K/TCD-1118

Vapor Pressures of Mixtures
of CFC-114 with the
Potential Replacement Coolants
 C_4F_{10} and $c-C_4F_8$

L.D.Trowbridge
Technical Division,
Oak Ridge K-25 Site

and

M.G.Otey
Technical Services Division,
Paducah Gaseous Diffusion Plant

Date Published -- September 1994

Prepared for the
UNITED STATES ENRICHMENT CORPORATION
Bethesda, MD
under inter-agency agreement

Prepared by Oak Ridge K-25 Site, managed by
Martin Marietta Energy Systems, Inc.
Oak Ridge, Tennessee 37831-7266
for the U.S. Department of Energy
under contract DE-AC05-84OR21400

and by
Martin Marietta Utility Services, Inc.
Paducah Gaseous Diffusion Plant
Paducah, KY 42002
for the United States Enrichment Corporation
under Contract No. USECHQ-93-C-0001

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ds*

TABLE OF CONTENTS

TABLE OF CONTENTS	iii
ABSTRACT	v
INTRODUCTION	1
EXPERIMENTAL	5
RESULTS	9
DATA ANALYSIS	12
DISCUSSION	30
CONCLUSIONS	31
ACKNOWLEDGEMENTS	32
BIBLIOGRAPHY	33

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

The U.S. Enrichment Corporation's production of isotopically enriched uranium depends solely on two plants which utilize the gaseous diffusion process. This process uses large quantities of CFC-114 as an evaporative coolant. CFC-114, however, will be phased out of production at the end of 1995 due to its potential to deplete stratospheric ozone. A search has been underway for substitutes for a number of years. The initial search (1988-89) for an ozone-friendly, commercially available, chemically compatible substitute yielded two candidates, FC-c318 ($\text{c-C}_4\text{F}_8$) and FC-3110 (C_4F_{10}).

The intended mode of replacing coolant was to stage the new coolant into independent subsystems of the plants, so that some systems would continue to operate on CFC-114, and an increasing number would operate on the new coolant. During that changeover process, the possibility of coolant mixing arises in variety of scenarios. This work was intended to generate sufficient experimental information to be able to predict the vapor pressure of coolant mixtures over the range of operating conditions likely to be found in the diffusion plants. Specifically, vapor pressures were measured over the temperature range 322 to 355 K (120°F to 180°F) and over the full range of mole fractions for binary mixtures of CFC-114 with FC-3110, and of CFC-114 with FC-c318.

INTRODUCTION

The U.S. Enrichment Corporation's production at present depends solely on isotopic enrichment of uranium by gaseous diffusion. The gaseous diffusion process uses large quantities (ca. 7000 tons total) of CFC-114 as a primary evaporative coolant. Of this quantity, a small percentage is lost annually to fugitive leaks. CFC-114, however, is to be phased out of production due to potential to deplete stratospheric ozone¹, and a search has been underway for substitutes for a number of years. The initial search (1988-89) for an ozone-friendly, commercially available, chemically compatible substitute yielded two candidates, FC-c318 (c-C₄F₈) and FC-3110 (C₄F₁₀).

Both candidates appear to satisfy the current requirements for a replacement coolant, though both have vapor pressures somewhat higher than that of CFC-114. A changeover to a replacement coolant would take place in a phased manner, with independent cooling subsystems of the plant being drained of CFC-114, then filled with the new coolant. The CFC-114 removed would be used to replace fugitive losses in those subsystems of the plant still using CFC-114.

Over the course of evaluating and reviewing the use of these coolants, a number of scenarios have been discussed in which CFC-114 and the replacement coolant might be mixed. One such scenario would be inadvertent mixing of significant quantities of the two coolants, due to misvalving, mislabeling or similar errors. In such a scenario, mixtures of virtually any composition might be produced. The vapor pressures of the two perfluorocarbon coolants are higher than that of CFC-114; their use in systems designed years ago for CFC-114 reduces the margin of safety between operating conditions and failure conditions (e.g. activation of pressure relief systems) which could vent several tons of coolant. Should an inadvertent mixture of coolants be created, it would be desirable to be able to predict the vapor pressure of that mixture. If the vapor pressure of the mixture were significantly higher than that of either component, then safety margins would be further reduced, increasing the risk of accidental venting of several tons of coolant. The only options in such an event would be to resort to costly purification or even more costly disposal of the mixture. On the other hand, if the vapor pressure of the mixture could be demonstrated to be low enough, then the possibility of use of the mixture for cooling could

at least be considered.

A second scenario derives from a suggestion that coolant losses might be reduced by intentionally using mixtures, if the vapor pressure of mixtures were depressed from that of the pure compounds. In such a case, outleakage, the rate of which is roughly proportional to vapor pressure, would be reduced.

A third scenario derives from the practical inability to completely remove all CFC-114 from a cooling subsystem prior to changeover to the new coolant. In this last case, a system nominally using the new coolant would actually contain a mixture of the new coolant with a fraction of a percent CFC-114. If the mixture were a strongly non-ideal solution, the vapor pressure even for trace mixtures could be significantly higher than that of the PFC coolant.

At the outset of this work, the conditions of concern in second and third scenarios were not considered to be likely. In all three scenarios, however, there was a need to predict the vapor pressures of coolant mixture.

