PHYSICAL PROPERTIES OF ALTERNATIVES TO THE
FULLY HALOGENATED CHLOROFLUOROCARBONS

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1. INTRODUCTION

The physical properties of a fluid largely determine its suitability for use in a given application. The present study is concerned with properties of possible alternatives to the fully halogenated chlorofluorcarbons, a class of compounds widely used as working fluids (refrigerants) in refrigeration and air-conditioning equipment, as solvents and foam blowing agents, and in a wide variety of other applications. As examples, the thermophysical properties such as enthalpy, the pressure-volume-temperature (PVT) behavior, and viscosity are necessary to predict the performance of a fluid in refrigeration equipment. The thermal conductivity of the blowing agent has a large effect on the insulating value of a foam. The normal boiling point is important for solvent uses.

This paper, as part of the larger Alternative Fluorocarbon Environmental Assessment Study (AFEAS), focuses on those properties that influence the environmental acceptability of alternative fluorocarbon fluids. Specifically considered are the fluid fixed point parameters (triple point, normal boiling point, and critical point parameters), vapor pressure, saturated liquid density, solubility in water, and hydrolysis rates. The environmental implications of the first five properties listed are indirect. These properties are, however, often required as inputs for various models and estimation techniques. The last two properties can directly affect the fate of a fluorocarbon once it is emitted to the environment. One possible mechanism for the removal of a fluorocarbon from the environment is its dissolution in the ocean or in water droplets in clouds and subsequent reaction of the fluorocarbon with water (hydrolysis). This paper addresses the basic data associated with this mechanism of decomposition in the environment; the effectiveness of this mechanism is assessed by Wine and Chameides (1989).

The fluids to be considered in this report are the leading candidates to replace the fully halogenated CFCs such as R12 (CCl_2F_2) and R11 (CCl_3F). All are hydrogen-containing halogenated methanes and ethanes. The range of normal boiling points for these candidate fluids is similar to the range seen with the fully halogenated compounds.

In many cases, the fluids considered here have never been commercially produced and as a consequence, the data for many of them are sparse; thus, all possible sources of data have been utilized. These include the published literature (as revealed by a search of Chemical Abstracts and surveys such as that by Stewart, et al. (1981)), compilations such as that by the Japanese Association of Refrigeration (1975), unpublished data provided by several chemical manufacturers which are members of the AFEAS group, and, finally, experimental work in progress at the National Institute of Standards and Technology (NIST). Where available, preference is generally given to published over unpublished sources and to actual experimental values over information presented graphically or in terms of a correlation. The data differ greatly in quality and reliability and, as will be seen, are sometimes conflicting.

To be of maximum and immediate utility to the other AFEAS groups which may need to make use of this information, all data are fit with standard forms and presented primarily in terms of the resulting correlations. In this report a summary section containing coefficients to the correlations, etc. precedes a detailed discussion of the data themselves.

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2. SUMMARY

Fluid Fixed Points

The triple point, normal boiling point, and critical point parameters are fundamental characteristics of a fluid. The triple point is the state at which three phases (solid, liquid and vapor) coexist; it is virtually identical with the more often reported freezing point. The normal boiling point is simply the temperature at which the vapor pressure of a fluid is one standard atmosphere (101.325 kPa). Since the vapor pressures of nearly all fluids are approximately parallel when plotted as the logarithm of pressure versus inverse temperature, the normal boiling point is a rough predictor of the vapor pressure at all temperatures. The critical point is the state at which the properties of the saturated liquid and vapor become indistinguishable; coexisting liquid and vapor are possible only at temperatures and pressures below the critical point values.

These parameters, often in the absence of any other information, are frequently used in screening among many different compounds to select a more limited set for further study. For many applications they define the temperature limits for the use of a particular fluid. Clearly a solvent or refrigerant cannot be used below the triple point temperature. For many refrigeration applications, operation at sub-atmospheric pressures is avoided and, thus, the normal boiling point is a more practical lower limit. Vapor compression refrigeration equipment transports heat through condensation and evaporation (i.e. two-phase) processes and thus the critical point represents an upper temperature and pressure limit. The critical point parameters are the essential inputs to estimation techniques based on the law of corresponding states, which is the observation that, when scaled by the critical parameters, the properties of nearly all fluids are similar.

The triple point, normal boiling point, and critical point parameters are given in Table 1. (In this table, and all subsequent tables, the fluids are listed in order of increasing normal boiling point temperature.) The selection of these values is discussed in detail in the Discussion section.

Vapor Pressure

The experimental vapor pressure data were fit to the following equation, which is a modification of a form suggested by Goodwin & Haynes (1982):

$$\ln p = a_1/T + a_2 + a_3T + a_4(1 - T/T_c)^{1.5} \tag{1}$$

where p is pressure, T is absolute temperature (kelvins) and T_c is the critical temperature. Theories for asymptotic critical behavior predict a value of approximately 1.9 for the exponent in the last term in Equation (1); a value of 1.5, however, was empirically found to yield a better fit over a wide temperature range for R134a and R123 (Weber 1989). The coefficients for each of the fluids considered, along with the temperature range of the data, are given in Table 2. Modest extrapolations outside this range should yield fairly accurate results. This table also gives the RMS deviations between Equation (1) and the input data. These RMS values serve as indications of the precision of the data and the agreement between different sources. Particularly for those fluids with only one data source, the method of computing RMS deviations cannot detect any systematic errors in the data, and thus RMS values provide little information on

the accuracy of the data and the resulting correlation. In most cases the accuracy of the correlation cannot be stated because of insufficient documentation; this is considered in more detail in the Discussion section. The vapor pressures as functions of temperature are also tabulated along with the other properties in the Appendix.

Saturated Liquid Density

Liquid densities along the saturation line, ϱ, were fit to the commonly used form:

$$\varrho/\varrho_c = 1 + d_1\tau^\beta + d_2\tau^{2/3} + d_3\tau + d_4\tau^{4/3} \tag{2}$$

where $\tau = (1 - T/T_c$ and ϱ_c is the critical density. The critical exponent, β, is properly evaluated from experimental measurements near the critical point. For most of the fluids considered here a value of 1/3 is assumed because of the lack of data. Equation (2) is well-grounded in theory, has the proper form over a wide range of temperature including the vicinity of the critical point, and is often used in the correlation of saturated liquid densities. The fit of density data to Equation (2) is summarized in Table 3. As with vapor pressure, the temperature range of the data and the RMS deviation are also given. The critical temperature and density required in Equation (2) may be found in Table 1.

Solubility in Water

The fluids considered in this report are all highly volatile (most have normal boiling points well below typical ambient temperatures) and thus their presence in the environment will be predominantly as trace gases in the atmosphere. Atmospheric gases will, however, dissolve to some extent into the oceans and into water droplets in clouds. The magnitude of this solubility will influence the importance of hydrolysis as a degradation mechanism. The dissolution of trace gases into water is well-represented by Henry's law:

$$x_a = p_a/H_a \tag{3}$$

which states that the concentration of substance "a" dissolved in a solvent, x_a, is proportional to the partial pressure of substance "a" over the solution, p_a. Henry's law strictly applies only in the limit of x_a approaching zero but in practice holds very well for gas partial pressures up to a few hundred kPa and even higher for gases of low solubility (such as the fluorocarbons). The proportionality factor in Equation (3), H_a, is called the Henry's law constant. The units of H_a are pressure divided by a concentration (e.g. kPa/mass % or atm/ppm). The Henry's law constant is not constant but is a function of temperature which can be well represented by:

$$\ln (1/H_a) = h_1 + h_2/(T + h_3) \tag{4}$$

Solubility data have been used to evaluate the coefficients in Equation 4; they are given in Table 4. Note that the term h_3 is used only for R22. Equation 4 has been used to calculate solubilities in water at the commonly referenced conditions of 298.15 K (25°C) and a fluorocarbon partial pressure of one standard atmosphere. (While this is an unrealistically large partial pressure for gases in the environment, it is useful for comparisons between compounds.) For several of the fluids there was considerable disagreement (as much as a factor of two) in measured solubility from different sources; these are flagged by comments in Table 4.

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At least limited solubility data were obtained (mostly from unpublished sources) for all of the compounds considered as part of AFEAS. For other fluids which may be of interest and for which data may not exist, the method of Irmann (1965) (as reported by Lyman, et al. 1982) can be used to estimate the solubilities of the halogenated hydrocarbons. This method requires only the molecular structure and vapor pressure at 298.15 K (25°C) of the compound in question and yields the solubility in water at 298.15 K. The results of applying this estimation technique to the nine compounds considered here are given in Table 5. For most of the fluids the agreement is very good (within 15%), validating this method. The estimated values for R125 and R141b, however, differ by factors of two and five, respectively from the reported values. In view of the good agreement for the other fluids, this discrepancy casts some doubt on the reported values for R125 and certainly for R141b.

The above results are for solubilities in pure water. The solubilities in saline solutions can be represented by the following form reported by Lyman, et al. (1982):

$$\ln (x_a/x_{a,s}) = K_s C_s \tag{5}$$

where x_a is the solubility in pure water and $x_{a,s}$ is the solubility in a saline solution of concentration C_s. The term K_s is an empirical salting parameter. Values of K_s are positive, so solubilities in salt water are lower than those in pure water. For the compounds of interest here, data were found only for R22 and methyl chloroform. Zhang, et al. (1985) report R22 solubilities in sodium chloride solutions over the temperature range 283-323 K. Their data confirm Equation (5) and can be used to compute values of K_s ranging from 0.0060 L/g at 283 K to 0.0082 L/g at 333 K. These correspond to solubilities in sea water which are 81-75% of those in pure water. Walraevens, et al. (1974) report a salting parameter of 0.0073 L/g for methyl chloroform corresponding to a solubility in sea water which is 78% of that in pure water.

Limited data for the solubility of other fluorocarbons in salt solutions were also found. Data for R21 ($CHCl_2F$) (Downing 1988) and R114 ($CClF_2CClF_2$) (Stepakoff and Modica 1973) give values of K_s of 0.0061 and 0.029 L/g respectively; these correspond to solubilities in sea water which are 81 and 36% of those in pure water. This range for the ratio of sea water to pure water solubilities is similar to those observed with other classes of fluids (Lyman, et al. 1982). The polar, hydrogen-containing R22, R21, and methyl chloroform are better analogues to the full set of fluids considered here than the weakly polar, fully halogenated R114. The effect of salt on the solubilities of the fluids considered in this report is, thus, probably closer to those observed with R22 and R21 than with R114. Considering the similarity of salting parameters for R22, R21, and methyl chloroform, a salting parameter of 0.007 L/g is recommended for the other fluids in the absence of data. This corresponds to a solubility in sea water which is 78% of that in pure water.

Hydrolysis Rates

Hydrolysis refers to the reaction of a compound in aqueous solution. For the fluorocarbons, two mechanisms are possible (Ellenrieder and Reinhard 1988). In nucleophilic substitution, or hydrolysis proper, the fluorocarbon reacts with water or the hydroxide ion (OH-) to form an alcohol plus an acid:

$$R\text{-}C\text{-}R'X + H_2O/OH^- \rightarrow R\text{-}C\text{-}R'OH + HX \tag{6}$$

where X represents a halogen (F or Cl) and R and R' are nonreacting groups. In the second mechanism, known as elimination or dehydrohalogenation, water or hydroxide catalyzes the reaction to form an alkene plus acid:

$$R\text{-}CH\text{-}CR'X + H_2O/OH^- \rightarrow RC=CR' + H_2O/OH^- + HX \tag{7}$$
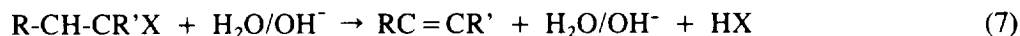
In this work, the term "hydrolysis" will refer to the general reaction in aqueous solution; the terms "substitution" and "elimination" will be used when it is necessary to distinguish between the different mechanisms. A single-carbon compound (such as R22) can obviously undergo only the substitution process. Other mechanisms occur for the fully halogenated compounds (Downing 1988) but will not be considered here.

