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EXPLICIT REPRESENTATION OF THE  
THERMODYNAMIC PROPERTIES OF REFRIGERANTS 12 AND 22  
IN THE SUPERHEAT REGION

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ABSTRACT

Algebraic relationships are presented relating temperature and pressure to specific volume, enthalpy and entropy for refrigerants 12 and 22. The equations provide for explicit representation of each variable as a function of the other two while affording accuracy unobtainable with the ideal gas approximation.

INTRODUCTION

The need for a quick and accurate means of relating the thermodynamic properties of superheated fluoromethane refrigerants is one of the first problems facing the investigator wishing to perform a comprehensive analysis of refrigeration machinery. The desirability of property relations explicit in more than a single variable has taken precedence over the need to represent accurately the thermodynamic properties of these refrigerants in previous studies. For example, the ideal gas equation of state was used by both Brunner [1] and Wambsganss and Cohen [2], despite the fact that it is in error by as much as 40% for R-22 (chlorodifluoromethane,  $\text{CHClF}_2$ ) and 25% for R-12 (dichlorodifluoromethane,  $\text{CCl}_2\text{F}_2$ ) near the saturated vapor curve.

Accurate equations relating the thermodynamic properties of these fluids have long been available [3,4]. However, all of these are explicit in but a single variable, usually pressure. Therefore, if temperature and pressure are known, an iterative procedure is required to determine the specific volume of the substance. In a computational model with a large number of such calculations, the time required to determine the various properties in this way is appreciable. In an effort to overcome this problem an investigation was undertaken to discover a relationship between the thermodynamic properties of refrigerants 12 and 22 that would improve upon the ideal gas approximation while permitting re-arrangement leading to equations explicit in pressure

temperature, specific volume, entropy, or enthalpy as required.

MATHEMATICAL REPRESENTATIONS OF PROPERTY RELATIONSHIPS

The desire for ease of mathematical manipulation supplied the starting point for this work, as it would be of little value to determine a relationship that fit the thermodynamic data precisely but was explicit in only one variable. Numerous forms were considered and tested in some detail with the following form giving the closest agreement with published data:

$$\begin{aligned}
 X = & (A_x(1, 1) + A_x(2, 1)T + A_x(3, 1)T^2)P^I \\
 & + (A_x(1, 2) + A_x(2, 2)T + A_x(3, 2)T^2)P^J \\
 & + (A_x(1, 3) + A_x(2, 3)T + A_x(3, 3)T^2)P^K \\
 & + (A_x(1, 4) + A_x(2, 4)T + A_x(3, 4)T^2)P^L
 \end{aligned} \tag{1}$$

This expression can be re-arranged to appear in the following form:

$$\begin{aligned}
 X = & (A_x(1, 1)P^I + A_x(1, 2)P^J + A_x(1, 3)P^K + A_x(1, 4)P^L) \\
 & + (A_x(2, 1)P^I + A_x(2, 2)P^J + A_x(2, 3)P^K + A_x(2, 4)P^L)T \\
 & + (A_x(3, 1)P^I + A_x(3, 2)P^J + A_x(3, 3)P^K + A_x(3, 4)P^L)T^2
 \end{aligned} \tag{1a}$$

where X can be thought of as specific volume (v), enthalpy (h) or entropy (s), with I, J, K, and L determined as follows:

$$\begin{aligned}
 I &= n \\
 J &= 1-4n^2 \\
 K &= 2-n-8n^2 \\
 L &= 3-2n-12n^2
 \end{aligned}$$

with n equal to 1/2, -1/2, 0 for X equal to v, s or h respectively. The matrix of constants denoted by  $A_x$  are presented in tables 1, 2, and 3.

Table 1

EQUATION 1 COEFFICIENTS FOR  
SPECIFIC VOLUME-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-12

	VTP(1,Q)	VTP(2,Q)	VTP(3,Q)
VTP(P,1)	-0.4969165E-03	-0.6340910E-05	0.9401889E-08
VTP(P,2)	-0.3046153E 00	0.7140947E-03	-0.4628525E-06
VTP(P,3)	-0.7414212E 00	0.1893646E-02	-0.1159975E-05
VTP(P,4)	-0.2132239E 00	0.9071642E-01	-0.2601888E-05

RANGE OF APPLICABILITY  
14.0 - 160. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

Table 2

EQUATION 1 COEFFICIENTS FOR  
ENTHALPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-12

	HTP(1,Q)	HTP(2,Q)	HTP(3,Q)
HTP(P,1)	0.3007994E 02	0.7860322E-01	0.6028411E-04
HTP(P,2)	-0.4166715E 00	0.1109862E-02	-0.7757546E-06
HTP(P,3)	0.1363164E-02	-0.4690105E-05	0.3892924E-08
HTP(P,4)	-0.4171020E-05	0.1375500E-07	-0.1119506E-10

RANGE OF APPLICABILITY  
14.0 - 160. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
SPECIFIC VOLUME-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-12