Earlier work

Vapor pressures of the pure compounds under consideration in this work have been measured by a number of workers. We will use the equations listed below, which derive from data of Wilson & Hules² for CFC-114, Brown & Mears³ for FC-3110 and Downing⁴ for FC-c318. Wilson & Hules' equation reproduced their data with an average deviation of 0.32% over the range 290 to 415K; Brown & Mears' data are reproduced by their equation to an average deviation of 2% over the range 270 to 380K; no deviation or temperature range were given for the Downing's vapor pressure equation.

Prior to this work, measurements were taken in our experimental system on the three compounds of interest here and compared to literature data. Individual measurements over a temperature range of 295 to 368 K (73 to 202° F) on FC-3110 showed deviations from Brown and Mears' data³ of between 0.4 and 2.4%. Similar measurements on FC-c318 showed deviations from Downing's data⁴ ranging from 0.01 to 1.3%.

Table 1: Vapor Pressure Equations for Pure Compounds
(Units of P are atm; units of T are Kelvin)

$$\text{CFC-114:} \quad \log_{10} P = A_P + B_P/T + C_P T + D_P T^2$$

$$\text{FC-3110 \& FC-c318:} \quad \log_{10} P = A_P + B_P/T + C_P \log_{10} T + D_P T$$

Vapor Pressure Equation Coefficient Values:

	<u>CFC-114</u>	<u>FC-c318</u>	<u>FC-3110</u>
A_P :	4.70513	55.2701	51.5505
B_P :	-1238.39	-2727.38	-2589.94
C_P :	-0.00114527	-19.9064	-18.5852
D_P :	1.34580×10^{-6}	0.012159	0.0118856
Ref:	[2]	[4]	[3]

Coolant miscibility and vapor pressure experiments for mixtures of CFC-114 and FC-3110 were previously done by Orlett⁵. His work demonstrated that these two materials were miscible over entire temperature and composition range of interest (0 to 100% CFC-114; 322 to 355 K), which is an important point, as the vapor pressures of the two compounds would be additive if the two components were immiscible. The vapor pressures of a range of mixtures were measured, but the pressure measurements were somehow flawed. Reported experimental vapor pressures of the pure components (i.e. the "0%" and "100%-mixtures") disagreed with literature values by as much as 11% (i.e., about 800 Torr or 15 psia) at the highest pressures and temperatures. Without definite knowledge of the reason for this discrepancy, the reliability of the vapor pressure measurements of mixtures of intermediate composition was in question.

We have, in essence, repeated the measurements of Orlett for CFC-114:FC-3110 and made similar measurements for CFC-114:FC-c318 mixtures. The equipment and techniques used are substantially the same as those used to measure the vapor pressures of pure coolants, as described in the experimental section of this document.

The experiments reported here measure the saturated vapor pressure of a range of mixtures from pure CFC-114 to pure PFC; for each composition, vapor pressure measurements were made at 4 temperatures, i.e. at nominally 322, 333, 344, and 355 K (120, 140, 160, and 180°F). The experiments did not measure the full range of P-V-T data (i.e. sub-saturated vapor, fully condensed liquid, or supercritical fluid ranges).

The data obtained are fit to a regular solution model for purposes of interpolation and prediction. A regular solution is a variety of non-ideal solution in which deviations from an ideal solution are characterized by a function of composition which contains a single adjustable parameter.

EXPERIMENTAL

The experimental system used in making the vapor pressure measurements is shown in Figure 1. Briefly, the system consists of a 300 cc stainless steel cylinder to contain the mixture, a simple manifold system, and a rupture disk, all located inside a Blue M oven. The mixtures were heated to nominal temperatures of 322, 333, 344, and 355 K (120, 140, 160, and 180°F) and the corresponding vapor pressures were measured with a Sensotec electronic pressure transducer having a range of 0 - 15,514 Torr (0 - 300 psia). The transducer was located in a separate controlled and heated chamber on top of the Blue M oven and maintained at a temperature higher than the test temperature (357 to 358 K). This was done to prevent instability in the transducer due to the changes in the test temperature and to prevent condensation of the coolant in the transducer.

The Sensotec pressure transducer is sensitive to gross temperature changes and can produce very erroneous results. Therefore, the transducer cabinet was maintained at the controlled temperature of 357 to 358 K throughout the entire study. Once the controlled temperature was reached and the pressure readings were stable, the Sensotec was calibrated against a Mensor secondary pressure standard also having a range of 0 - 15,514 Torr (0 - 300 psia). This pressure standard is periodically sent back to Mensor for recalibration and at this time was not due for recalibration. The Sensotec transducer was found to be linear over the pressure range of 0 to 12,428 Torr (the maximum output pressure range of an available nitrogen cylinder regulator) and once zero and span adjustments were made, no corrections in the pressure readings were necessary. Prior to each set of measurements on a given mixture, the zero and span of the Sensotec transducer was checked against the Mensor. Only very minor adjustments were required throughout this study. The Sensotec measured pressure to a precision of 1 Torr; we estimate the accuracy of our measurements as ± 2 Torr.

