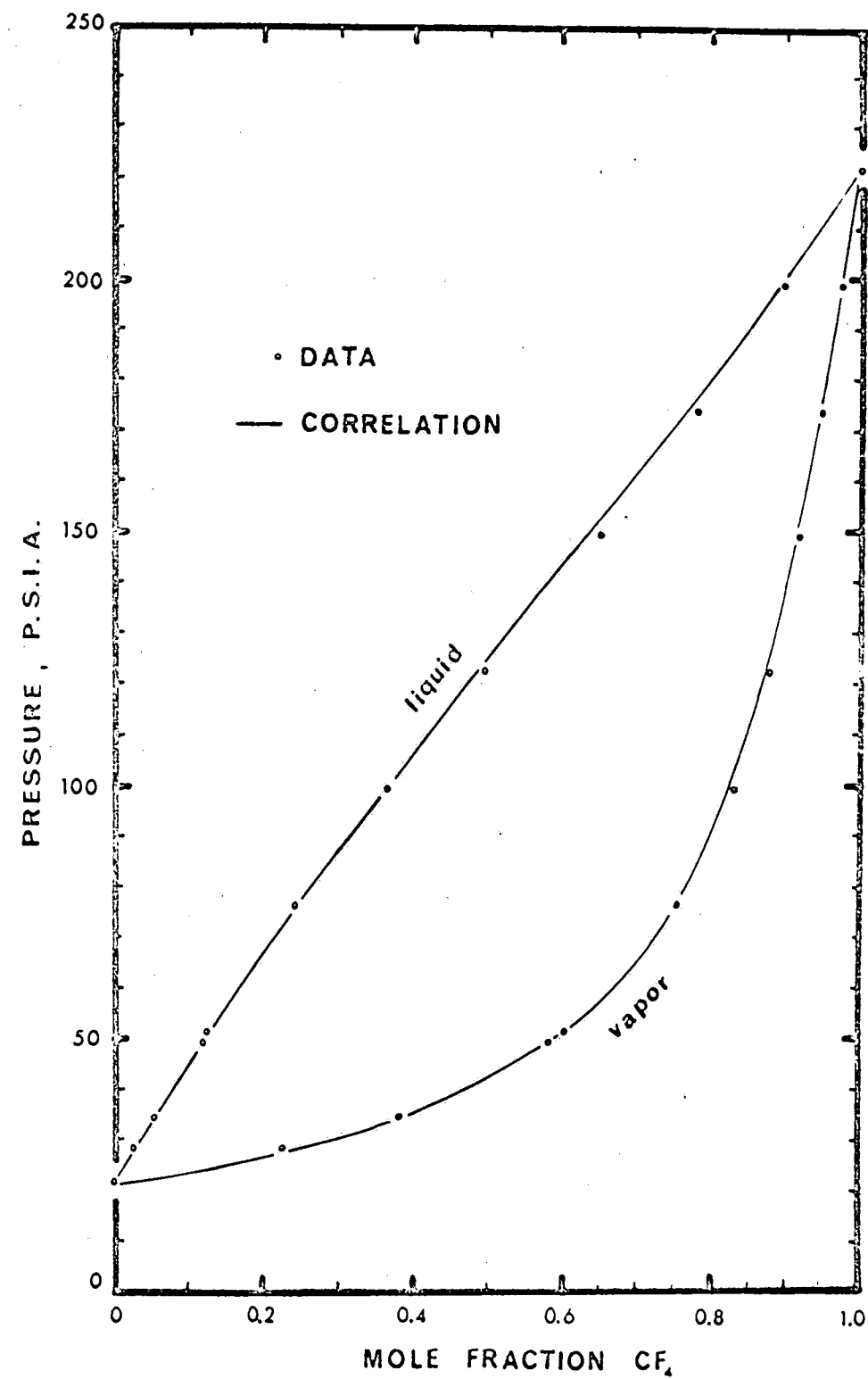


Fig. 2 Pressure - Composition Diagram for the Binary System

$\text{CF}_4$  -  $\text{CClF}_3$  at  $-100^\circ \text{F}$