	VTP(1,Q)	VTP(2,Q)	VTP(3,Q)
VTP(P,1)	-0.14141734E-01	0.62532708E-04	-0.12851609E-07
VTP(P,2)	-0.21717529E-01	-0.14255421E-02	-0.20088435E-07
VTP(P,3)	-0.21850738E 01	0.25198213E-01	-0.34856111E-05
VTP(P,4)	0.00000000E 00	0.00000000E 00	0.00000000E 00

RANGE OF APPLICABILITY  
120. - 300. P.S.I.A.  
SAT. TEMP.-SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
ENTHALPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-12

	HTP(1,Q)	HTP(2,Q)	HTP(3,Q)
HTP(P,1)	0.40350563E 02	0.54086603E-01	0.74290859E-04
HTP(P,2)	-0.53582132E 00	0.13390812E-02	-0.85748468E-06
HTP(P,3)	0.15015422E-02	-0.42026931E-05	0.28937470E-08
HTP(P,4)	-0.28544454E-05	0.76196666E-08	-0.50661627E-11

RANGE OF APPLICABILITY  
120. - 300. P.S.I.A.  
SAT. TEMP.-SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
SPECIFIC VOLUME-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-22

	VTP(1,Q)	VTP(2,Q)	VTP(3,Q)
VTP(P,1)	-0.7789202E-02	0.1700799E-04	-0.9056337E-08
VTP(P,2)	-0.1785181E 00	0.2926419E-03	-0.1213291E-06
VTP(P,3)	-0.1746960E 01	0.5253877E-02	-0.3895423E-05
VTP(P,4)	0.1972133E 01	0.1187866E 00	0.3374420E-05

RANGE OF APPLICABILITY  
10.0 - 300. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
ENTHALPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-22

	HTP(1,Q)	HTP(2,Q)	HTP(3,Q)
HTP(P,1)	0.5632460E 02	0.7745772E-01	0.7154574E-04
HTP(P,2)	-0.3046307E 00	0.7463918E-03	-0.4870323E-06
HTP(P,3)	0.2340083E-03	-0.9443053E-06	0.8501064E-09
HTP(P,4)	-0.6022906E-06	0.1905331E-08	-0.1511901E-11

RANGE OF APPLICABILITY  
10.0 - 300. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
SPECIFIC VOLUME-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-22

	VTP(1,Q)	VTP(2,Q)	VTP(3,Q)
VTP(P,1)	-0.26638474E-01	0.74685289E-04	-0.30033220E-07
VTP(P,2)	0.41570597E 00	-0.19883476E-02	0.52991174E-06
VTP(P,3)	-0.62810335E 01	0.34308359E-01	-0.86670079E-05
VTP(P,4)	0.00000000E 00	0.00000000E 00	0.00000000E 00

RANGE OF APPLICABILITY  
250. - 540. P.S.I.A.  
SAT. TEMP.-SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
ENTHALPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-22

	HTP(1,Q)	HTP(2,Q)	HTP(3,Q)
HTP(P,1)	0.31634143E 02	0.13713106E 00	0.34915290E-04
HTP(P,2)	-0.85458472E-01	0.18048088E-03	-0.11302998E-06
HTP(P,3)	-0.40542264E-03	0.85784495E-06	-0.44784204E-09
HTP(P,4)	0.00000000E 00	0.00000000E 00	0.00000000E 00

RANGE OF APPLICABILITY  
250. - 540. P.S.I.A.  
SAT. TEMP.-SAT. TEMP + 300 DEG. F

Table 3

EQUATION 1 COEFFICIENTS FOR  
ENTROPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-12

	STP(1,Q)	STP(1,Q)	STP(3,Q)
STP(P,1)	0.1230670E 00	-0.1079542E-03	0.6754932E-07
STP(P,2)	-0.6719676E-02	0.4588917E-03	-0.1619739E-06
STP(P,3)	-0.2374717E-02	-0.4322555E-05	0.2800583E-08
STP(P,4)	-0.3076593E-03	0.8269586E-06	-0.4504050E-09

RANGE OF APPLICABILITY  
14.0 - 160. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
ENTROPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-12

	STP(1,Q)	STP(1,Q)	STP(3,Q)
STP(P,1)	0.65919218E 01	-0.16879301E-01	0.11091497E-04
STP(P,2)	-0.14717590E 01	0.42286673E-02	-0.26248030E-05
STP(P,3)	0.10725490E 00	-0.28378120E-03	0.18429886E-06
STP(P,4)	-0.30191214E-02	0.76571050E-05	-0.48582258E-08

RANGE OF APPLICABILITY  
120. - 300. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
ENTROPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-22

	STP(1,Q)	STP(2,Q)	STP(3,Q)
STP(P,1)	0.1463046E 00	0.1274049E-04	-0.5323955E-07
STP(P,2)	0.5463370E-01	0.4420192E-03	-0.1211753E-06
STP(P,3)	-0.2690976E-02	-0.2790766E-05	0.2602275E-10
STP(P,4)	-0.3776649E-03	0.9079179E-06	-0.4415235E-09

