
COMPUTER BASED THERMODYNAMIC PROPERTIES OF ALTERNATIVE REFRIGERANT R-134A

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Abstract: Depletion of ozone layer in the stratosphere and global warming caused due to the use of different CFC and HCFC refrigerants have forced for the search of alternative refrigerants. R-134a is found to be a suitable alternative to CFC R-12 having similar thermodynamic properties. For the basic as well as complex cycle calculations, the accurate determination of the thermodynamic properties is essential. Keeping this in mind, this paper aims to formulate different thermodynamic properties of refrigerant R-134a using four basic equations, namely liquid density, vapour pressure at saturation, equation of state and constant volume specific heat available in the literature. Those above-said four equations are combined with basic thermodynamic equations and Maxwell's relationships to calculate enthalpy and entropy for vapour state. Clapeyron-Clausius equation for a single component system has been used to evaluate latent heat of vaporization. The virial coefficient type of equation of state is solved using binary search method. Other equations are solved and a FORTRAN code has been developed. The program accepts temperature as input and calculates different saturated thermodynamic properties, i.e., specific volume, enthalpy, entropy etc. in the temperature range of -80°C to $+80^{\circ}\text{C}$. It is observed that the data predicted from the present formulation are within the acceptable limit for all practical purposes.

Keywords: alternative refrigerant, R-134a, thermodynamic properties, enthalpy, entropy

Introduction: A refrigerant is a substance used as the working substance in a refrigeration cycle to get cooling effect in the evaporator. The halogen derivatives of hydrocarbon discovered by Midgley were used as excellent refrigerants having favorable thermodynamic properties. With the discovery of ozone hole in the stratosphere as stated first by Molina and Rowland [1] and the subsequent protocols, the hydro-chlorofluorocarbon (HCFC) and chlorofluorocarbons (CFC) are to be phased out. Other common refrigerants used in various applications are ammonia, sulfur dioxide, and non-halogenated hydrocarbons such as propane. The primary global environmental impacts from air conditioning and refrigeration systems occur due to emissions of halogenated refrigerants and of gases associated with energy use. Those gases usually are released at the power plants, chillers, cold storages. In this context most of the developed countries reduced the production and consumption of halogenated refrigerants, which demands for suitable alternatives. The discovery of the ozone-depleting properties of CFCs and HCFCs refrigerants, and of their global warming potential, led to the Montreal Protocol (1987) and the London (1990) and Copenhagen amendments (1992), which scheduled the end of production of CFCs by the end of 1995 and of HCFCs by 2030 [2]. Hence HC and HFC based refrigerants with zero ODP and low GWP are considered to be long-term alternatives. Although the ozone-depletion potential (ODP) of some HFCs is zero, their global warming potential (GWP) related to the greenhouse effect-can be large. On the other

hand, HC refrigerants have a flammability issue, which restricts the usage in existing systems. However the flammability issue can be avoided by blending HC refrigerants with HFC refrigerants. The solubility of HC/HFC mixtures with mineral oil has been found to be good. The GWP of HC/HFC mixtures is less than one third of HFC, when it is used alone. The refrigerant R-134a has similar thermodynamic properties (as shown in table 1) as that of R-12 and also has zero ODP (table 2). This fact encouraged scientists to replace R-12 by R-134a on a short term basis. This also have motivated the authors to formulate and develop a computer code for the accurate determination of the thermodynamic properties of R-134a needed for the analysis of simple as well as complex refrigeration cycles.

Mathematical formulation: Downing [4] developed equations for four basic properties of refrigerants based on the work of Professor Martin at the University of Michigan. The equations related to liquid density, vapour pressure at saturation, equation of state and constant volume specific heat of vapour at zero pressure. A complete review of correlations and equations used in calculating thermodynamic properties of Freon refrigerants was published by Martin [5]. Later Schofield [6] restated the thermodynamic relationships and listed the results of some computer calculations for various refrigeration cycles. Kartsounes and Earth [7] published a complete computer program for calculating properties of refrigerants R-12, R-22 and R-502. Hewitt et al. [8] provided the engineering data for the most common of the new refrigerants (R-134a,

TABLE 1: Properties of Refrigerants [3]

Refrigerant	Molecular (wt)	Critical temperature (°C)	Boiling Point (°C)
R134a	102.03	101.1	-26.5
R152a	66.05	113.3	-24
R600a	58.12	134.7	-11.6
R600	58.12	152	-0.5
R290	44.1	96.7	-42.1
R717	17.03	132.3	-33.3
R744	44.01	31.1	-78.4
R507	98.9	70.9	-47.1
R12	120.93	112	-29.79
R22	86.47	96.2	-40.8
R11	137.37	23.7	198
R143A	84.04	-47.3	72.9
R718	18.02	100	373

R-125, R-32, R-124 and R-143a) that can replace

TABLE 2: Refrigerants and their ODP and GWP values [3]