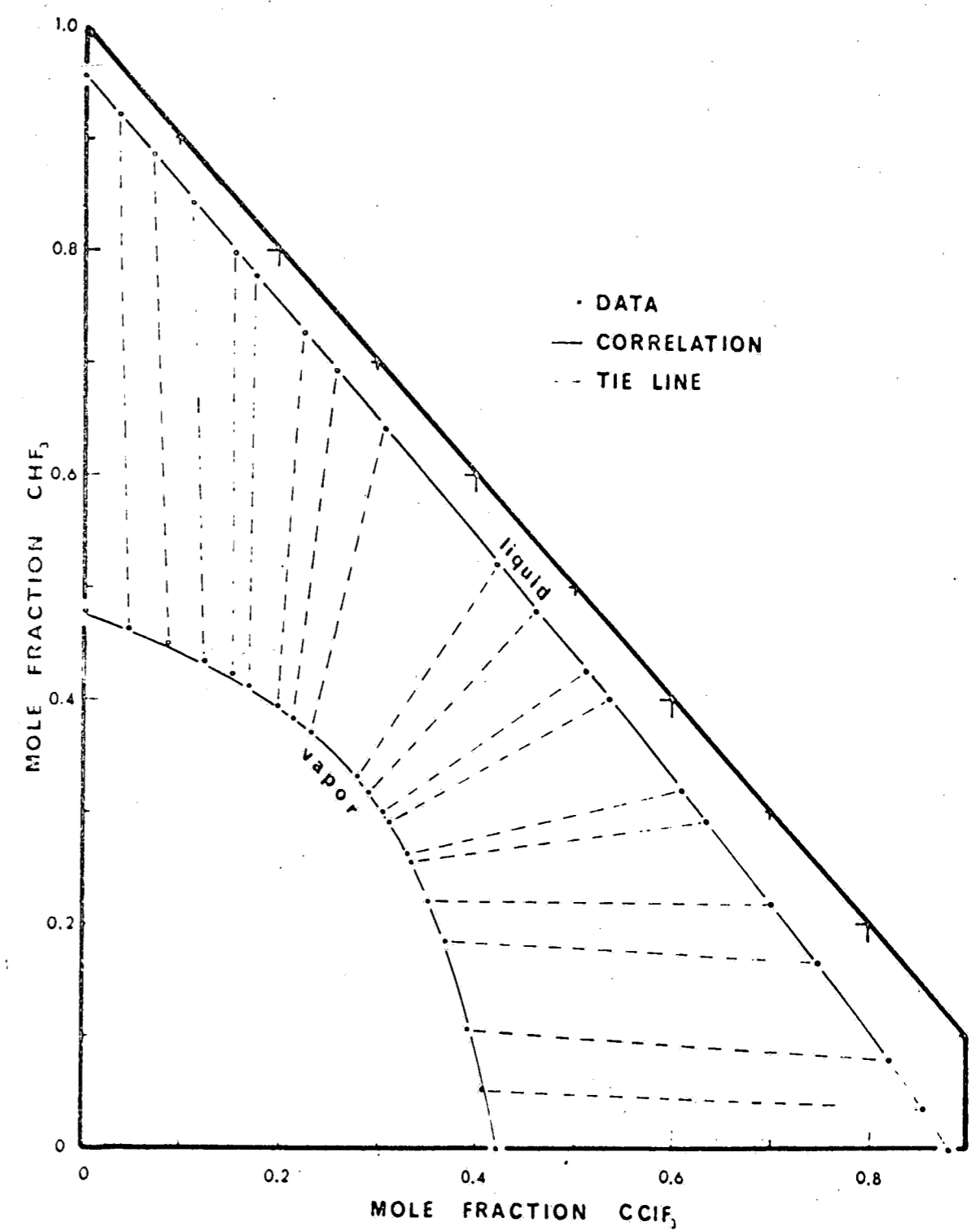


Fig. 3 Equilibrium Compositions for the Ternary System CF<sub>4</sub> - CClF<sub>3</sub> - CHF<sub>3</sub> at -100° F and 50 p.s.i.a.