Temperature readings were made with the use of a Hewlett Packard (HP) 85 computer with a 3421A Data Acquisition/Control unit. Two chromel-alumel thermocouples were taped to the outside surface of the stainless steel cylinder near the bottom of the cylinder where the liquid coolant exists. Two thermocouples were used in the study to provide duplicate temperature readings. However, only one thermo-

couple reading will be reported since temperature readings by both thermocouples agreed throughout the study. Both thermocouples and the readout of the HP were calibrated against a recently purchased and calibrated Altek Thermocouple Calibrator which serves as a secondary temperature standard. The HP system and thermocouples were found to read low by approximately 0.6 K (1°F) and the Altek data vs the thermocouple data were fitted to linear regression equations and corrections were made to all temperature readings. Temperature measurements were recorded to a precision of 0.006 K (0.01°F), (and reported at that level in Tables 2 and 3, below), but our estimate of the accuracy of the measurements is ± 0.06 K.

Prior to making the vapor pressure measurements, the volume of the stainless steel cylinder was measured by determining the weight of water necessary to fill the cylinder and found to be 294.7 cc. Knowing the cylinder volume, the volume of the remaining part of the system was measured by pressure - volume techniques and found to be 29.4 cc, for a total system volume of 324.1 cc.

Measurements were first made on pure CFC-114 followed by mixtures of 25, 50, 60, 70, 80, and 90 % FC-3110 or FC-c318 in CFC-114. These were then followed by measurements of the pure proposed substitute coolants. The mixes were prepared on a separate manifold from that used in the vapor pressure measurements. A sample of pure CFC-114 was first transferred to the evacuated and tared stainless steel cylinder and the mass of material determined. The cylinder and CFC-114 was then frozen down in liquid nitrogen and the desired amount of proposed coolant (either FC-3110 or FC-c318) was added to the cylinder. Mass was determined (and reported) to a precision of 0.01 gm, but our estimate of the accuracy is ± 0.02 gm. In most cases, while at liquid nitrogen temperature, any noncondensable gases were removed from the mix by pumping.

After the cylinder containing the material was installed in the oven, the zero and span were checked on the transducer by evacuating the manifold, checking zero and filling the manifold with nitrogen to approximately 12,000 Torr and comparing the transducer reading to the Mensor. Once the zero and span were checked, the manifold was again evacuated and the Mensor valved out of the system. At this time, the cylinder was valved to the isolated manifold and the oven was

turned on. After any temperature change was made, at least two hours were allowed for system equilibration prior to taking pressure and temperature readings. Three successive readings were taken, one minute apart, after the equilibrium period. If any significant change in pressure or temperature was observed, these readings were voided and additional time was allowed for equilibration.

Once the measurements were completed on the mix, the oven was turned off and liquid nitrogen was poured into a stainless steel beaker containing the cylinder with the mixture in order to cold trap the coolant in the manifold back to the cylinder. The cylinder was reweighed and any loss of coolant recorded. In several cases, if the loss was minimal, the next subsequent mix was prepared by adding more FC-3110 or FC-c318 to reach the next desired concentration. With one exception, losses of the mixture during any given set of measurements were much less than 1 g. During the nominal 25 % FC-3110 test, a minor leak developed and the material loss was 2 g. Actual mass losses in the CFC-114 : FCc318 experiments for mixtures (i.e. not for pure CFC-114 or pure FC-c318 runs), in the order the experiments are listed in Table 3, were 0.07, 0.22, 0.13, 0.29, 0.16, and 0.36 g. Losses for the CFC-114:FC-3110 experiment, again in the order the mixtures are listed in Table 2, were 0.39, 2.03, 0.96, 0.01, 0.08, 0.12, and 0.18 g. These losses should not have had a significant effect on the conclusions drawn later in this report.

Experimental System For Vapor Pressure Measurements

* Surface Contact Thermocouple

RESULTS

The raw data for these experiments consist of measurements of overall mass of each mixture component, the overall volume of the system, and, at each specific experimental condition, the temperature and pressure. Auxiliary data was taken in the form of before-after mass balance checks (total weight of system before and after an experiment), and residual pressure in the system when frozen to liquid nitrogen temperature. Experimental data are listed in Tables 2 and 3.

In those experiments in which the mixture was made up by adding material to the previous experiment's mixture, the (small) material losses were apportioned to each species proportionally to that species mass fraction in the earlier mixture. Such experiments are indicated in Tables 2 and 3 by an asterisk. This adjustment had no significant influence on the results of the data analysis.

Table 2: FC-3110 : CFC-114 Mixtures - Experimental Data

M ₃₁₁₀ gm	M ₁₁₄ gm	T K	Expt. VP Torr	Lit. VP Torr	Pct Dev.	Notes
0.00	35.00	322.17	3259	3257	0.07%	
13.70	34.30	322.84	3756			
35.39	33.29	322.51	4000			
46.73	26.97	322.19	4023			
60.13	24.99	322.89	4121			
100.13	24.95	322.96	4167			*
237.92	24.92	322.72	4173			*
41.96	0.00	321.97	4001	4034	-0.83%	
0.00	35.00	333.67	4402	4387	0.34%	
13.70	34.30	333.83	4969			
35.39	33.29	334.61	5449			
46.73	26.97	334.37	5500			
60.13	24.99	335.08	5635			
100.13	24.95	334.09	5561			*
237.92	24.94	334.28	5631			*
41.96	0.00	334.55	5559	5604	-0.80%	
0.00	35.00	344.63	5750	5724	0.46%	
13.70	34.30	344.33	6361			
35.39	33.29	344.01	6822			
46.73	26.97	344.66	7017			
60.13	24.99	344.19	7002			
100.13	24.95	344.40	7111			*
237.92	24.94	344.14	7081			*
62.01	0.00	343.58	6917	6987	-1.01%	
0.00	35.00	356.19	7384	7448	-0.86%	
13.70	34.30	356.29	8258			
35.39	33.29	356.11	8874			
46.73	26.97	356.97	9196			
60.13	24.99	355.67	8995			
100.13	24.95	355.61	9120			*
237.92	24.94	356.21	9308			*
62.01	0.00	355.78	9108	9251	-1.54%	