The elimination process becomes more important as the number of halogens in the molecule increases (Vogel, et al. 1987). Either process may be neutral (reaction primarily with water) or base-promoted (reaction primarily with hydroxyl). A third possibility, acid promotion by the hydronium ion, H^+, does not occur (Mabey and Mill 1978).

The rate of reaction, expressed in terms of the disappearance of fluorocarbon, is proportional to the fluorocarbon concentration. Thus the solubility of the compound will have an influence on its reaction rates. For base-promoted processes, the reaction rate is also proportional to the hydroxyl concentration, which in turn is related to the pH. Where the neutral process dominates, the rate is independent of pH. For the general case of base-promoted and neutral processes occurring simultaneously, the reaction rate can be expressed as:

$$-d[RX]/dt = [RX](k_B[OH^-] + k_N) \tag{8}$$

where square brackets denote a concentration in moles/liter, RX is the reacting fluorocarbon, and k_B and k_N are the rate constants for the base-promoted and neutral processes, respectively. Both k_B and k_N may be further broken down into additive contributions from the substitution and elimination mechanisms. Each of the rate constants are functions of temperature, typically expressed in terms of an Arrhenius expression:

$$k = A \exp(-E/RT) \tag{9}$$

where E is the activation energy of the reaction and R is the gas constant.

The hydrolysis of a fluorocarbon is thus seen to be a rather complex process with several possible mechanisms. To fully describe the temperature and pH dependence of a reaction requires up to eight parameters. To further complicate the situation, metals can catalyze hydrolysis and increase reaction rates by an order of magnitude or more (Downing 1988). The information located for the hydrolysis rates of the fluorocarbons considered here was limited.

Downing 1988 gives information on both the temperature and pH dependence of R22 hydrolysis rates:

$$-d[R22]/dt = k[R22][OH^-] \tag{10}$$

The temperature dependence of k is given by Equation (9) with:

$$A = 1.87 \times 10^8 \text{ L/(mol·s)}$$

$$-E/R = -7692. \text{ K}$$

One must infer from Equation (10) that either the neutral and base-promoted processes have been lumped together into a single rate constant or that the former process is insignificant, i.e. k_N is small.

At a temperature of 298 K and a concentration of hydroxide of 1×10^{-7} mol/L (corresponding to pure water of pH = 7) the above expression yields an overall rate constant (i.e. $k_B[OH^-] + k_N$) of 1.15×10^{-10} s^{-1}; at an R22 concentration of 0.033 mol/L (the solubility of R22 at a partial pressure of 101.3 kPa) the corresponding hydrolysis rate is 3.8×10^{-12} mol/(L·s). This is in reasonable agreement with the value of 4.5×10^{-12} mol/(L·s) given by DuPont (1989) at the same conditions.

Ellenreider and Reinhard (1988) have developed an interactive, computerized data base for the calculation of hydrolysis rates as functions of temperature and pH. While this would be an ideal method of presenting hydrolysis data, of the compounds of interest here, only methyl chloroform is presently included in this data base. In the paper by Ellenreider and Reinhard, methyl chloroform is presented as an example. At 293 K in pure water (pH = 7) the rate constant for the substitution reaction is 8.1×10^{-9} s^{-1} with the neutral process dominant by several orders of magnitude over the base-promoted process; for the elimination mechanism the rate constant is 2.0×10^{-9} s^{-1} for the neutral process (no data are given for the base-promoted elimination process). The overall rate constant is 1.0×10^{-8} s^{-1}. For a concentration of 0.033 mol/L (the saturation concentration of methyl chloroform) the hydrolysis rate is 3.3×10^{-10} mol/(L·s). The temperature dependence is also given by Ellenreider and Reinhard. The overall rate constant can be expressed in terms of Equation (9) with:

$$A = 1.28 \times 10^{13} \text{ s}^{-1}$$

$$-E/R = -14244. \text{ K}$$

This implies that the hydrolysis reaction is a factor of five faster at 303 K than at a temperature of 293 K.

Perhaps a more convenient means of expressing the rate of a first order reaction is in terms of the half-life of the reacting species. The half-life is independent of reactant composition. Ellenreider and Reinhard report a half-life of 0.96 year for methyl chloroform at 298 K and pH = 7. The hydrolysis rate constant for R22 yields a half-life of 191 years at the same conditions. Thus, there is a vast difference in the effectiveness of hydrolysis in breaking down a compound in the environment.

For R123, DuPont (1989) reports a hydrolysis rate approximately 4.3 times that for R22 for a test of 100 days at 328 K. A series of 3-day tests at 358 K indicated that R141b is less stable than R123 but considerably more stable than methyl chloroform. In these short-term test the amount of decomposition was less than 5 ppm for R123 and R141b and 0.006% for methly chloroform. "Stability" data of Allied (1989), however, report that the production of acid from R123 in aqueous solution is 38% of that with R22. The Allied information also indicates that the acid production rates with R124 and R142b are, respectively, 1.35 and 1.65 times that observed with R22. The Allied data are for tests at 314 K and result from measurements of the decomposition of fluorocarbon over a period of three months. The differences in the DuPont and Allied results suggest caution in the use of any hydrolysis rate data.

The database of Ellenreider and Reinhard, along with a survey by Mabey and Mill (1978), unfortunately, do not contain information on any of the other compounds of interest here. In general terms, chlorine is much more reactive than fluorine (Hine, et al. 1961) so the chlorine-free compounds (R125, R134a, R152a) will probably have lower hydrolysis rates than those reported for R22 or R123. The data for the relative reaction rates of R22, R142b, R124, R123, and R141b suggest that the hydrolysis rates for all of these chloroflouro compounds will be of the same order of magnitude. Thus, for the nine fluids considered here, only methyl chloroform is likely to have a hydrolytic half-life on the order of a year; all the others will likely have half-lives on the order of a century or more.

3. DISCUSSION

<u>R125</u>

The data for R125 (pentafluoroethane) are limited. Both Allied (1989) and DuPont (1989) report a critical temperature of 339.4 K. DuPont also gives a freezing point temperature and critical density. None of these values are documented, but they are adopted here in the absence of any other data.

The saturated liquid density and vapor pressure data reported by Allied were selected over the single liquid density value and graphical presentation of vapor pressure given by DuPont in fitting the coefficients to Equations (1) and (2). A comparison of these data with the correlations is presented in Figure 1. The critical pressure (reported in Table 1) was calculated by an extrapolation of Equation (1) to the

Table 1. Fluid Fixed Points

Fluid	Chemical formula	Mol. mass (g/mol)	Tr. Pt. temp. (K)	Norm. temp. (K)	Boiling Pt. liq. den. (kg/m³)	Critical Point temp. (K)	pres. (kPa)	density (kg/m³)
R125	CF_3CHF_2	120.020	170.	224.6	1515.	339.4	3631.	571.5
R22	$CHClF_2$	86.468	113.	232.4	1409.	369.30	4990.	513.0
R134a	CF_3CH_2F	102.030	172.	247.1	1373.	374.21	4056.	515.3
R152a	CHF_2CH_3	66.050	156.	249.0	1011.	386.44	4520.	368.0
R124	$CHClFCF_3$	136.475	74.	261.2	1472.	395.65	3640.	560.0
R142b	CH_3CClF_2	100.495	142.	264.0	1193.	410.25	4246.	435.0
R123	$CHCl_2CF_3$	152.930	166.	301.0	1456.	456.94	3674.	549.9
R141b	CH_3CCl_2F	116.950	170.	305.3	1216.	481.5	4540.	464.1
methyl chlr.	CH_3CCl_3	133.405	243.	347.3	1250.	545.	4300.	470.0

*Note: None of the critical densities are known to four significant figures; they are given to this level for consistency with Eqn (2).
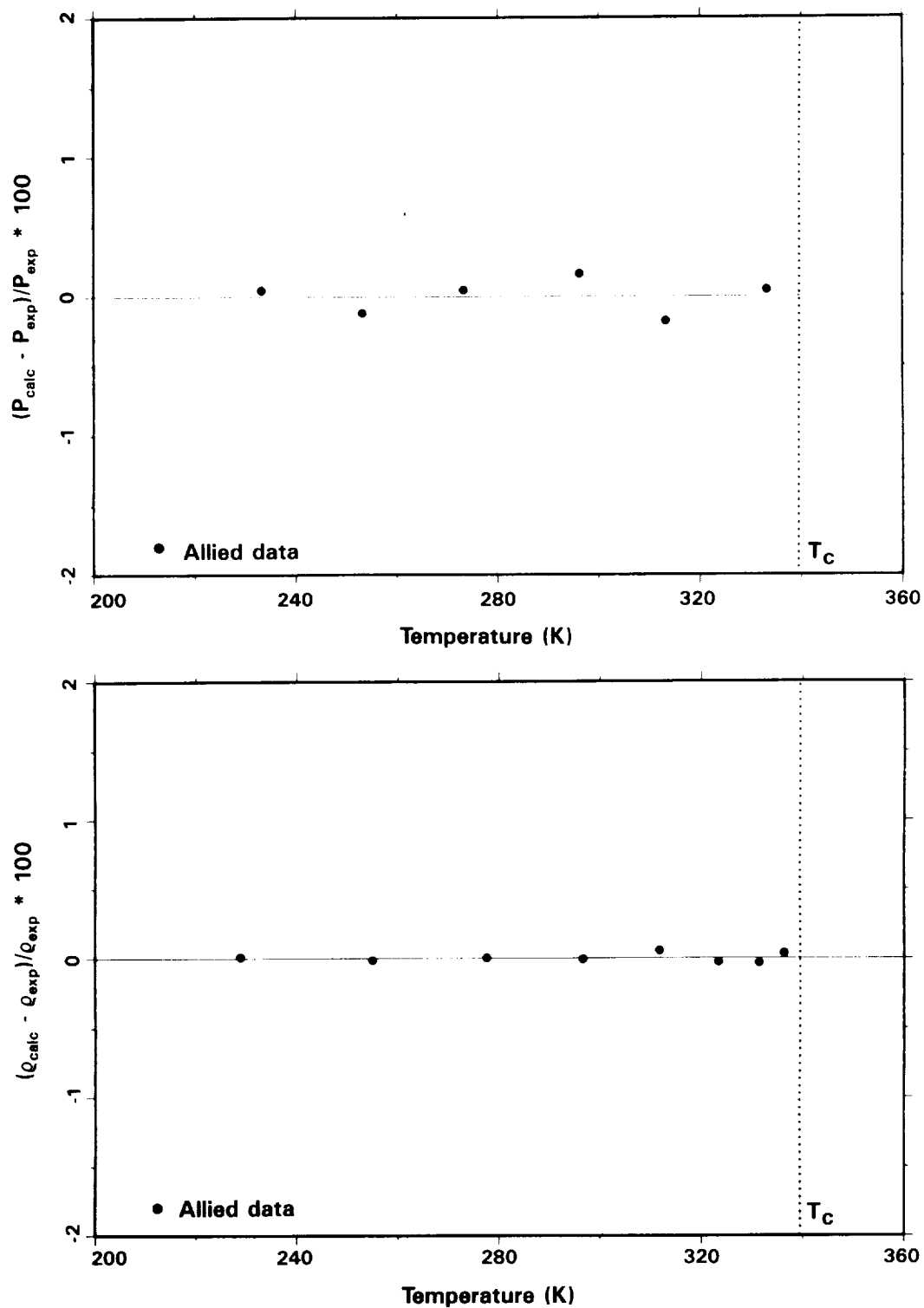
Figure 1. Comparison of correlations with data for R125; a) vapor pressure; b) saturated liquid density.

critical temperature (an extrapolation of only 6.3 K) rather than the value of 3520 kPa reported by DuPont, (1989). As with all the fluids in this report, the normal boiling point temperature reported in Table 1 is obtained by finding the temperature at which Equation (1) yields a pressure of one standard atmosphere (101.325 kPa).