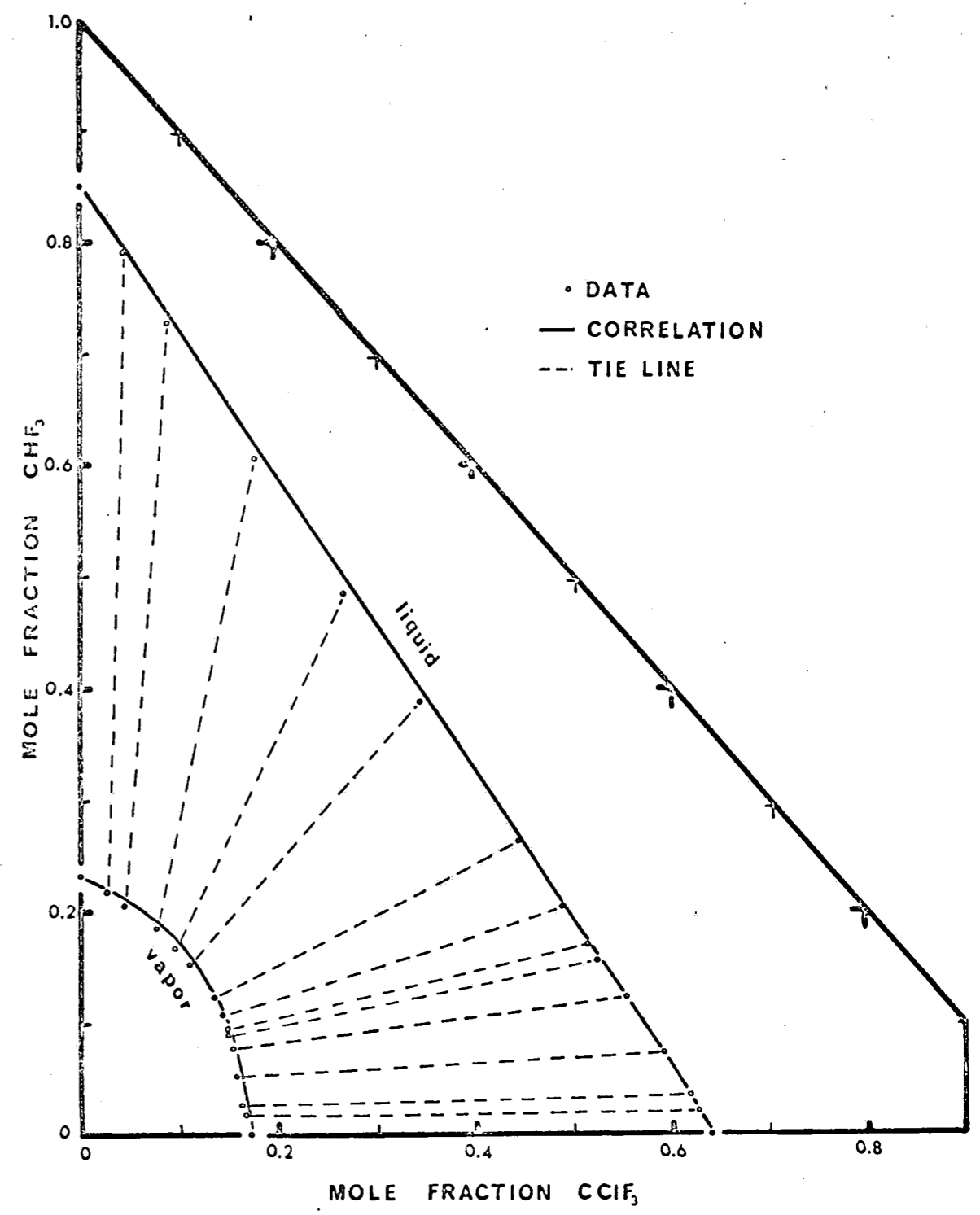


Fig. 4 Equilibrium Compositions for the Ternary System CF<sub>4</sub> - CClF<sub>3</sub> - CHF<sub>3</sub> at -100° F and 100 p.s.i.a.