Note: Entries marked by an asterisk have been adjusted to account for mass loss.

Table 3: FC-c318 : CFC-114 Mixtures - Experimental Data

M ₃₁₈ gm	M ₁₁₄ gm	T K	Expt. VP Torr	Lit. VP Torr	Pct. dev.	Notes
0.00	32.34	322.18	3257	3258	-0.02%	
11.16	38.69	322.67	3735			
35.50	38.52	322.53	4180			*
61.29	38.45	322.76	4404			*
95.51	38.34	322.34	4480			*
105.70	25.90	322.52	4607			
211.89	22.58	323.08	4774			
103.78	0.00	322.53	4777	4784	-0.15%	
0.00	32.34	334.18	4470	4444	0.58%	
11.16	38.69	334.06	5015			
35.50	38.52	334.42	5666			*
61.29	38.45	334.49	5955			*
95.51	38.34	334.79	6212			*
105.70	25.90	335.05	6365			
211.89	22.58	334.55	6428			
103.78	0.00	333.74	6394	6378	0.24%	
0.00	32.34	344.08	5652	5650	0.03%	
11.16	38.69	344.08	6350			
35.50	38.52	344.34	7167			*
61.29	38.45	344.25	7514			*
95.51	38.34	343.82	7673			*
105.70	25.90	344.14	7882			
211.89	22.58	344.63	8165			
103.78	0.00	343.33	8050	8029	0.26%	
0.00	38.93	356.58	7483	7511	-0.37%	
11.16	38.69	356.56	8333			
35.50	38.52	356.61	9353			*
61.29	38.45	356.11	9708			*
95.51	38.34	355.50	9897			*
105.70	25.90	356.53	10378			
211.89	22.58	356.09	10536			
103.78	0.00	356.33	10766	10746	0.19%	

Note: Entries marked by an asterisk have been adjusted to account for mass loss.

DATA ANALYSIS

The data for an experiment consisted of measurements of the system volume, temperature, and the overall masses of each component in the system. To use the experimental data for predictive purposes, it is necessary to know the compositions of the liquid and vapor phases. These were, however, not known (except trivially in the case of the pure compound experiments). The raw data included only the overall composition in the system, not phase-specific information. We (the authors) discussed early on the desirability of obtaining such information by sampling and chemical analysis. We concluded that, considering the likely accuracy of phase-specific measurements, the degree of accuracy needed, the cost and time such measurements would take, and the likely ability to adequately mathematically approximate (rather than measure) the needed values, that phase-specific measurements were not needed. Instead, liquid and vapor phase compositions were determined by computer simulation of the experimental system.

For purposes of analysis, the vapor pressure behavior of the mixtures under study was provisionally assumed to follow that of a "regular solution", a class of non-ideal solution behavior involving a single adjustable parameter, R_0 , for the excess free energy of the solution. In a regular solution⁶, the excess free energy of a single component of the solution, $G_{\text{excess},i}$ is given by:

$$G_{\text{excess},i} = R_0 (1-X_{l,i})^2$$

where $X_{l,i}$ is the liquid phase mole fraction of either of the components of the solution. The vapor pressure, P_i , of that component above the solution is given by

$$P_i = P_i^0 X_{l,i} \exp(R_0(1-X_{l,i})^2/RT)$$

where P_i^0 is the vapor pressure of the pure component at the same temperature. Pure component vapor pressures were taken from the literature-derived equations listed in Table 1. The vapor pressure of the mixture as a whole is just the sum of that of its constituents:

$$P = \sum_{i=1}^2 P_i$$

In this model, the value of the parameter R_0 determines the degree to which the solution vapor pressure deviates from ideal solution behavior. When the parameter R_0 approaches zero, the exponential term approaches unity, and the vapor pressure of that component will approach the ideal solution value ($P_i^0 X_{l,i}$). Values of R_0 less than zero result in solution vapor pressures that are less than that of the ideal solution; values of R_0 greater than zero result in solution vapor pressures greater than that of the ideal solution.

This model provides a means of estimating the mole fraction of the gas phase as a function of the composition of the liquid phase. Experimentally, we have measured the total mass of each component in the system, and have measured the system volume. To estimate the quantities of each material in each phase (gas and liquid), we need to know the densities of the phases, which will in general vary as a function of composition. We do not have explicit data or formulae for calculating these densities, but will resort to estimation methods, which will be described in more detail below.