RANGE OF APPLICABILITY  
10.0 - 300. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

EQUATION 1 COEFFICIENTS FOR  
ENTROPY-TEMPERATURE-PRESSURE RELATIONSHIP  
FREON-22

	STP(1,Q)	STP(2,Q)	STP(3,Q)
STP(P,1)	-0.86277370E 01	0.19117731E-01	-0.10068391E-04
STP(P,2)	0.12006218E 01	-0.20837108E-02	0.11999484E-05
STP(P,3)	-0.46143703E-01	0.95076611E-04	-0.50525045E-07
STP(P,4)	0.00000000E 00	0.00000000E 00	0.00000000E 00

RANGE OF APPLICABILITY  
250. - 540. P.S.I.A.  
SAT. TEMP. - SAT. TEMP + 300 DEG. F

The versatility of equation (1) is worthy of note. Defining  $C_m(T)$  and  $D_m(P)$  as follows.

$$C_m(T) = A_x(1, m) + A_x(2, m)T + A_x(3, m)T^2$$

$$D_m(P) = A_x(m, 1)P^1 + A_x(m, 2)P^2 + A_x(m, 3)P^3 + A_x(m, 4)P^4$$

equations (1) and (1a) can be written in the following form:

$$X = C_1(T)P^1 + C_2(T)P^2 + C_3(T)P^3 + C_4(T)P^4 \quad (2)$$

$$X = D_1(P) + D_2(P)T + D_3(P)T^2 \quad (2a)$$

From the examination of equation (2a), it is recognized that equation (1) reduces to a quadratic in T provided that X and P are known. Thus, using the quadratic formula two values of temperature, T1 and T2, can be determined which satisfy equation (2a).

The task of determining which of these roots, T1 or T2, is preferred would not be necessary if the property relationship given by (1) were explicit in both X and T. However, for the purposes of a computational model where a continuous system is modeled by considering a number of very small discrete increments, the additional complexity is insignificant due to the fact that only very small changes in thermodynamic properties occur. Thus, if T is known at State 1 and we wish to use equation (2a) to determine its value at State 2 (knowing X and P at State 2), the desired quantity will be the value of T1 or T2 nearest in magnitude to T.

Examination of the form of equation (2) suggests little without evaluating the values of I, J, K, and L for X equal to v, s, and h. However, for X

X	I	J	K	L
v	1/2	0	-1/2	-1
s	-1/2	0	1/2	1
h	0	1	2	3

equal to v and s, equation (2) assumes the form of a cubic equation in terms of  $p^{1/2}$  and for X equal to h, it reduces to a cubic equation in terms of P. The three roots of a cubic equation can be determined directly similar to the case for a quadratic equation. The selection of the correct root from among the three can be handled in the manner described above.

Thus, it can be concluded that while equation (1) is explicit only in X, given T and P, it can be used to produce a single value of T, given X and P, or of P, given X and T, where it is known a priori that the next value of the desired property will be close to its last value.

It is of course, impossible to prove that equation (1) or any other form is the best equation for the job. However, considerable time was spent in checking other property relationships. Multiplying the powers of P in equation (1) by  $P^{-3/2}$ ,  $P^{-1}$ ,  $P^{-1/2}$ ,  $P^{1/2}$ , P, and  $P^{3/2}$  gave results with larger standard deviations. Similarly, it was not possible to improve the approximation by introducing higher powers of T or shifting the equation by the introduction of a multiplier of the form  $T^n$ . Thus, the only justification for equation (1) lies in the fact that it was found to correlate well with the published thermodynamic data for R-12 and R-22 while having the proper form to permit the mathematical manipulations necessary in a computational model.

The property relationships are such that the greatest error occurs at saturated vapor conditions and high pressure. The equations are most accurate at low pressures and temperatures far removed from saturation. The error is at least a factor of 10 less than the ideal gas prediction throughout the superheat region.

#### CONCLUDING REMARKS

Equation (1) was developed for use in a digital computer simulation of the cyclic behavior of a reciprocating refrigeration compressor [5]. A summary of the coefficients for the low pressure ranges only, together with tables of maximum percentage error, was presented by Gatecliff and Lady in an earlier paper [6]. The additional coefficients presented here double the range of pressures over which the equations are usable. The computer must be programmed to choose the applicable set of coefficients as a function of pressure.

These equations have been used extensively for several years and have never failed to produce rapid and accurate results. Several partial differentials derived from these equations have also been used in the mathematical simulation of compressors and the results have been equally valid. In addition, the specific volume form of equation (1) has been used to yield a concise expression for the speed of sound, the results of which agree well with published data. In summary, the explicit representations of the thermodynamic properties of R-12 and R-22 given here do the job for their intended purpose.

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