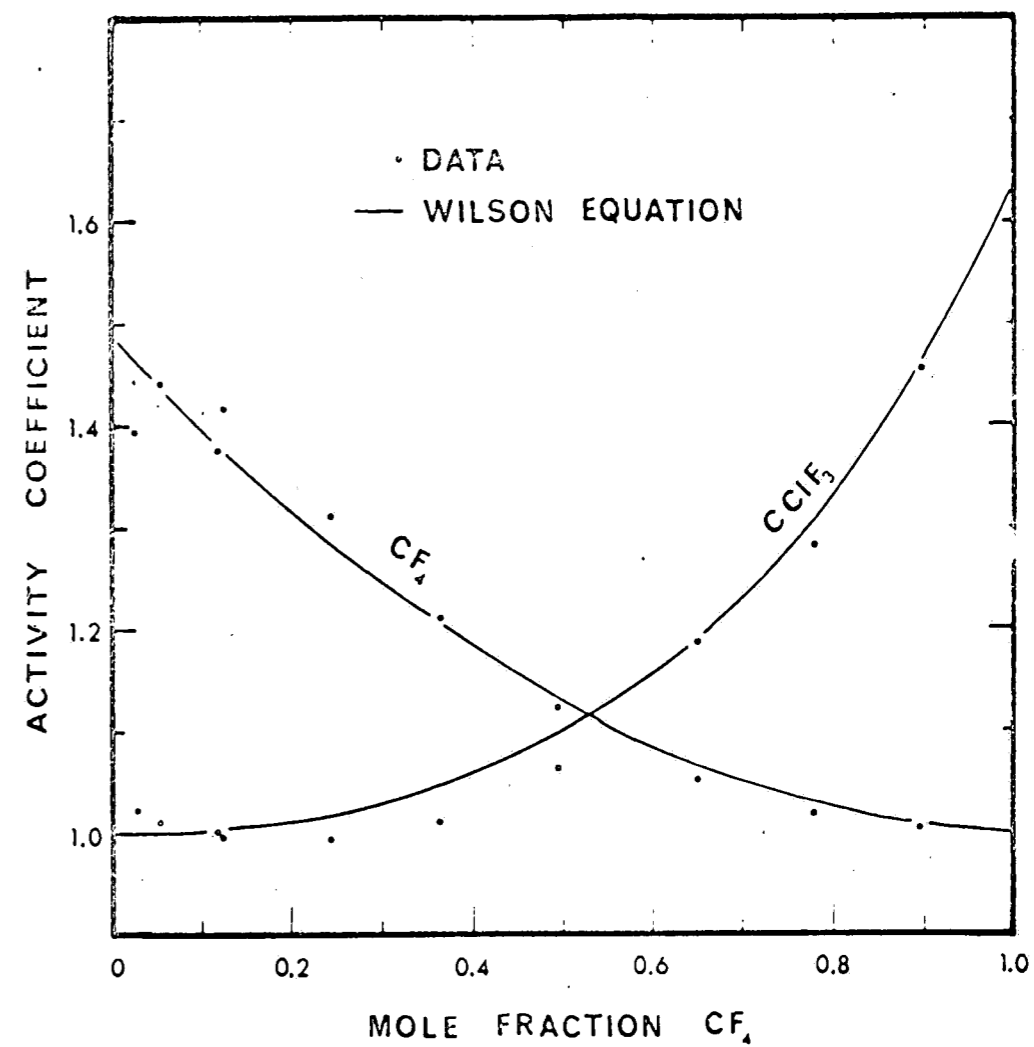


Fig. 5 Activity Coefficients for the Binary System

$CF_4 - CClF_3$  at  $-100^\circ F$

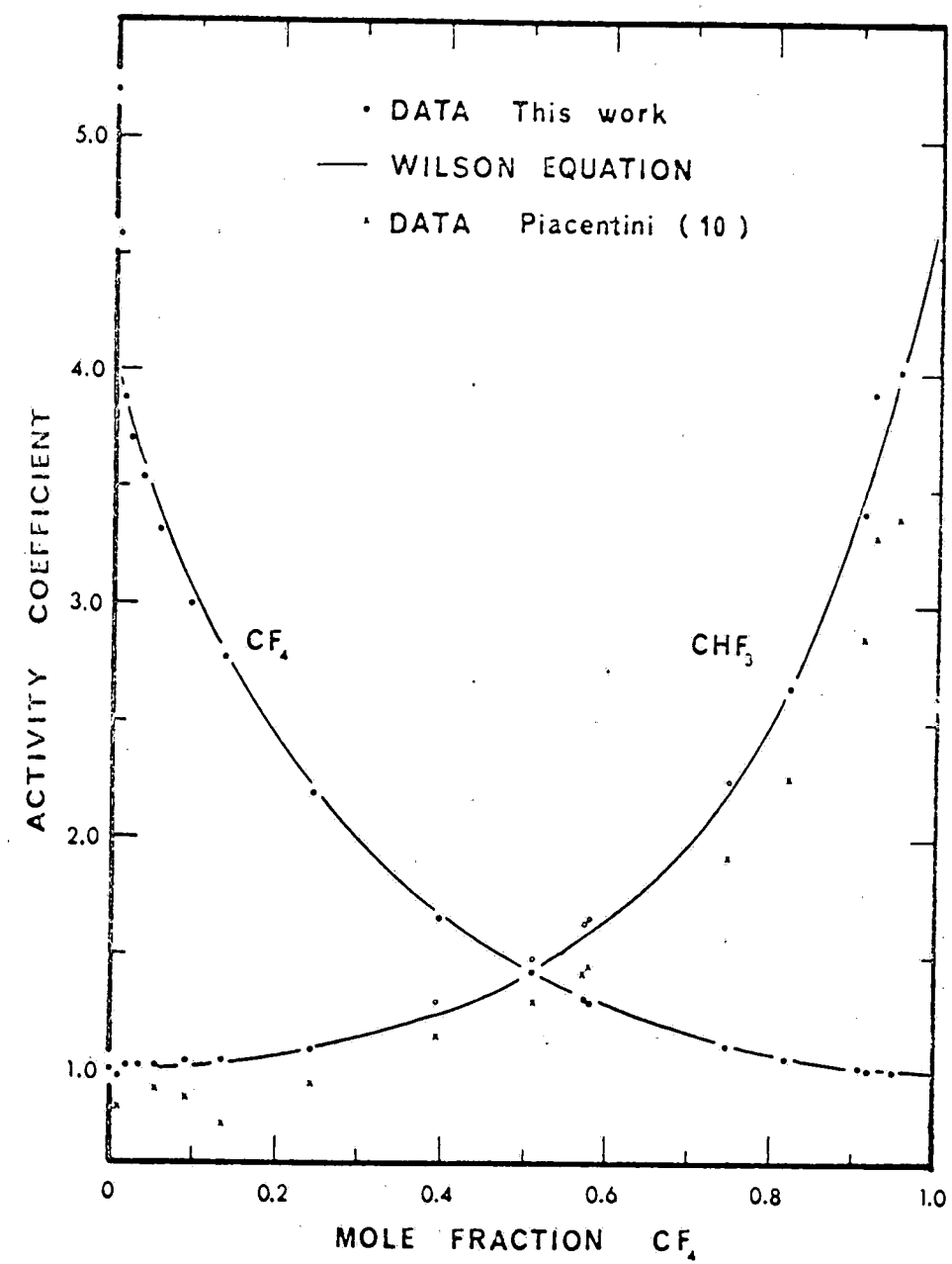


Fig. 6 Activity Coefficients for the Binary System

$CF_4 - CHF_3$  at  $-100^\circ F$ .

## 6. CONCLUSIONS

1. The experimental apparatus is well suited for the determination of the vapor-liquid equilibria of a ternary system under isothermal and isobaric conditions.
2. Analysis of ternary samples can be accomplished using only binary reference samples.
3. No ternary azeotrope was found at either 50 or 100 p.s.i.a. and  $-100^{\circ}\text{F}$ . However, at 50 p.s.i.a.,
  - a) For  $\text{CClF}_3$  mole fractions smaller than about 0.15, the vapor phase is richer in this heavy component than the liquid phase.
  - b) For  $\text{CHF}_3$  mole fractions smaller than about 0.23, the vapor phase is richer in this heavy component than the liquid phase.
4. The experimental equilibrium conditions are adequately correlated using only data of the pure substances and of the corresponding binary systems.
5. It is believed that the correlating scheme can be used to predict the vapor-liquid equilibria of the ternary system at  $-100^{\circ}\text{F}$  and any pressure between the vapor pressures of the pure components, that is to say, 25 and 220 p.s.i.a. approximately.