Refrigerant	R-12 (CFC)	R-22 HCFC	R-134a (HFC)	R-717 (NH ₃)	R-744 (CO ₂)	R-290 propane	R-600 (butane)	R-718 (H ₂ O)	R-728 (air)
ODP	0.9	0.05	0	0	0	0	0	0	0
GWP	3	0.34	0.29	0	0	<0.03	<0.03	0	0

Vapour Pressure at Saturation: The saturated vapour pressure is expressed as function of saturation temperature and expressed in terms of different constants like P₁, P₂, and P₃ etc. The equation is written as

$$\ln P_s = P_1 + \frac{P_2}{T_s} + P_3 T_s + P_4 T_s^2 + \frac{P_5(P_6 - T_s)}{T_s} \ln(P_6 - T_s) \quad (2)$$

Where P_s is in kPa, and the constants are

P₁= 24.803398, P₂= -0.398048 × 10⁴,
 P₃= -0.2405332 × 10⁻¹, P₄= 0.224521 × 10⁻⁴,
 P₅= 0.1995548, P₆= 0.3748473 × 10³

Equation of State: The equation of state plays a very important role to predict the thermodynamic properties accurately. A13-constant virial coefficient type Martin - Hou equation of state is considered here and is written as

$$P = \frac{RT}{(v-b)} + \frac{E_1 + E_2 T + E_3 e^{-kT_r}}{(v-b)^2}$$

chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) in refrigeration and air-conditioning systems using the Martin-Hou equation of state.

Wilson and Basu [9] presented those four equations as given by Downing for R-134a. In the present work, these equations have been used as the basic equations. The equations are as follows:

Liquid Density: The equation for liquid density of the refrigerant is given in terms of saturation temperature, critical temperature and different constants like D₁, D₂, D₃ etc., as

$$\rho_c = \rho_L + \sum_{N=1}^4 D_N (1 - T_r)^{N/3} \quad (1)$$

Where ρ_L is in kg/m³, T_r is the ratio of saturation temperature and critical temperature and the constants are:

D₁= 81906183, D₂= 1023.582,

D₃= -1156.757, D₄= 789.7191

The temperature and the critical temperature both are expressed in absolute scale of temperature.

$$\begin{aligned} & + \frac{E_4 + E_5 T + E_6 e^{-kT_r}}{(v-b)^3} + \frac{E_7}{(v-b)^4} \\ & + \frac{E_8 + E_9 T + E_{10} e^{-kT_r}}{(v-b)^5} \\ \therefore P = & \frac{RT}{(v-b)} + \sum_{i=2}^5 \frac{A_i + B_i T + C_i e^{-kT_r}}{(v-b)^i} \end{aligned} \quad (3)$$

Where

$$T_r = T / T_c \quad (4)$$

P is in kPa, v is in m³/kg, and the constants are:

b= 0.3455467 × 10⁻³, k= 5.475,
 E₁= -0.1198051, E₂= 0.1137590 × 10⁻³,
 E₃= 3.531592, E₄= 0.1447797 × 10⁻³,
 E₅= -0.894255 × 10⁻⁷, E₆= 0.6469248 × 10⁻², E₇= -1.049005 × 10⁻⁷,
 E₈= -6.953904 × 10⁻¹², E₉= 1.269806 × 10⁻¹³, E₁₀= 2.051369 × 10⁻⁹, R= 0.081488162 kJ/kg. K

Where P is the pressure, v is specific volume, T is absolute temperature, T_c is critical temperature, and b, k, E₁, E₂, and E₃ etc. are constants for particular refrigerant R-134a.

Constant Volume Specific Heat of Vapour at Zero

Pressure: The specific heat at constant volume of the refrigerant in vapour phase is expressed as a polynomial function of absolute temperature with different coefficients like C_{p1} , C_{p2} and C_{p3} etc. which are constant for the particular refrigerant R-134a. This is given by the following equation.

$$C_p^0 = C_{p1} + C_{p2} T + C_{p3} T^2 + C_{p4} T^3 + \frac{C_{p5}}{T} \tag{5}$$

Here C_p^0 is in kJ/kg. K and the constants are:

$$C_{p1} = -0.5257455 \times 10^{-2},$$

$$C_{p2} = 0.3296570 \times 10^{-2},$$

$$C_{p3} = -2.017321 \times 10^{-6},$$

$$C_{p4} = 0.0, \quad C_{p5} = 15.82170$$

Derivation of Enthalpy: Now from the equation of state (equation 3) we obtain

$$\left[\frac{dP}{dT} \right]_p = \frac{R}{(v-b)} + \frac{E_2 - E_3 k e^{-kT_r} / T_c}{(v-b)^2} + \frac{E_5 - E_6 k e^{-kT_r} / T_c}{(v-b)^3} + \frac{E_9 - E_{10} k e^{-kT_r} / T_c}{(v-b)^5} \tag{6}$$