The eight liquid densities reported by Allied were measured over the temperature range 228.7-336.3 K using glass flotation beads of known density. In this technique, the temperature of the fluid is adjusted so that the density of the fluid matches that of one of the beads. In another work by the same group (Wilson and Basu 1988), the accuracy of this method is claimed to be 0.2 kg/m³. The values for R125 were apparently not corrected for the effects of temperature on the densities of the glass beads. Judging by other results by this method, these corrections should be less than 0.1 kg/m³ for the temperature range of the measurements for R125. The excellent fit of Equation (2) to within 6 K of the critical temperature gives some credence to the critical density of DuPont used in the correlation.

The only information on solubility in water were coefficients to a correlation similar in form to Equation (4) reported by DuPont (1989). The experimental technique was similar to that employed by Parmalee (1953). No data were given but an "experimental data range" of 298-333 K was indicated. These coefficients are reported in Table 4 after the appropriate conversion of units.

R22

The extensive body of data on R22 (chlorodifluoromethane) is summarized, evaluated, and correlated in the treatise by the Japanese Association of Refrigeration (1975). Although additional data have been meas-

Table 2. Vapor Pressure

Fluid	Temperature low (K)	limits high (K)	a_1	Coefficients to Equation (1) a_2	a_3 (p in kPa, T in K)	a_4	RMS error (%)
R125	233.	T_c	-2678.571	16.63306	-0.001602304	1.390420	0.12
R22	223.	T_c	-2907.443	17.05244	-0.001796055	2.204052	0.09
R134a	210.	T_c	-3353.464	18.36056	-0.002908044	2.783663	0.19
R152a	273.	T_c	-3110.511	17.02405	-0.001445740	2.105154	0.05
R124	222.	T_c	-3471.946	18.16083	-0.002997217	2.703744	0.35
R142b	233.	369.	-3382.422	17.01384	-0.001012149	3.224924	0.30
R123	243.	T_c	-4060.080	18.20783	-0.002426370	3.164297	0.17
R141b	243.	475.	-4388.810	18.40668	-0.001808752	5.149630	2.20
methyl chlr.	295.	371.	-4809.873	17.93429	-0.001362322	4.617096	0.02

TABULATED VALUES OF VAPOR PRESSURE, LIQUID DENSITY AND SOLUBILITY IN WATER

Properties of R125
(Parentheses indicate extrapolation of data)

Temp.	Vapor Pressure	Sat. Liq. Density	Henry's const.
(°C)	(kPa)	(kg/m³)	(kPa/Mass%)
-40.0	150.6	1484.0	
-35.0	186.9	1465.4	
-30.0	229.8	1446.3	
-25.0	280.1	1426.8	
-20.0	338.5	1406.8	
-15.0	406.0	1386.2	
-10.0	483.3	1365.0	
-5.0	571.4	1343.1	
0.0	671.2	1320.4	(242.)
5.0	783.7	1296.8	(331.)
10.0	909.8	1272.2	(448.)
15.0	1050.7	1246.4	(599.)
20.0	1207.2	1219.3	(794.)
25.0	1380.6	1190.4	1042.
30.0	1571.9	1159.6	1355.
35.0	1782.4	1126.2	1747.
40.0	2013.4	1089.7	2234.
45.0	2266.2	1048.8	2835.
50.0	2542.5	1001.8	3572.
55.0	2844.1	945.3	4469.
60.0	3173.5	870.5	(5553.)
65.0	3534.4	735.8	(6857.)
NBP:-48.6	(101.3)	(1515.2)	
T_c: 66.3	(3630.6)	(571.5)	

Properties of R22
(Parentheses indicate extrapolation of data)

Temp.	Vapor Pressure	Sat. Liq. Density	Henry's const.
(°C)	(kPa)	(kg/m³)	(kPa/Mass⁷)
-40.0	105.3	1406.5	
-35.0	132.0	1391.8	
-30.0	163.8	1376.9	
-25.0	201.2	1361.8	
-20.0	245.1	1346.4	
-15.0	295.9	1330.6	
-10.0	354.5	1314.6	
-5.0	421.6	1298.2	
0.0	498.0	1281.5	(82.)
5.0	584.3	1264.3	(122.)
10.0	681.3	1246.7	171.
15.0	789.9	1228.6	227.
20.0	910.8	1210.0	288.
25.0	1044.9	1190.7	354.
30.0	1193.1	1170.8	425.
35.0	1356.1	1150.1	498.
40.0	1534.8	1128.6	573.
45.0	1730.3	1106.0	650.
50.0	1943.4	1082.3	727.
55.0	2175.3	1057.1	805.
60.0	2427.1	1030.3	883.
65.0	2700.0	1001.3	961.
70.0	2995.4	969.7	1038.
75.0	3315.1	934.4	1114.
80.0	3660.8	893.9	(1189.)
85.0	4035.1	845.2	(1263.)
90.0	4441.6	780.6	(1336.)
95.0	4886.2	660.9	(1408.)
NBP: -40.8	101.3	(1408.9)	
T_c: 96.2	(4995.6)	(513.0)	

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ured since the publication of this work, the recommendations of the JAR were adopted here so that the limited time available for this project could be better expended on other fluids for which no such compilations exist.

The triple point and critical point values of the JAR are adopted here. The saturated-liquid densities were fit by the JAR based largely on the data of Zander (1968) to the same form used here (Equation (2)) and thus the coefficients given in Table 3 are those reported by the JAR. This correlation is valid from 204 K to the critical temperature with an RMS deviation of approximately 0.1%.

The vapor pressure data of Kletskii (1964), Kohlen (1985), and Zander (1968) were fit to Equation (1); the residuals are shown in Figure 2. The three lowest temperature (203.3-211.3 K) points of Zander and his point at 366.1 K were excluded from the fit. The high temperature point appeared to be anomalously high compared to the other data sets while the three low temperature points could not be fit without seriously affecting the correlation at higher temperatures. (In Figure 2 and all similar residual plots, points used in the correlation are shown as filled-in symbols; points excluded from the fit are shown as open symbols.)

R22 solubility data are reported by Parmelee (1953). Fourteen data points at three temperatures were measured with an estimated accuracy of 5% using a gas volumetric technique. Parmelee correlated his data to a form similar to Equation (4) and his coefficients are reported in Table 4 after the appropriate conversion of units.
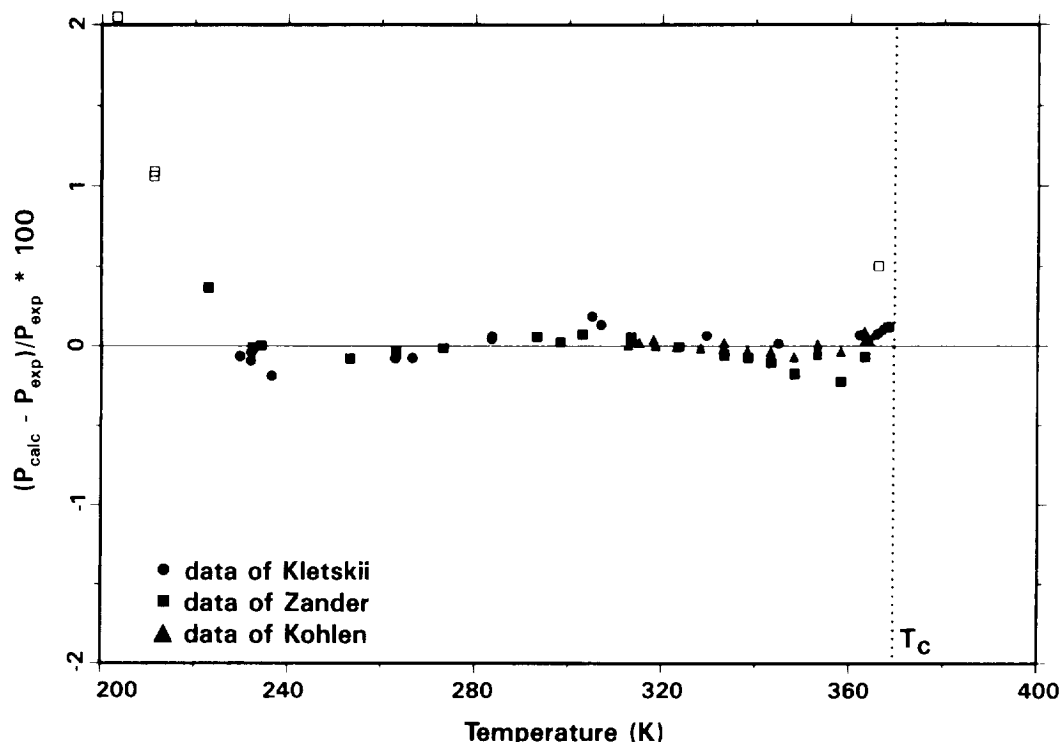

Figure 2. Comparison of vapor pressure correlation with data for R22; filled-in and open symbols indicate points used and not used, respectively, in fitting correlation.

PHYSICAL PROPERTIES

<u>R134a</u>

Refrigerant 134a (1,1,1,2-tetrafluoroethane) has been the focus of considerable attention in the fluid property community recently, and considerable data have become available. The critical point has been measured by Kabata, et al. (1988), Wilson and Basu (1988), and Morrison (1989). Morrison's determination, carried out at NIST, is adopted here, although all three sets of critical parameters are in excellent agreement. DuPont (1989) and Daikin (1989) both report freezing temperatures of 172 K.

Two reliable sources of vapor pressure data are available; together they span the temperature range from 211.0 K to within 1 K of the critical temperature. Weber (1989) measured 22 values with an estimated accuracy of 0.2 kPa. Wilson and Basu (1988) report 32 values with an accuracy of 0.7-7. kPa (depending on the pressure). As shown in Figure 3, the two data sets are in excellent agreement over the temperature range of overlap. The correlation presented here is identical with that presented in McLinden, et al. (1989). Yamashita, et al. (1988) have measured the vapor pressure of R134a at 25 temperatures from 253-371 K. Unfortunately, their paper does not give the experimental points. Saturated liquid densities have been reported by three independent groups. Wilson and Basu (1988) report nine measurements over a fairly wide range of temperature (238.9-371.6 K) using the floating bead technique. Kabata, et al. (1988) report six measurements in the vicinity of the critical point. Morrison (1989) has measured 11 values from 268.2-368.2 K with a variable-volume, mercury-displacement apparatus. These three data sets were used in fitting Equation (2); the residuals are shown in Figure 3. (Further measurements by Morrison using a vibrating tube densimeter were not available in time to include in this work.) The different data sets are in reasonable agreement, although differences of as much as 1.5% exist, especially near the critical point.

The solubility of R134a in water has been measured by DuPont (1989) at 298 and 353 K. These two points were read off their graphical presentation and used to fit the coefficients in Equation (4).

<u>R152a</u>

The primary source of data for R152a (1,1-difluoroethane) was the work of Higashi, et al. (1987). Their critical point determination is consistent with the earlier determination by Mears, et al. (1955), which is the basis of the critical parameters listed on many manufacturer's data sheets. The determination by Higashi, et al. is, however, of much higher accuracy (0.01 K for temperature, 1.0 kPa for pressure, and 2 kg/m³ for density) and is adopted here. The freezing point reported by DuPont (1989) is used here.