Gas Density Estimate: In the range of experimental conditions studied, all three pure compounds have densities somewhat in excess of what would be predicted from the ideal gas law. A fairly simple P-V-T formula is that of Beattie and Bridgeman:

$$P = (A_g T + B_g)d^3 + (C_g T + D_g)d^2 + E_g T d$$

where P is pressure, T is absolute temperature, and d is molar density. Parameters for this equation were reported for CFC-114 and FC-c318 in references 7 and 4, respectively. Converted to common units, the values of these parameters are listed in Table 4. Temperature ranges and average deviations were not cited for these equations. Experimental P-V-T data for FC-3110 from reference 3 was fit to this equation. The fit reproduced that reference's experimentally measured $P(d,T)$ to an average deviation of 0.5% throughout the reported temperature range of 340 to 450K. The fitted coefficients for FC-3110 are listed in Table 4.

Table 4: Coefficients for P-V-T Equation for Pure Compounds:

$$P = (A_g T + B_g)d^3 + (C_g T + D_g)d^2 + E_g T d$$

where P is in atm,
 T is in K, and
 d is in mol/liter.

Coeff.	CFC-114	FC-c318	FC-3110	units
A_g	0.00919393	-0.00539387	-0.00737867	$l^3 \text{atm/mol}^3 \text{K}$
B_g	-1.64416	3.85009	5.08795	$l^3 \text{atm/mol}^3$
C_g	0.0395591	0.0373349	0.0579469	$l^2 \text{atm/mol}^2 \text{K}$
D_g	-29.5395	-27.4419	-36.9413	$l^2 \text{atm/mol}^2$
E_g	0.0823084	0.0823199	0.0816715	$l \text{atm/mol K}$
Ref	[7]	[4]	[data of 3]	

The above equation of state gives the pure compound pressure as a function of molar density and temperature. At conditions of interest, the molar densities of all three compounds deviate somewhat from ideality, but to a similar degree. For example, at a pressure of 7 atm (5320 Torr) and a temperature of 344 K, the molar densities of gaseous CFC-114, FC-c318, and FC-3110 are calculated to be 0.294, 0.288, and 0.301 mol/liter, respectively, versus the ideal gas molar density of 0.248 mol/liter.

We will approximate the density of a mixture as a linear combination of the densities of the mixture's components as follows:

1. The equation of state for each component will be used to calculate the gas density of that component ($d_{g,i}$) as a function of the temperature and total system pressure (i.e., not from the partial pressure of each component)
2. The mixture gas density will be taken to be the mole fraction-weighted average density:

$$d_g = \sum_{i=1}^2 d_{g,i} X_{g,i}$$

The rationale for this approximation is somewhat subjective. Based on the similarity of behavior and the near ideality of solution behavior (to be established below), we conclude that interaction between molecules of the different species shouldn't be too much different than that between like molecules, since the deviation from ideal gas behavior (in terms of mol/liter) is fairly similar for each compound at the conditions of interest. Certainly this approximation should be more accurate than the alternative of assuming that the two mixture components do not interact with one another. A more elaborate treatment might attempt to extract from the experimental data not only the excess free energy of the liquid, but also the inter-species P-V-T relationships. Such a level of elaboration would require more extensive data than we have obtained to date.

Liquid Density Estimate:

Density data for the pure compounds came from Wilson & Hules² for CFC-114 and from Martin⁸ (as reported by Harkins⁹) for FC-c318. In both references, density data had been fit to an equation of the form:

$$d_l = A_1 + B_1 f + C_1 f^2 + D_1 f^3 + E_1 f^4$$

where $f = (1-T/T_c)^{1/3}$
and T_c is the critical temperature.

The coefficients for each compound are presented in Table 5. The CFC-114 data in Reference 8 are reproduced with an average deviation of 0.05% over the range 210 to 420K; the FC-c318 data are reproduced with an average deviation of 1% over the range 260 to 388K. For FC-3110, experimental data of Schlessner & Schramm¹⁰ and Brown & Mears³ (as reported by Harkins⁹) were fit to an abbreviated version of the same functional form yielding the coefficients listed in Table 5. This fit reproduces the cited data, taken over the range 270 to 360 K, with an average deviation of 0.2%.

Table 5: Coefficients for computation of pure compound liquid densities

$$d_l = A_1 + B_1 f + C_1 f^2 + D_1 f^3 + E_1 f^4$$

$$\text{where } f = (1 - T/T_c)^{1/3},$$

T_c is the critical temperature

d_l is in units of gm/cc

	<u>CFC-114</u>	<u>FC-c318</u>	<u>FC-3110</u>
$T_c(K)$	419.03	388.37	386.40
A_1	0.55668	0.619934	0.728008
B_1	1.227001	1.135077	0.786847
C_1	-0.13979	0.378204	0.771867
D_1	0.589876	0.256127	0
E_1	-0.1009	-0.14296	0
	[2]	[8]	[data 3 & 10]

For purposes of estimating the liquid density of the mixture, each liquid component is assumed to occupy a volume $V_{l,i}$ at its calculated pure material density:

$$V_{l,i} = M_{l,i} / d_{l,i}$$

and the total liquid volume is taken to be the sum of these volumes:

$$V_l = \sum_{i=1}^2 V_{l,i}$$

While this approximation won't be exact, error in estimation of the liquid density of the mixtures will have very little effect on the resulting computed gas-liquid distribution of material.