## NOMENCLATURE

- a - constant in the Redlich-Kwong equation of state
- $A_2, B_2, C_2$  - constants in the Martin-Hou equation of state
- b - constant in the Martin-Hou or Redlich-Kwong equation of state
- B - second virial coefficient, cu.ft per lb.mole
- $f$  - fugacity in the pure state, p.s.i.a.
- $\bar{f}$  - fugacity in a mixture, p.s.i.a.
- G - Gibbs free energy, Btu per lb.mole
- k - constant in the Martin-Hou equation of state
- $k_{ij}$  - interaction parameter
- n - moles, lb.mole
- N - number of components
- P - pressure, p.s.i.a.
- R - gas constant
- T - temperature, °R
- V - molar volume of vapor phase, cu.ft. per lb.mole
- $V^l$  - molar volume of liquid phase, cu.ft. per lb.mole
- x - liquid-phase mole fraction
- y - vapor-phase mole fraction

- $\gamma$  - liquid-phase activity coefficient  
 $\Lambda$  - parameter in the Wilson equation  
 $\phi$  - vapor-phase fugacity coefficient  
 $\Omega_a, \Omega_b$  - dimensionless constants in the Redlich-Kwong equation  
of state  
 $\omega$  - acentric factor

Subscripts

- c - critical  
i, j, k - component i, j, k  
r - reduced  
T - total  
1, 2, 3 - component 1, 2, 3

Superscripts

- E - excess  
l - liquid phase  
r - reference  
s - saturation  
v - vapor phase  
o - standard state

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