Higashi, et al. report 44 vapor pressure measurements from 273.1 K to within 0.4 K of the critical temperature with a precision better than 0.17%. Additional data, of lower accuracy but covering a wider temperature range (203.7 K and above), are reported by Mears, et al. The data sets of Higashi, et al. and Mears, et al. are in reasonable agreement above 290 K but diverge rapidly at lower temperatures; see Figure 4. (In Figure 4 and all similar figures, points drawn just outside the frame of the plot indicate residuals greater than the limits of the ordinate and are not to scale.) All attempts to extend the range of Equation (1) to lower temperatures by including selected low temperature points of Mears resulted in a much poorer fit at the higher temperatures. The accuracy of the data by Mears, et al. is difficult to ascertain but is probably no better than 5-10 kPa; this uncertainty would be equivalent to an error of as much as 10% at the lowest temperatures. Thus, only the vapor pressure data of Higashi, et al. were used in fitting Equation (1).
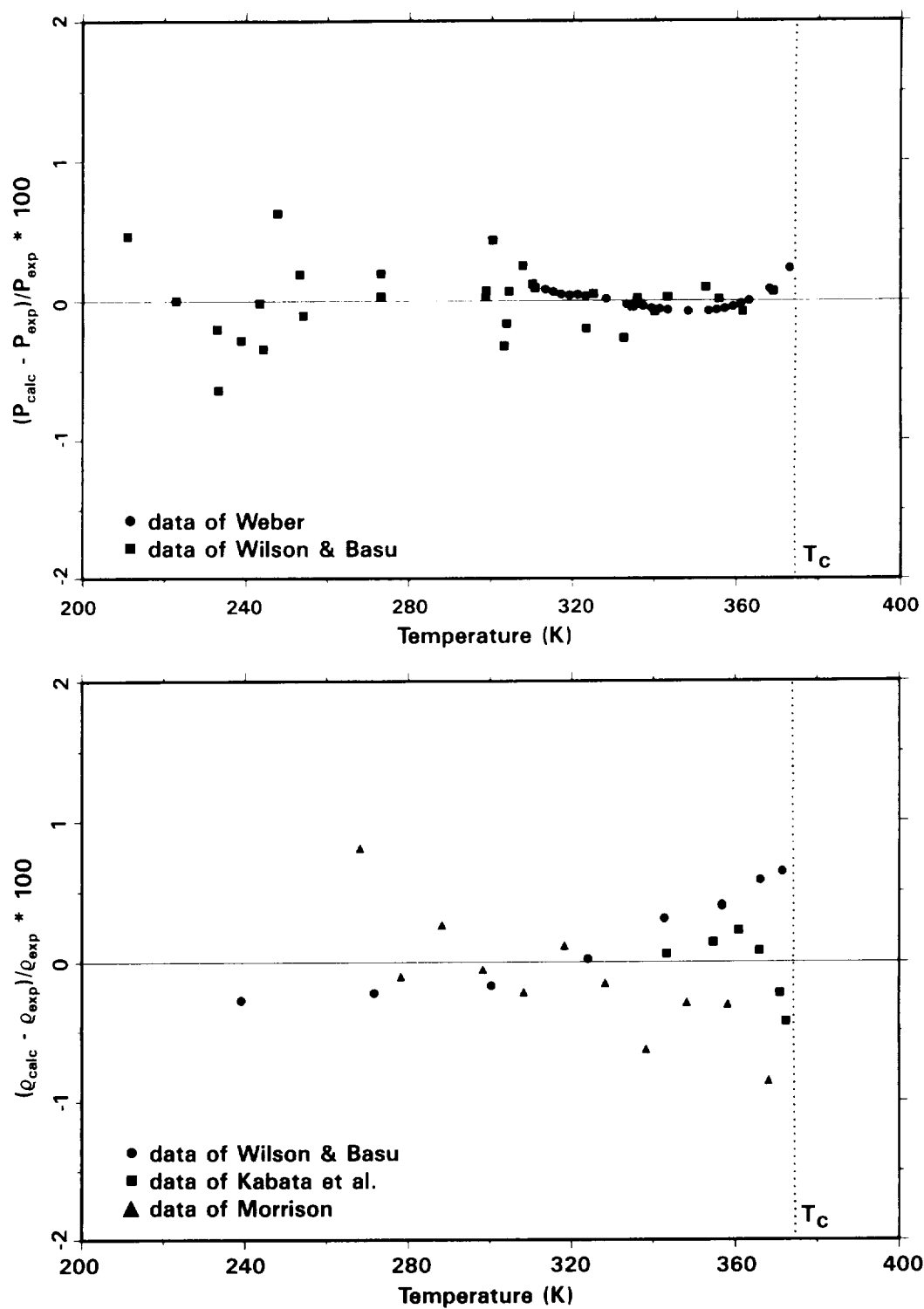
Figure 3. Comparison of correlations with data for R134a; a) vapor pressure; b) saturated liquid density.

PHYSICAL PROPERTIES

Properties of R134a
(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	51.6	(1413.5)	
-35.0	66.5	(1399.2)	
-30.0	84.7	1384.6	
-25.0	106.6	1369.8	
-20.0	132.9	1354.8	
-15.0	164.1	1339.5	
-10.0	200.7	1324.0	
-5.0	243.4	1308.2	
0.0	292.9	1292.1	(302.)
5.0	349.8	1275.7	(359.)
10.0	414.8	1258.8	(425.)
15.0	488.7	1241.5	(499.)
20.0	572.1	1223.8	(583.)
25.0	665.8	1205.5	678.
30.0	770.7	1186.7	784.
35.0	887.4	1167.1	903.
40.0	1017.0	1146.8	1035.
45.0	1160.1	1125.7	1181.
50.0	1317.8	1103.4	1342.
55.0	1491.0	1080.0	1520.
60.0	1680.7	1055.1	1714.
65.0	1888.2	1028.5	1927.
70.0	2114.6	999.6	2158.
75.0	2361.5	967.9	2409.
80.0	2630.4	932.4	(2682.)
85.0	2923.4	891.4	(2976.)
90.0	3243.1	841.7	(3293.)
95.0	3593.0	775.3	(3634.)
100.0	3979.6	650.9	(3999.)
NBP:-26.1	101.3	1373.1	
T_c: 101.1	4067.9	515.3	

Properties of R152a
(Parentheses indicate extrapolation of data)

| Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(48.0)	1043.0	
-35.0	(61.5)	1033.2	
-30.0	(77.9)	1023.1	
-25.0	(97.6)	1013.0	
-20.0	(121.2)	1002.6	
-15.0	(149.0)	992.1	
-10.0	(181.8)	981.3	
-5.0	(219.9)	970.3	
0.0	263.9	959.1	178.
5.0	314.6	947.7	207.
10.0	372.5	936.0	239.
15.0	438.2	924.0	275.
20.0	512.5	911.7	316.
25.0	596.0	899.0	360.
30.0	689.4	886.0	409.
35.0	793.4	872.6	462.
40.0	908.9	858.8	521.
45.0	1036.5	844.5	584.
50.0	1177.1	829.7	654.
55.0	1331.5	814.2	729.
60.0	1500.5	798.1	809.
65.0	1685.1	781.1	896.
70.0	1886.2	763.2	990.
75.0	2104.8	744.2	(1090.)
80.0	2342.1	723.9	(1197.)
85.0	2599.3	701.8	(1310.)
90.0	2877.9	677.5	(1432.)
95.0	3179.4	650.1	(1560.)
100.0	3505.8	618.1	(1696.)
NBP: -24.2	101.3	1011.2	
T_c: 113.3	4519.8	368.0	
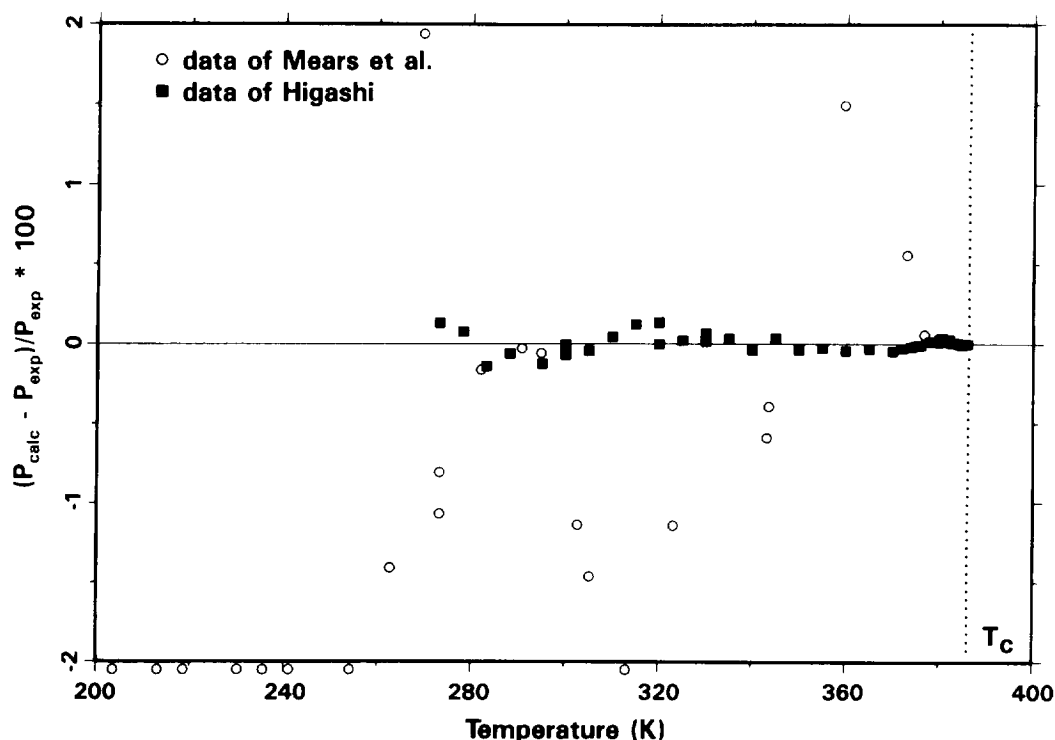
Figure 4. Comparison of vapor pressure correlation with data for R152a.

Higashi, et al. give a correlation of the saturation density based on a total of 48 measurements including their own work, the data of Mears, et al. and the 23 values of Kanome and Fujita (1986). Because of the unavailability of this last reference (published only in a thesis of Keio University), 12 densities from 220-385 K were calculated with Higashi's correlation and used as input data to fit Equation (2). The correlation of Higashi represented the experimental data with an RMS deviation of 0.21 % over the temperature range 221.0-386.4 K. The RMS deviation between Equation (2) and Higashi's correlation was 0.001 % implying that Equation (2) would also fit the data to 0.21%.

The solubility data of DuPont (1989) were again the basis of fitting the coefficients to Equation (4). They report three measurements by a technique similar to Parmalee (1953) over the temperature range 298-353 K as well as four additional measurements from unspecified other sources from 273-303 K. A single value at 294 K reported by Allied (1989) is in excellent agreement with the DuPont values.

R124

Measurements of the thermodynamic properties of R124 (1-chloro-1,2,2,2-tetrafluoroethane) have been published by Kubota, et al. (1988). Their measurements include a critical point determination which is in excellent agreement with the parameters reported by Allied (1989) and DuPont (1989). The values of Kubota, et al. are used here because of the preference for published, documented measurements over unpublished values. Again, the only information on the triple point was an undocumented value reported by DuPont.