Mass balance: A final constraint on the system is that of mass balance. For each component, the mass of material in the gas and liquid phases must sum to the measured quantity initially introduced into the system:

$$M_i = M_{l,i} + M_{g,i}$$

Determination of Gas-Liquid Material Distribution

Within the constraints imposed by the equations above, values for the unknown parameters (mass of each component in the gas and liquid and the mixture non-ideality parameter R_0) were sought using numerical techniques. An iterative series of calculations was done using relationships for the densities, vapor pressures, and mass balance formulae, the experimentally measured data (total mass of each coolant in the system, system volume, and temperature), adjusting the unknowns until a self-consistent set of values was determined by which the calculated system vapor pressure best reproduced (in the least squares sense) the experimentally measured vapor pressures.

In more detail, the iteration scheme operated as follows:

I. Outer loop:

A: Postulate a value of R_0

B: For each experimental measurement (P, T, M_1, M_2, V), in a data set (e.g., for all CFC-114:FC-c318 experiments run nominally at 322 K) execute the following "inner loop":

1. Calculate pure species vapor pressures at T , P_i^0 .
2. Calculate pure component liquid density at T , $d_{l,i}$.
3. Postulate a value for the mass of each gas species, $M_{g,i}$.
4. Calculate the mole fraction of gas, $X_{g,i}$.
5. From mass balance, calculate the liquid mass of each component, $M_{l,i}$.
6. Calculate the liquid mole fractions, $X_{l,i}$.
7. Calculate the liquid volume from liquid density values and the liquid masses, V_l .

8. Calculate volume available to gas ($V_g = V - V_l$)
9. Calculate the partial pressure, P_i , of each component over the liquid mix.
10. Calculate the total vapor pressure, P , of the mixture.
11. Calculate the gas density $d_{g,i}$ of each pure component at P , T , and $X_{l,i}$.
12. Calculate the mass of each gas component, $M_{g,i}^*$, from gas density and gas volume.
13. Check for convergence: If the mass for either component calculated in step 12 differs from the mass postulated in step 3 by more than the convergence criterion, then go back to step 3, using the values $M_{g,i}^*$ as the postulated $M_{g,i}$. Repeat steps 3 through 13 until the difference is less than the convergence criterion (taken as 1 microgram).

C: Steps 1 through 13 yield a predicted mixture vapor pressure for each experiment. Calculate the mean square deviation s^2 between this set of calculated vapor pressures and the experimentally measured vapor pressures:

$$s^2 = \frac{1}{n} \sum_{j=1}^n (P_{\text{exp},j} - P_{\text{calc},j})^2$$

where n is the number of experiments in the data set, $P_{\text{exp},j}$ is the experimentally measured pressure of the j^{th} experiment, and $P_{\text{calc},j}$ is the vapor pressure calculated by the inner loop (steps 1-13) for that experiment.

D. Repeat steps A..C, varying R_0 until the root mean square difference is minimized. This yields a value for the "best" R_0 at the temperature of the data set.

E. Repeat steps A..D for each of the 4 data sets derived from the 4 nominal experimental temperatures.

This iterative scheme yields, for each experiment, a computed estimate of the quantity (and hence mole fraction) of each compound in each phase. Figures 2 through 9 show pressure vs. composition plots for each set of experimental data. Experimental vapor pressures (solid squares), annotated as to their particular experimental temperature and calculated vapor pressures (open squares) at that same temperature are plotted against the calculated liquid mole fraction. Calculated vapor pressure curves, computed at the average temperature of the data set, are plotted vs. liquid (solid line) and gaseous (dotted line) mole fractions. The upper set of curves shows the non-ideal solution model using the value of the non-ideality parameter R_0 which best reproduces that data set; for reference, a lower set of curves, depicting the behavior of an ideal solution, is also displayed.

As can be seen from the figures, the regular solution model fits observed behavior reasonably well. Most of the deviations of experimental data points from the corresponding calculated pressure vs. liquid composition line are the result of the temperature difference between a particular experimental point and the average temperature of the data set (from which the calculated line was derived).

The adjustable parameter R_0 does not have an identical value at all temperatures, but does not vary a great deal and follows a regular trend with temperature, suggesting that interpolation and perhaps short-range extrapolation is a viable procedure for predicting mixture behavior at temperatures in or near the range explored in these experiments. Table 6 lists the "best fit" values for R_0 for each data set, along with the standard deviation estimate for the fitted value.