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Although fairly comprehensive, the measurements of Kubota, et al. have two weaknesses. The first is a lower temperature limit of only 278 K. The second, more serious problem, is the fairly poor precision of the pressure measurements. An accuracy of 12 kPa is claimed for the vapor pressure measurements; this is equivalent to an error of 6% at the lowest temperature. The relative error would be smaller at higher temperatures and pressures, yet for temperatures between 300 and 350 K there are serious discrepancies between the data of Kubota, et al. and the 17 vapor pressure points reported by Allied (1989) (see Figure 5). The boiling point temperature given by DuPont (1989) is also significantly different. Because of the wider temperature range of the Allied data (222.3-389.8 K) and the good accuracy for other fluids measured by this group (e.g. Wilson and Basu 1988), only these data were used in fitting Equation (1). Further measurements on this fluid will be required to ascertain whether this was the proper choice.

For liquid density, the situation is considerably better. The three available data sources are in good agreement, as shown in Figure 5. The saturated liquid densities reported by Kubota, et al. were obtained by extrapolating compressed liquid measurements to the saturation pressure. The stated accuracy of the density measurements is 0.09% with the extrapolation adding perhaps a comparable uncertainty. The point at 323.2 K appeared to be an outlier and was excluded from the fit. Saturated liquid densities have been measured by Allied (1989) from 216-391 K using a vibrating tube densimeter. These results were available only as a correlation, and, thus, the points shown in Figure 5 have been calculated from this correlation for use in fitting Equation (2). The precision of measurements made with this type of device is very high, although the accuracy is dependent on calibration of the instrument. The two liquid density values reported by DuPont are also consistent with the other sources.

As with R125, the correlation coefficients presented by DuPont (1989) are the basis for the solubility of R124 in water. The applicable temperature range is stated as 313-348 K.

R142b

The long-standing reference for the thermodynamic properties of R142b (1-chloro-1,1-difluoroethane) has been Mears, et al. (1955); for example, the thermodynamic data of ASHRAE (1985 and 1987) are taken directly from Mears. A second source is that of Cherneeva (1958). Although the data of Cherneeva are claimed to be more accurate than those of Mears, et al., there is some reason to doubt Cherneeva's data (as discussed below) and thus the critical parameters of Mears were selected for this work. The freezing temperatures reported by DuPont (1989) and Solvay (1989) for Refrigerant 142b are consistent.

The vapor pressure data of Cherneeva and Mears, et al. are fairly consistent, although both exhibit considerable scatter as shown in Figure 6. The data of Cherneeva extended over a wider temperature range and gave a slightly better fit to Equation (1) and were thus selected over the data of Mears. A substantially improved correlation was obtained by omitting the points at 213, 218 and 284 K.

At temperatures above 320 K, the saturated liquid densities from Mears et al. and Cherneeva exhibit serious differences (see Figure 6). These differences are at least an order of magnitude larger than can be explained by the accuracies of 0.1 and 0.2% claimed by Cherneeva and Mears, respectively. A third
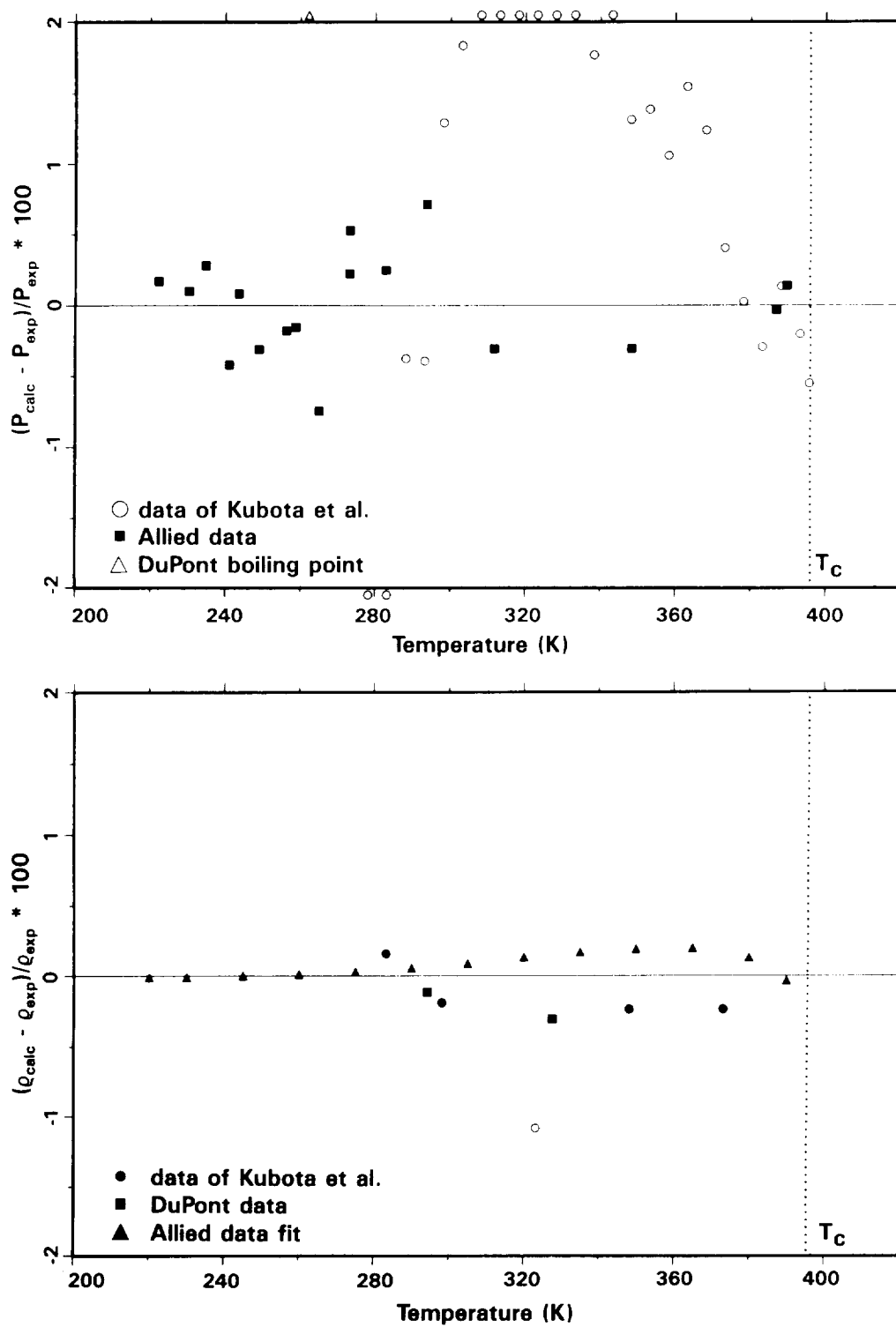
Figure 5. Comparison of correlations with data for R124; a) vapor pressure; b) saturated liquid density.

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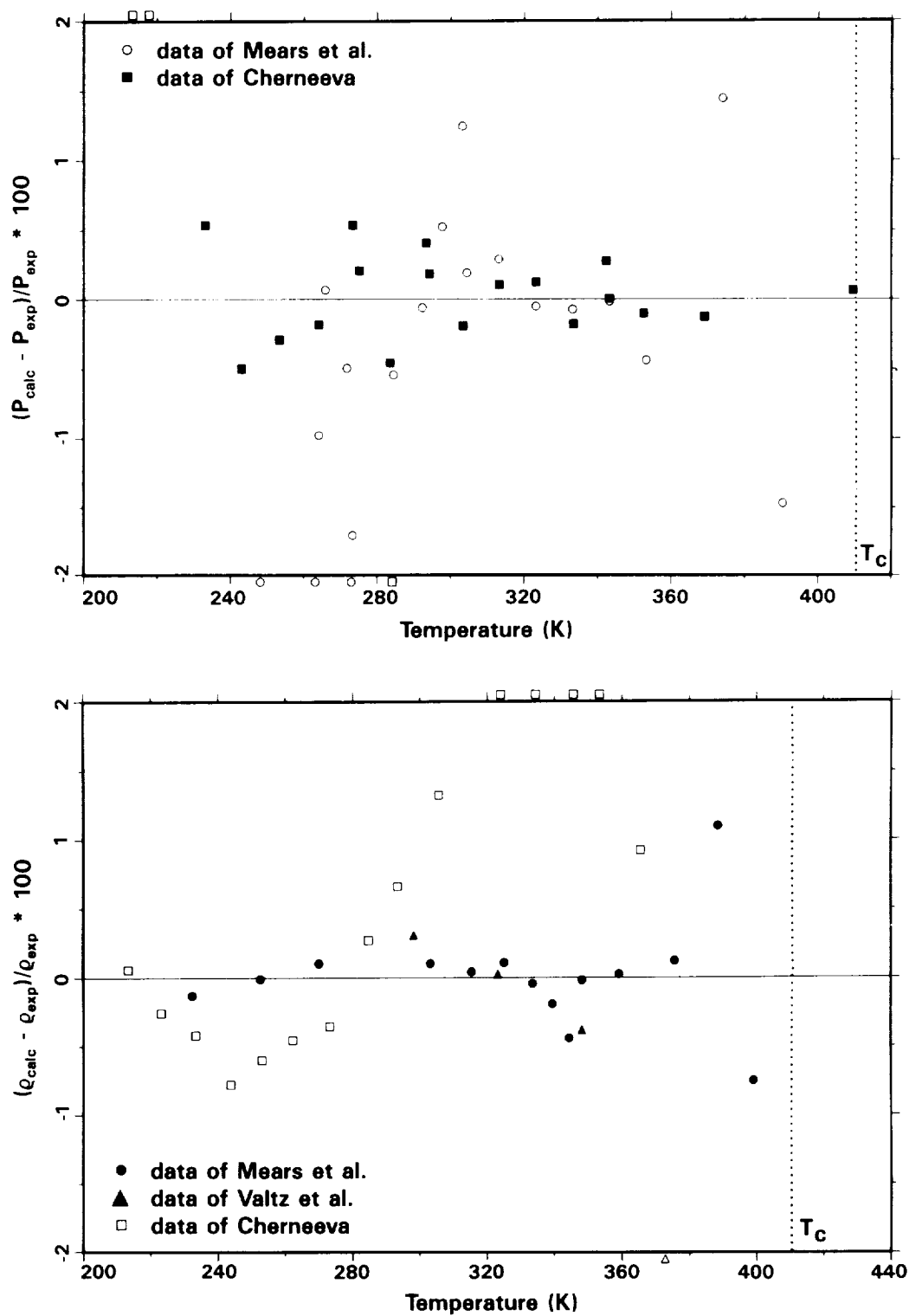**Figure 6.** Comparison of correlations with data for R142b; a) vapor pressure; b) saturated liquid density.

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Properties of R124
(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	26.6	1552.1	
-35.0	34.7	1538.3	
-30.0	44.7	1524.3	
-25.0	56.9	1510.1	
-20.0	71.6	1495.7	
-15.0	89.3	1481.1	
-10.0	110.2	1466.4	
-5.0	134.8	1451.3	
0.0	163.6	1436.1	(259.)
5.0	196.9	1420.5	(321.)
10.0	235.2	1404.7	(394.)
15.0	278.9	1388.5	(480.)
20.0	328.7	1372.1	(581.)
25.0	384.9	1355.2	(699.)
30.0	448.1	1337.9	(836.)
35.0	518.7	1320.2	(994.)
40.0	597.4	1302.0	1175.
45.0	684.5	1283.3	1381.
50.0	780.8	1263.9	1616.
55.0	886.7	1243.9	1882.
60.0	1002.7	1223.1	2181.
65.0	1129.6	1201.4	2517.
70.0	1268.0	1178.6	2893.
75.0	1418.4	1154.7	(3312.)
80.0	1581.6	1129.3	(3777.)
85.0	1758.4	1102.3	(4291.)
90.0	1949.7	1073.1	(4858.)
95.0	2156.3	1041.3	(5481.)
100.0	(2379.5)	1005.8	(6165.)
NBP:-12.0	(101.3)	1472.4	
T_c: 122.5	(3639.8)	560.0	

Properties of R142b
(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	24.2	1261.4	
-35.0	31.4	1250.6	
-30.0	40.3	1239.6	
-25.0	51.1	1228.6	
-20.0	64.1	1217.5	
-15.0	79.7	1206.2	
-10.0	98.1	1194.8	
-5.0	119.8	1183.3	
0.0	145.1	1171.6	(29.)
5.0	174.4	1159.7	(389.)
10.0	208.0	1147.7	(457.)
15.0	246.5	1135.4	(534.)
20.0	290.2	1122.8	(621.)
25.0	339.7	1110.0	719.
30.0	395.3	1096.9	827.
35.0	457.5	1083.5	948.
40.0	526.9	1069.7	1081.
45.0	603.8	1055.4	1229.
50.0	689.0	1040.7	1391.
55.0	782.8	1025.5	1568.
60.0	885.8	1009.7	1761.
65.0	998.7	993.2	1972.
70.0	1122.0	975.9	2200.
75.0	1256.4	957.8	2447.
80.0	1402.5	938.7	(2714.)
85.0	1561.1	918.4	(3001.)
90.0	1733.0	896.8	(3310.)
95.0	1919.1	873.6	(3640.)
100.0	(2120.4)	848.4	(3993.)
NBP:-9.2	(101.3)	1193.0	
T_c: 137.1	(4246.4)	435.0	

Table 3. Saturated Liquid Density

Fluid	Tem-perature limits low (K)	limits high (K)	β	d_1	d_2	d_3	d_4	RMS error (%)
					(dimensionless)			
R125	229.	T_c	1/3	1.642389	1.6539076	-1.729574	1.2250132	0.03
R22	210.	T_c	1/3	1.887739	0.5985853	-0.071134	0.4032765	0.1
R134a	239.	T_c	0.34	1.723892	1.7176130	-2.269035	1.7074390	0.38
R152a	220.	T_c	0.338	2.000849	-0.0176269	1.374012	-0.5664321	0.21
R124	220.	390.	1/3	1.723120	1.2093710	-1.189464	1.0189435	0.15
R142b	213.	365.	1/3	-0.276715	10.1472750	-13.917142	7.1135587	0.37
R123	240.	T_c	1/3	1.898571	0.2369317	0.654672	-0.0736059	0.22
R141b	263.	432.	1/3	-0.298060	9.6097677	-13.651652	7.3068081	0.09
methyl chlr.	263.	333.	1/3	8.751564	-24.2030418	28.987334	-10.7700329	

source of data (Valtz et al., 1986), although limited, is more consistent with the data of Mears, et al. There is a second, more subtle, means of deciding between conflicting data: the coefficients to Equation (2) are all of the same order of magnitude for the set of similar compounds considered here. When fit to the data of Cherneeva, however, the coefficients to Equation (2) are radically different from any other fluid considered in this report. The fit based on the data of Mears, et al. and Valtz, on the other hand, result in coefficients that are similar to those for the structurally analogous R141b (see Table 3). For these two reasons, the fit adopted here is based on the data of Mears, et al. and Valtz, et al.

For the solubility of R142b in water, Allied (1989) gives three data points over the temperature range 273-304 K; these were used in fitting Equation (4). The single datum (at 299 K) reported by Dupont (1989) is 19% higher than the solubility given by Equation (4) based on the Allied data.

R123

Refrigerant 123 (1,1-dichloro-2,2,2-trifluoroethane) is, along with R134a, one of the two most publicized new refrigerants, and, thus, property data are starting to become available. Critical parameters have been measured by Weber and Levelt-Sengers (1989), and have been reported on the data sheets of at least three chemical manufacturers (Allied, 1989; DuPont, 1989; and Daikin, 1989). The reported critical temperatures range from 456.94-459.45 K. An uncertainty involved with all R123 data is the isomeric purity of the sample. Commercial-grade R123 will likely contain a significant percentage, perhaps as much as 10%, of the isomer R123a (1,2-dichloro-1,2,2-trifluoroethane). For most of the available data there is no information on whether the measurements were conducted on isomerically pure R123 or on the R123/R123a mixture produced by the process of a particular company. The presence of a small amount of R123a will probably not affect the vapor pressure or liquid density significantly, but will likely affect the critical parameters. An isomerically pure sample of R123 was used in the critical point determination

of Weber and Levelt-Sengers at NIST (as well as all the other NIST measurements). For this reason, and others, the NIST critical parameters are recommended. A freezing temperature of 166 K is reported by both DuPont and Daikin.

Two sources for the vapor pressure of R123 were used in fitting Equation (1). Weber (1989) has measured 43 values at temperatures above 338.1 K. Allied (1989) provide 16 points extending down to 234K. Although the two data sets are consistent (see Figure 7), only Weber's data were used for the fit above 338 K because of their very high accuracy and precision. Yamashita, et al. (1988) have also measured the vapor pressure of R123 at 38 temperatures from 270 K to the critical temperature but do not present their data. Yamashita, et al. have also carried out a similar set of vapor pressure measurements for R123a. They indicate a normal boiling point of 302.7 K for R123a and 300.7 K for R123; their boiling point for R123 is 0.4 K lower than the value evaluated from Equation (2).

No less than six sets of data, measured at two laboratories using five different methods are available for the saturated liquid density of R123. At NIST, Schmidt (1988) has employed a buoyancy technique, Weber has used a constant volume cell described by Weber and Levelt-Sengers (1989), and Morrison

Table 4. Solubility in Water

Fluid	Tem-perature. low (K)	limits high (K)	Coefficients to Equation (4) h₁	h₂	h₃	Solubility @101. kPa, 25°C (mass%)	Comments
			(H in mass%/kPa, T in K)				
R125	298.	333.	-22.88	4750.	0.0	0.097	
R22	283.	353.	-8.689	205.9	-225.1	0.29	
R134a	298.	353.	-15.35	2633.	0.0	0.15	
R152a	273.	348.	-13.60	2300.	0.0	0.29	
R124	313.	348.	-17.38	3229.	0.0	0.14	(1)
R142b	298.	353.	-15.11	2544.	0.0	0.14	
R123	297.	348.	-14.06	2570.	0.0	0.40	(2,3)
R141b	298.	311.	-24.61	5248.	0.0	0.071	(2,3)
methyl chloroform	273.	323.	-20.29	4655.	0.0	0.15	(3)

Comments

(1) Solubility at 25°C is extrapolation of data.

(2) Other sources give solubilities 41% lower to 129% higher than those listed here (see Discussion section).

(3) Normal boiling point is greater than 25°C; values given at a partial pressure equal to the vapor pressure at 25°C.
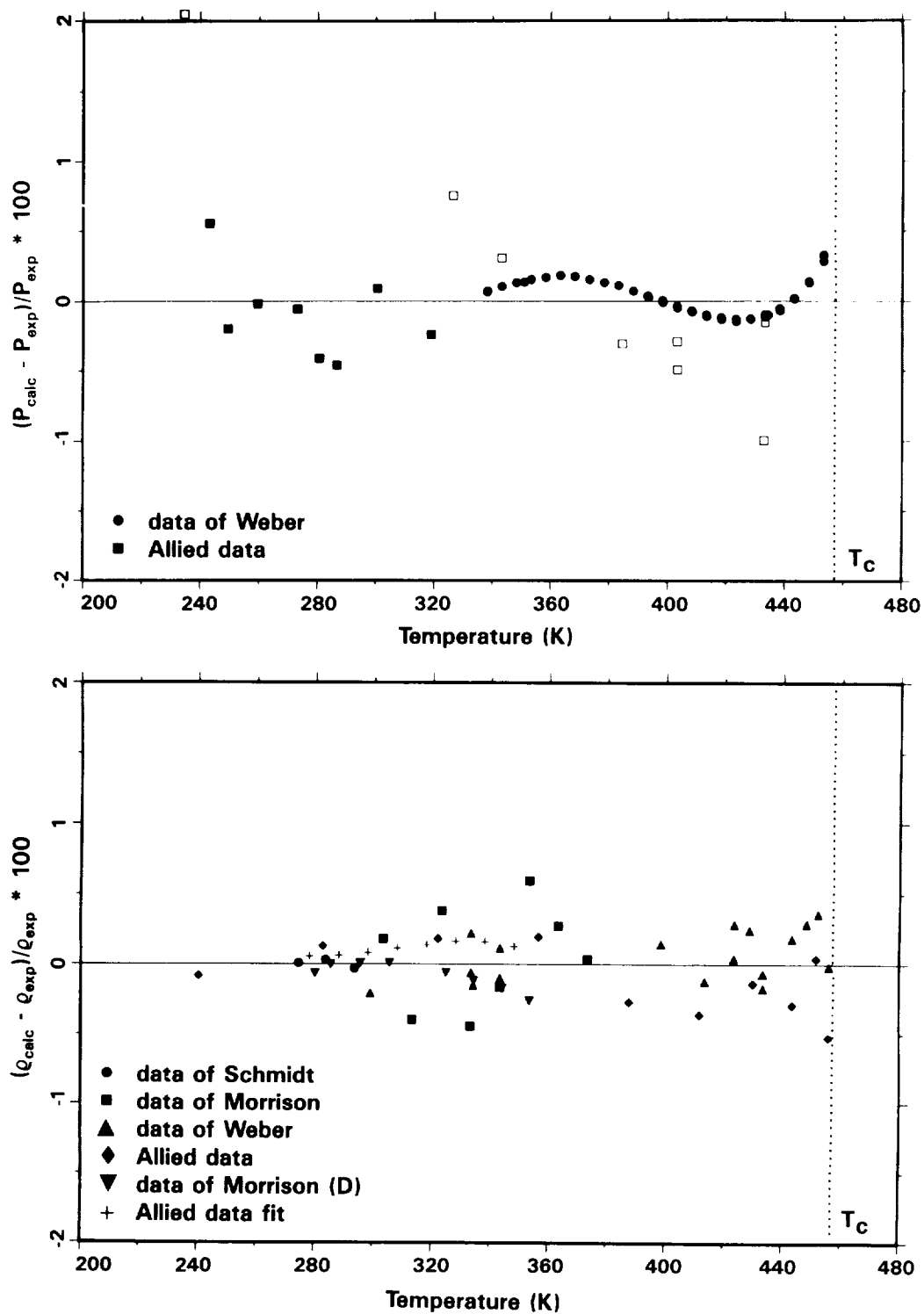
Figure 7. Comparison of correlations with data for R123; a) vapor pressure; b) saturated liquid density.

has used a mercury-displacement variable-volume cell as well as a vibrating-tube densimeter. Allied has employed their glass flotation beads and a vibrating tube densimeter; data for the latter method are available only as a correlation. All of these data were felt to be of comparable accuracy and all were included in the fit of Equation (2). As indicated in Figure 7, the different data sets are in essential agreement with an RMS deviation of 0.22%.

DuPont and Allied report solubility data. The data of DuPont cover the temperature range 297-348 K and are presented in terms of coefficients to a correlation similar to Equation (4); these coefficients are reported in Table 4 after the appropriate conversion of units. The single Allied datum at 295 K gives a solubility 41% lower than the DuPont data.

R141b

Although R141b (1,1-dichloro-1-fluoroethane) is being actively developed by several chemical manufacturers, only scattered unpublished data are available. Reported values for the critical temperature range from 480.9-483.4 K. The selection of the value of 481.5 K given by Solvay (1989) is largely arbitrary-- none of the values are documented nor are uncertainties given. The adopted critical density is based on the critical compressibility factor given by Solvay (1989). The critical pressure and estimated critical density reported by Dupont were rejected primarily because they yielded a critical compressibility factor that was felt to be unrealistically high (0.314). A freezing point of 170. K is one parameter that Daikin (1989), DuPont, and Solvay agree on.