To assist in interpolation of the value of $R_0(T)$, the values in Table 6 were fit to the following equation:

$$R_0(T) = A_R (1 - \exp(-(C_R - T)/B_R))$$

This form of this equation has the behavior that R_0 approaches the constant value A_R when the temperature is far below C_R , and approaches zero when the temperature approaches C_R . This equation is

Vapor Pressure of CFC-114 : FC-c318 Mixtures

at Ave. $T = 322.6 \text{ K}$; $R_o = 596 \text{ J/mole}$

Figure 2: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_o adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

Vapor Pressure of CFC-114 : FC-c318 Mixtures

at Ave. T = 334.4 K; $R_o = 647$ J/mole

Figure 3: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_o adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

Vapor Pressure of CFC-114 : FC-c318 Mixtures

at Ave. T = 344.1 K; $R_o = 614$ J/mole

Figure 4: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_o adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

at Ave. $T = 356.3\text{ K}$; $R_o = 514\text{ J/mole}$

Figure 5: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_0 adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

Vapor Pressure of CFC-114 : FC-3110 Mixtures

at $T = 322.5 \text{ K}$; $R_o = 925 \text{ J/mole}$

Figure 6: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_o adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

Vapor Pressure of CFC-114 : FC-3110 Mixtures at $T = 334.3 \text{ K}$; $R_o = 914 \text{ J/mole}$

Figure 7: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_o adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

Vapor Pressure of CFC-114 : FC-3110 Mixtures

at $T = 344.3 \text{ K}$; $R_o = 859 \text{ J/mole}$

Figure 8: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_o adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

Vapor Pressure of CFC-114 : FC-3110 Mixtures at $T = 356.1 \text{ K}$; $R_o = 742 \text{ J/mole}$

Figure 9: Solid curves depict (at the average system temperature) pressure vs. liquid composition; dotted curves depict pressure vs. gas composition. Lower set of curves depicts behavior of an ideal solution and upper curves that of a regular solution with R_o adjusted to best fit the experimental data. Solid rectangles plot observed pressure vs. liquid composition at the indicated temperature; open rectangles plot corresponding regular solution model pressure.

Table 6: Best fit values for solution non-ideality parameter R_0 , in units of J/mol.

Nominal Temperature (K)	CFC-114 + FC-c318	CFC-114 + FC-3110
322	596 $\pm$ 16	927 $\pm$ 19
333	647 $\pm$ 35	919 $\pm$ 23
344	614 $\pm$ 45	864 $\pm$ 38
355	514 $\pm$ 71	748 $\pm$ 46

completely empirical, and should not be considered valid much outside the temperature range of the experimental data (322 to 355 K). The parameters for this equation for each mixture are listed in Table 7. For FC-c318, this equation reproduces the fitted values of R_0 to within 5%, and the experimental mixture vapor pressure measurements to within 1.4%; for the FC-3110 parameters, R_0 is reproduced to within 1.1% and the vapor pressures to within 0.9%. The poorer performance of this equation for the CFC-114:FC-c318 mixtures is due to the 322K value for R_0 in that system, which is slightly low relative to the 333 and 344K points.

The model and fitted experimental results make it possible to devise a method by which one can predict the vapor pressure (within our experimental temperature range) of any mixture of CFC-114 and FC-3110 or FC-c318 whose liquid mole fraction, $X_{l,i}$, is known.

1. Calculate the solution non-ideality parameter $R_0(T)$ from:

$$R_0(T) = A_R (1 - \exp(-(C_R - T)/B_R))$$

where T is in K and A_R , B_R , and C_R come from Table 7.

2. For each solution component, i, calculate the excess free energy of that component in the solution:

$$G_{\text{excess},i} = R_0(T) (1 - X_{l,i})^2$$

Table 7: Parameters for empirical fit of solution non-ideality parameter to:

$$R_0(T) = A_R (1 - \exp(-(C_R - T)/B_R))$$

<u>Parameter</u>	<u>CFC-114 + FC-c318</u>	<u>CFC-114 + FC-3110</u>
$A_R(\text{J/mol})$	627.33	938.68
$B_R(\text{K})$	6.00	10.93
$C_R(\text{K})$	366.72	373.40

3. Calculate the partial pressure of each component:

$$P_i = P_i^0 X_{i,i} \exp(G_{\text{excess},i} / R T)$$

where P_i^0 is the vapor pressure of the pure component, calculated from the equations in Table 1.

4. Calculate the vapor pressure of the solution as the sum of the partial pressures of its components:

$$P = \sum_{i=1}^2 P_i$$

DISCUSSION

From Figures 2 through 9, it is apparent that the two binary mixtures examined were found to be slightly non-ideal, with both exhibiting a positive deviation of vapor pressure relative to that of an ideal solution. This vapor pressure deviation was, within the limits of experimental accuracy, well-depicted by a regular solution model.

The degree of non-ideality of solution behavior is embodied in the value of the parameter R_0 . For CFC-114:FC-c318 mixtures, R_0 was about 600 J/mole. For CFC-114:FC-3110 mixtures, R_0 was about 50% stronger, at about 900 J/mole. In both cases, as the temperature increased (perhaps toward the critical temperature?), the value of R_0 decreased. In neither case is the deviation from solution ideality strong (compare the values of R_0 to the heat of vaporization of these species, which is on the order of 20000 J/mole).

For FC-c318, the combination of the difference in its vapor pressure and that of CFC-114 and the relative weakness of R_0 , combine to result in mixture vapor pressures which, while higher than those of an ideal solution, are lower at all compositions than that of pure FC-c318.

For FC-3110, the vapor pressure difference between it and CFC-114 is smaller, and the value of R_0 is larger. The combination of these factors results in mixture vapor pressures exhibiting a maximum at intermediate compositions, especially at the lower temperatures examined. At 322 and 333 K, the pressure at this maximum is calculated to be about 50 Torr (1 psia) higher than that of pure FC-3110 at the same temperatures. This difference diminishes as the temperature is increased until at 355 K, the vapor pressure maximum is predicted to be only 7 Torr higher than the pure compound vapor pressure (a difference smaller than the experimental scatter of our data). This intermediate vapor pressure maximum also implies the existence of an azeotropic composition for this mixture, which has implications for distillation separation of such mixtures.