The vapor pressure data for R141b leave much to be desired. DuPont graphically presents 21 data points from 298-480 K and also a correlation of these data.The pressures could not be accurately read off their graph, and, thus, the vapor pressure was evaluated from their correlation at the temperatures corresponding to the data points. Another correlation from Allied (1989) for the temperature range 278-338 was handled in a similar fashion. Solvay reports six points from 243-368 K. Large differences are seen (Figure 8) for the residuals of these data fit to Equation (1). (Note that the range of the ordinate in this figure is twice that of the preceding figures.) Despite the inconsistencies in these data, all were included in the fit of Equation (1) because no single set spanned the full temperature range.

For liquid density, two data sets from Allied were used in fitting Equation (2). As seen in Figure 8, the densities measured with the glass bead technique agree very well with the densimeter data (presented in terms of a correlation).

The solubility data for R141b is particularly sparse and conflicting. The two data points of Allied at 298 and 311 K were used to fit Equation (4). The single datum of DuPont at 298 K gives a solubility 129% higher than the Allied datum at the same temperature.

Methyl chloroform

The critical temperature and pressure of methyl chloroform (1,1,1-trichloroethane) were determined by Ambrose, et al. (1973). The critical temperature of 545 K is subject to some uncertainty due to decomposition of the sample at high temperatures as discussed by Ambrose, et al. The critical density has appar-
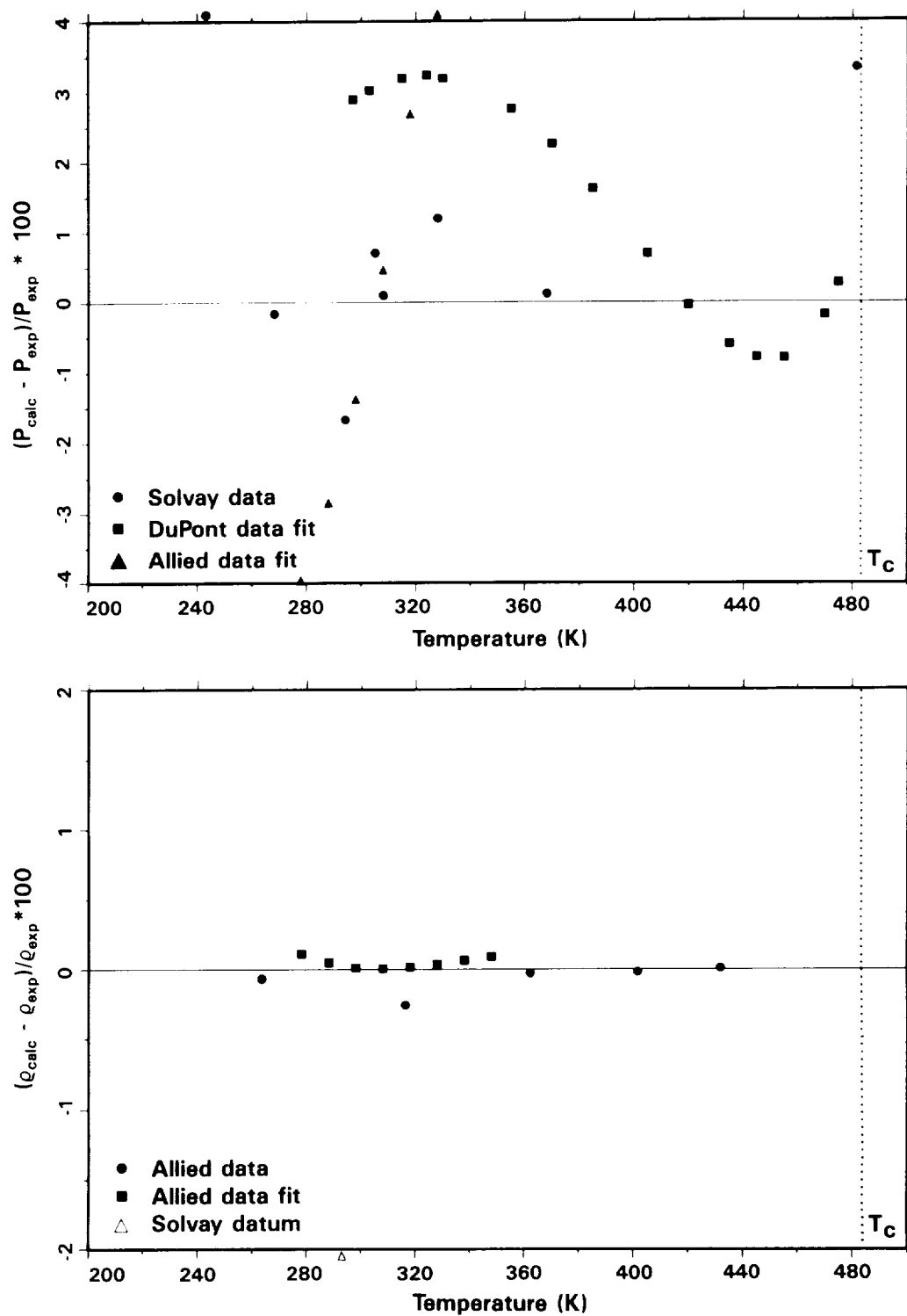
Figure 8. Comparison of correlations with data for R141b; a) vapor pressure; b) saturated liquid density.

$(P_{calc} - P_{exp})/P_{exp} * 100$

2

1

0

-1

-2

- data of Ambrose et al.
▫ tabulation of Ambrose et al.
△ data of Rubin et al.

T_c

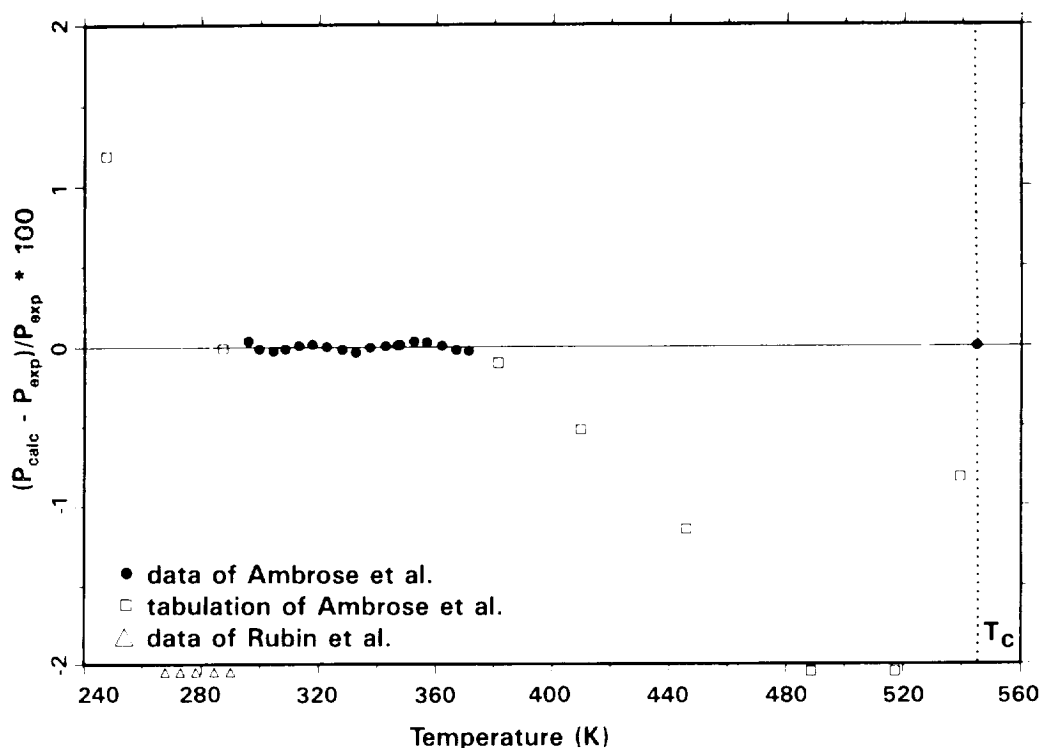240   280   320   360   400   440   480   520   560

Temperature (K)

Figure 9. Comparison of vapor pressure correlation with data for methyl chloroform.

ently not been measured and thus had to be estimated. The estimation techniques of Ambrose and the Joback modification of Lydersen's method (both as reported in Reid, et al. 1987)) yield values of 468 kg/m³ and 471 kg/m³, respectively. A value of 470 kg/m³ is used in this work. Different sources for the triple point temperature differ by as much as 3 K (Rubin, et al. 1944); the value of 243.1 K measured by Andon, et al. (1973) is selected because of the high stated accuracy and high purity sample used.

The vapor pressure of methyl chloroform was measured by Ambrose, et al. from 296-371 K. They also represent their data in terms of a Chebyshev polynomial which they state can be accurately used outside the temperature range of the data. Equation (1) fits the measured data very well but not the tabulated values obtained from the Chebyshev polynomial (Figure 9). The data of Rubin, et al. (1974) are not consistent with the data of Ambrose, et al. and were not included in the fit of Equation (1).

Liquid densities tabulated by the Thermodynamics Research Center of Texas A&M University (1986) were used in the fit of Equation (2). Although the RMS deviation between the fit and the tabulated values was 0.003%, the accuracy of the tabulation was not given, and, thus, the accuracy of the correlation presented here cannot be stated.

The correlation for the solubility in water is based on the correlation of solubility presented by Walraevens, et al. (1974). Because they do not present their solubility data, their correlation was used to generated points which were then used to fit Equation 4.

Properties of R123
(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(3.7)	(1614.5)	
-35.0	(5.1)	(1603.7)	
-30.0	6.9	1592.7	
-25.0	9.2	1581.6	
-20.0	12.2	1570.4	
-15.0	15.8	1559.1	
-10.0	20.4	1547.7	
-5.0	26.0	1536.1	
0.0	32.7	1524.4	(05.)
5.0	40.9	1512.5	(124.)
10.0	50.6	1500.5	(146.)
15.0	62.1	1488.4	(171.)
20.0	75.6	1476.0	(199.)
25.0	91.4	1463.5	230.
30.0	109.6	1450.9	266.
35.0	130.6	1438.0	305.
40.0	154.7	1424.9	348.
45.0	182.0	1411.7	396.
50.0	212.9	1398.2	449.
55.0	247.8	1384.4	507.
60.0	286.8	1370.5	570.
65.0	330.3	1356.2	639.
70.0	378.7	1341.6	714.
75.0	432.2	1326.8	(795.)
80.0	491.1	1311.6	(882.)
85.0	555.9	1296.0	(977.)
90.0	626.9	1280.1	(1078.)
95.0	704.3	1263.7	(1187.)
100.0	788.7	1246.9	(1303.)
NBP: 27.8	101.3	1456.4	
T_c: 183.8	3691.4	549.9	

Properties of R141b
(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(2.9)	(1356.3)	
-35.0	(4.0)	(1346.7)	
-30.0	5.5	(1337.1)	
-25.0	7.5	(1327.5)	
-20.0	9.9	(1317.9)	
-15.0	13.0	(1308.2)	
-10.0	16.9	1298.6	
-5.0	21.6	1288.9	
0.0	27.4	1279.2	(221.)
5.0	34.4	1269.5	(312.)
10.0	42.8	1259.8	(435.)
15.0	52.7	1250.0	(600.)
20.0	64.4	1240.1	(819.)
25.0	78.0	1230.2	1106.
30.0	93.9	1220.3	1478.
35.0	112.1	1210.2	1957.
40.0	132.9	1200.1	(2569.)
45.0	156.6	1189.9	(3343.)
50.0	183.5	1179.7	(4315.)
55.0	213.6	1169.3	(5527.)
60.0	247.4	1158.7	(7026.)
65.0	285.1	1148.1	(8868.)
70.0	326.8	1137.3	(11119.)
75.0	372.9	1126.3	(13850.)
80.0	423.7	1115.2	(17145.)
85.0	479.4	1103.8	(21098.)
90.0	540.2	1092.3	(25814.)
95.0	606.5	1080.4	(31412.)
100.0	678.5	1068.4	(38023.)
NBP: 32.1	101.3	1216.0	
T_c: 208.4	4541.0	464.1	

Properties of methyl chloroform
(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(.4)	(1435.6)	
-35.0	(.5)	(1427.5)	
-30.0	(.8)	(1419.5)	
-25.0	(1.1)	(1411.4)	
-20.0	(1.5)	(1403.3)	
-15.0	(2.0)	(1395.2)	
-10.0	(2.8)	1387.0	
-5.0	(3.7)	1378.9	
0.0	(4.9)	1370.7	26.
5.0	(6.3)	1362.6	35.
10.0	(8.2)	1354.4	47.
15.0	(1.4)	1346.2	63.
20.0	(13.2)	1338.1	82.
25.0	16.5	1329.9	107.
30.0	20.5	1321.7	139.
35.0	25.2	1313.6	178.
40.0	30.9	1305.4	227.
45.0	37.4	1297.3	287.
50.0	45.1	1289.1	(360.)
55.0	54.0	1281.0	(448.)
60.0	64.2	(1272.9)	(554.)
65.0	75.9	(1264.8)	(681.)
70.0	89.2	(1256.8)	(833.)
75.0	104.2	(1248.8)	(1012.)
80.0	121.2	(1240.8)	(1222.)
85.0	140.3	(1232.9)	(1469.)
90.0	161.5	(1224.9)	(1757.)
95.0	185.2	(1217.1)	(2092.)
100.0	(211.4)	(1209.3)	(2478.)
NBP: 74.1	(101.3)	(1250.3)	
Tc: 271.9	(4300.0)	(470.0)	

Table 5. Comparison of Solubilities Evaluated from Data with Those Estimated by Method of Irmann

Fluid	Solubility (mass%) @ 25°C (partial pres = 101.325 kPa)	
	data	estimated
R125	0.097	0.044
R22	0.29	0.31
R134a	0.15	0.13
R152a	0.29	0.29
R124	0.14	0.13
R142b	0.14	0.15
R123*	0.40	0.38
R141b*	0.071	0.39
methyl chloroform*	0.15	0.13

*Normal boiling point is greater than 25°C; values given for a partial pressure equal to the vapor pressure at 25°C.

4. CONCLUDING REMARKS

This report presents recommended values and correlations of selected physical properties of several alternatives to the fully halogenated chlorofluorocarbons. The quality of the data used in this compilation varies widely, ranging from well-documented, high accuracy measurements from published sources to completely undocumented values listed on anonymous data sheets. That some properties for some fluids are available only from the latter type of source is clearly not the desired state of affairs. While some would reject all such data, the compilation given here is presented in the spirit of laying out the present state of knowledge and making available a set of data in a timely manner, even though its quality is sometimes uncertain. The correlations presented here are certain to change quickly as additional information becomes available. Indeed, one use of this report could be to identify areas where additional work is needed.

III. REACTION RATE CONSTANTS

Evaluated Rate Constants for Selected HCFC's and HFC's with OH and $O(^1D)$

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EXECUTIVE SUMMARY

The chemistry of HCFC's and HFC's in the troposphere is controlled by reactions with OH in which a hydrogen atom is abstracted from the halocarbon to form water and a halo-alkyl radical. The halo-alkyl radical subsequently reacts with molecular oxygen to form a peroxy radical. The reactions of HCFC's and HFC's with $O(^1D)$ atoms are unimportant in the troposphere but may be important in producing active chlorine or OH in the stratosphere.

In this chapter, the rate constants for the reactions of OH and $O(^1D)$ with many HFC's and HCFC's have been evaluated. Recommendations are given for the five HCFC's and three HFC's specified by AFEAS as primary alternatives as well as for all other isomers of C_1 and C_2 HCFC's and HFC's where rate data exist. In addition, recommendations are included for CH_3CCl_3, CH_2Cl_2, and CH_4.

The format used for the presentation of the recommended rate constant data is the same as that used by the NASA Panel for Data Evaluation (see DeMore et al., JPL Publication 87-41, September 15, 1987). The rate constant tabulation is given in Arrhenius form, $k(T) = A \exp(-E/RT)$, and contains the following information:

1. Reaction stoichiometry and products (if known).
2. Arrhenius A factor (in units of cm^3 molecule^{-1} s^{-1}).
3. Temperature dependence ("activation temperature," E/R) and associated uncertainty ($\Delta E/R$).
4. Rate constant at 298 K (in units of cm^3 molecule^{-1} s^{-1}).
5. Uncertainty factor at 298 K.

All of the uncertainties are one standard deviation, 1σ. Hence, 95% confidence limits are given by 2σ. The uncertainty (1σ) at any temperature can be calculated from the expression:

$$f(T) = f(298)\exp\{\Delta E/R(1/T - 1/298)\}$$

For all of the OH reactions, the recommendations were derived from linear least squares Arrhenius fits of the selected data bases for temperatures below 400 K. This temperature restriction was made due to the observed Arrhenius curvature for several of the reactions over more extended temperature ranges. For some reactants, the necessary temperature dependent data do not exist, and the E/R values were estimated by comparison with other similar reactants and the A factor back-calculated using k_{298}. Reasonable values of E/R can be estimated from compounds appearing in a homologous series and by noting that most values of E/R for reactions of OH with halocarbons lie between 1000 and 2000 K. An alternative approach would have involved estimating, or calculating from transition state theory, the A factor and using k_{298} to obtain E/R. These two approaches yield similar results if the data are not extrapolated very far from room temperature and, thus, are nearly equivalent for the calculation of ozone depletion or greenhouse warming potentials. These two estimation procedures can result in significant differences when used for extrapolations over a wide temperature range. In addition, they can yield disparate predictions when there are no direct kinetic data for either the species of interest or for one of similar structure.

Rate constants for the $O(^1D)$ reactions are associated with actual chemical reaction (leading to chemical breakdown of the HCFC or HFC) and do not include contributions due to simple physical deactivation (quenching) of the excited oxygen atom. Temperature data do not exist for most of the $O(^1D)$ reactions and the estimated temperature independencies are taken from comparisons with the few HCFC's and CFC's for which such data do exist. The following two tables summarize the results of this evaluation.

RATE CONSTANTS

Recommended rate constants and uncertainties for reactions of OH with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A^1	$E/R \pm \Delta E/R^2$	k_{298}^1	$f(298)$
OH + CHFCl$_2$	HCFC-21	1.2(-12)	1100 ± 150	3.0(-14)	1.1
OH + CHF$_2$Cl	HCFC-22	1.2(-12)	1650 ± 150	4.7(-15)	1.1
OH + CHF$_3$	HFC-23	1.5(-12)	2650 ± 500	2.1(-16)	1.5
OH + CH$_2$Cl$_2$	30	5.8(-12)	1100 ± 250	1.4(-13)	1.2
OH + CH$_2$FCl	HCFC-31	3.0(-12)	1250 ± 200	4.5(-14)	1.15
OH + CH$_2$F$_2$	HFC-32	2.5(-12)	1650 ± 200	1.0(-14)	1.2
OH + CH$_3$F	HFC-41	5.4(-12)	1700 ± 300	1.8(-14)	1.2
OH + CH$_4$	50	2.3(-12)	1700 ± 200	7.7(-15)	1.2
OH + CHCl$_2$CF$_3$	HCFC-123	6.4(-13)	850 ± 250	3.7(-14)	1.2
OH + CHFClCF$_3$	HCFC-124	6.6(-13)	1250 ± 300	1.0(-14)	1.2
OH + CHF$_2$CF$_3$	HFC-125	8.9(-13)	1750 ± 500	2.5(-15)	2.0
OH + CH$_2$ClCF$_2$Cl	HCFC-132b	3.6(-12)	1600 ± 400	1.7(-14)	2.0
OH + CH$_2$ClCF$_3$	HCFC-133a	5.2(-13)	1100 ± 300	1.3(-14)	1.3
OH + CHF$_2$CHF$_2$	HFC-134	8.7(-13)	1500 ± 500	5.7(-15)	2.0
OH + CH$_2$FCF$_3$	HFC-134a	1.7(-12)	1750 ± 300	4.8(-15)	1.2
OH + CH$_3$CCl$_3$	140	5.0(-12)	1800 ± 300	1.2(-14)	1.3
OH + CH$_3$CFCl$_2$	HCFC-141b	4.2(-13)	1200 ± 300	7.5(-15)	1.3
OH + CH$_3$CF$_2$Cl	HCFC-142b	9.6(-13)	1650 ± 250	3.8(-15)	1.2
OH + CH$_2$FCHF$_2$	HFC-143	2.8(-12)	1500 ± 500	1.8(-14)	2.0
OH + CH$_3$CF$_3$	HFC-143a	6.0(-13)	1750 ± 500	1.7(-15)	2.0
OH + CH$_2$FCH$_2$F	HFC-152	1.7(-11)	1500 ± 500	1.1(-13)	2.0
OH + CH$_3$CHF$_2$	HFC-152a	1.5(-12)	1100 ± 200	3.7(-14)	1.1
OH + CH$_3$CH$_2$F	HFC-161	1.3(-11)	1200 ± 300	2.3(-13)	2.0

1 units are cm^3 molecule^{-1} s^{-1}
2 units are K

Recommended rate constants and uncertainties for reactions of $O(^1D)$ with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A^1	$E/R \pm \Delta E/R^2$			k_{298}^1	$f(298)$
$O(^1D)$ + $CHFCl_2$	HCFC-21	1.9(-10)	0	±	100	1.9(-10)	1.3
$O(^1D)$ + CHF_2Cl	HCFC-22	1.0(-10)	0	±	100	1.0(-10)	1.3
$O(^1D)$ + CHF_3	HFC-23	1.9(-12)	0	±	500	1.9(-12)	3.0
$O(^1D)$ + CH_2F_2	HFC-32	5.0(-11)	0	±	100	5.0(-11)	2.0
$O(^1D)$ + CH_3F	HFC-41	1.0(-10)	0	±	100	1.0(-10)	2.0
$O(^1D)$ + $CHCl_2CF_3$	HCFC-123	2.3(-10)	0	±	100	2-3(-10)	2.0
$O(^1D)$ + $CHFClCF_3$	HCFC-124	1.0(-10)	0	±	100	1.0(-10)	3.0
$O(^1D)$ + CHF_2CF_3	HFC-125	5.0(-11)	0	±	100	5.0(-11)	2.0
$O(^1D)$ + CH_2ClCF_2Cl	HCFC-132b	1.7(-10)	0	±	100	1.7(-10)	2.0
$O(^1D)$ + CH_2ClCF_3	HCFC-133a	1.6(-10)	0	±	100	1.6(-10)	2.0
$O(^1D)$ + CH_2FCF_3	HFC-134a	5.0(-11)	0	±	100	5.0(-11)	3.0
$O(^1D)$ + CH_3CFCl_2	HCFC-141b	1.5(-10)	0	±	100	1.5(-10)	3.0
$O(^1D)$ + CH_3CF_2Cl	HCFC-142b	1.4(-10)	0	±	100	1.4(-10)	2.0
$O(^1D)$ + CH_3CF_3	HFC-143a	6.0(-11)	0	±	100	6.0(-11)	2.0
$O(^1D)$ + CH_3CHF_2	HFC-152a	1.0(-10)	0	±	100	1.0(-10)	3.0

1 units are cm^3 molecule^{-1} s^{-1}
2 units are K