CONCLUSIONS

The vapor pressure of CFC-114 : FC-3110 and CFC-114: FC-c318 mixtures has been measured over the temperature range 322 to 355 K (120 to 180°F). The vapor pressure of these mixtures will be higher than that of an ideal solution. The pressures observed follow the behavior of the class of non-ideal solutions termed a regular solution, with an excess free energy parameter whose temperature dependence implies that the solution becomes more ideal as temperature rises.

The data have been used to create a formula for calculating mixture vapor pressure anywhere within this range, and which is probably reasonably valid for modest extrapolations to lower temperature.

Some diffusion plant operational implications can be drawn from the mixture data. On the issue of inadvertent overpressure, this should not be an issue with FC-c318, since the vapor pressures of mixtures of FC-c318 and CFC-114 will always be lower than that of pure FC-c318. For FC-3110, the vapor pressures of mixtures rich in FC-3110 will be only slightly higher than those of the pure compound. Thus, trace contamination of FC-3110 with CFC-114 won't cause a dramatic (and perhaps not even a noticeable) increase in the overall vapor pressure.

Second, use of inadvertent coolant mixtures could at least be considered. The economics and operational uncertainties in use of the mixture would have to be balanced against the cost or cost avoidance of either purification or disposal of an inadvertent mixture, but the vapor pressure data do not yield any clear reason for outright rejection of the notion of utilizing mixtures.

Third, intentional dilution of FC-3110 or FC-c318 with CFC-114 (as a means of lowering the vapor pressure) would not appear to offer useful benefits. Mixtures of either PFC coolant with CFC-114 will have a higher vapor pressure than the mole fraction weighted average vapor pressure. Thus, the outleakage from systems containing mixtures will be greater (other factors being equal) than the leakage of an equivalent combination of systems containing pure PFC and pure CFC-114.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. J.M.Leitnaker for helpful discussions and criticism of the data analysis methods used in this work.

BIBLIOGRAPHY

- 1 *Montreal Protocol on Substances that Deplete the Ozone Layer*, U.N.E.P., 1987.
- 2 D.P.Wilson & K.R.Hules, "Experimental Study of Thermodynamic Properties of 1,2 Dichlorotetrafluoroethane", in *Proc. of 8th Sym. on Thermophysical Properties*, J.V.Sengers, ed., NBS, Gaithersburg, MD 6/15/1981.
- 3 J.A.Brown & W.H.Mears, *J. Phys. Chem.*, v. 62, p 960, 1958.
- 4 R.C.Downing, "Physical Properties of Freon-C318, Perfluorocyclobutane", Technical Bulletin B-18B, E.I.DuPont de Nemours, Wilmington, DE, 1960.
- 5 M.J.Orlett, *Laboratory Measurement of Miscibility and Pressure Temperature Relationships of n-C₄F₁₀/CFC-114 Mixtures*, POEF-T-3599, Martin Marietta Energy Systems, Inc, Portsmouth, OH, 1992.
- 6 P. Benedek and F.Olti, *Computer and Chemical Thermodynamics of Gases and Liquids*, J. Wiley & Sons, New York, 1985.
- 7 A.F.Benning & R.C.McHarness, DuPont data sheet entitled "Thermodynamic Properties of "Freon-114", undated.
- 8 J.J.Martin, "Thermodynamic Properties of Perfluorocyclobutane", *J.Chem Eng. Ref. Data* 7(1), p 68, 1962.
- 9 D.A.Harkins, *Evaluation of Available Perfluorobutane Data for Selected Physical Properties*, K/QT-331, ORGDP, Martin-Marietta Energy Systems, Inc., Oak Ridge TN, Jan 1990.
- 10 C. Schlessor & S.R.Schramm, eds., *Preparation, Properties and Technology of Fluorine and Organic Fluorine Compounds*, McGraw-Hill, New York, 1951.

DISTRIBUTION

Oak Ridge - 4 Oaks Office Complex

G.B.Boroughts
R.L.Higgins
P.L.McKenney

Oak Ridge K-25 Site

W.D.Altman
E.C.Angel
D.P.Armstrong
E.J.Barber
D.A.Harkins
J.A.Hoffmeister
J.M.Leitnaker
F.W.Nehring
A.S.Quist (3)*
R.L.Ritter
L.D.Trowbridge
Appl. Techn. Library
K-25 Site Records

Oak Ridge National Laboratory

P.D.Fairchild
J.R.Sand

Paducah Gaseous Diffusion Plant

P.B.Kreitz
J.D.Lewis
M.G.Otey
B.W.Pilgrim
R.G.Russell
D.L.Weishaar
P.D.Wooldridge
Technical Library

Portsmouth Gaseous Diffusion Plant

C.F.Harley
D.M.Manuta
W.D.Netzer
M.J.Orlett
A.J.Saraceno
Technical Library

USEC/HQ

O.L.Ewing

University of Tennessee, Knoxville

J.L.Adcock

* 2 copies intended for OSTI