Substituting from above, we obtain the expression for vapour phase enthalpy. For a given reference temperature and pressure (T_0 , P_0), the enthalpy at any temperature T and pressure P is obtained by integrating the above equations between the reference state and the given state as

$$h = h_0 + \int_{T_0}^T (C_p^0 - R) dT + \sum_{i=2}^5 \left[\frac{A_i}{(i-1)(v-b)^{(i-1)}} \right] + \sum_{i=2}^5 \left[\frac{C_i e^{-kT_r} (1 + kT_r)}{(i-1)(v-b)^{(i-1)}} \right] + (Pv - RT_0) \tag{7}$$

The first term (specific heat integral term) on the right hand side of the above equation is evaluated using expression as for C_p^0 .

$$h = h_0 + C_{p1} (T - T_{ref}) + C_{p2} (T^2 - T_{ref}^2) / 2 + C_{p3} (T^3 - T_{ref}^3) / 3 + C_{p4} (T^4 - T_{ref}^4) / 4 + C_{p5} \ln(T / T_{ref}) - R (T - T_{ref}) + \sum_{i=2}^5 \left[\frac{A_i}{(i-1)(v-b)^{(i-1)}} \right] + \sum_{i=2}^5 \left[\frac{C_i e^{-kT_r} (1 + kT_r)}{(i-1)(v-b)^{(i-1)}} \right] + (Pv - RT_0) \tag{8}$$

Derivation of Entropy: In a similar manner, the expression for vapour phase entropy at given temperature T and pressure P with specified reference condition is then given by vapour phase entropy we obtain is

$$s = s_0 + \int_{T_0}^T \frac{C_p^0 dT}{T} - R \ln \left[\frac{RT}{P_0(v-b)} \right] + \sum_{i=2}^5 \left[\frac{B_i}{(i-1)(v-b)^{(i-1)}} \right] + \sum_{i=2}^5 \left[\frac{C_i (k/T_c) e^{-kT_r}}{(i-1)(v-b)^{(i-1)}} \right] \tag{9}$$

The above equation can be re-written as

$$s = s_0 + C_{p1} \ln(T / T_{ref}) + C_{p2} (T - T_{ref}) + C_{p3} (T^2 - T_{ref}^2) / 2 + C_{p4} (T^3 - T_{ref}^3) / 3 + C_{p5} (T - T_{ref}) / T \times T_{ref} - R \ln \left[\frac{RT}{P_0(v-b)} \right] + \sum_{i=2}^5 \left[\frac{B_i}{(i-1)(v-b)^{(i-1)}} \right] + \sum_{i=2}^5 \left[\frac{C_i (k/T_c) e^{-kT_r}}{(i-1)(v-b)^{(i-1)}} \right] \tag{10}$$

To specify the thermodynamic state of a single component pure substance, generally two independent properties like pressure, volume, temperature are required. But when it is either saturated liquid or saturated vapour, one property is sufficient to identify the state. So, for saturated state, temperature alone is required and for the superheated or sub cooled zone, degree of superheat or sub-cool is also required as the case may be. For saturated liquid or saturated vapour, the pressure (P_{sat}) is first calculated using equation for saturated pressure.

Latent Heat of Vaporization: From Clausius-Clapeyron equation for a single component system, we get

$$\left(\frac{dP}{dT} \right)_{sat} = \frac{H_{fg}}{T(V_g - V_f)} \tag{11}$$

The saturated vapour specific volume V_g is obtained from the numerical solution of the equation of state described in the later section. The saturated liquid specific volume V_f is determined by the equation for

saturated liquid density. The differential term $\frac{dP}{dT}$ is

obtained from the vapor pressure equation.

Saturated Liquid Enthalpy and Entropy: For a given temperature T , the saturated vapour enthalpy and entropy are obtained from the equations described already for enthalpy and entropy

respectively. The liquid enthalpy and entropy can be calculated as

$$H_f = H_g - H_{fg} \text{ And} \quad (12)$$

$$S_f = S_g - H_{fg}/T$$

Solution methodology: These four basic equations can be combined by exact thermodynamic relationships to calculate different properties required in refrigeration system design. Chan and Haselden [10] outlined the procedure for the solution of these equations and provided a set of subroutines also.

Since the equation of state considered here is explicit in pressure but not in specific volume or temperature, it has to be solved iteratively if the volume is unknown. Thus the specific volume values required in enthalpy and entropy calculations can only be obtained by numerical methods. Two approaches may be considered, one is the binary search method and the other is Newton-Raphson method. Both the methods iterate in pressure. In the Newton-Raphson method, the new estimate is given by

$$V_{est(new)} = V_{est(old)} + (P - P') / \frac{dP}{dV} \quad (13)$$

In the binary search method, the new estimate is obtained by adding a positive or negative increment, depending on the approach to convergence to the old

value. When the desired value is within the range of the increment, the increment is halved successively until the tolerance is met.

At temperature between -50°C to 20°C, the Newton-Raphson method is faster. But when the temperature is more than this it requires greater number of iterations and its performance deteriorates. The binary search method is stable and has proved robust under all conditions. Therefore, this method is adopted for the present work throughout the whole temperature domain of interest. Initial estimation of volume for a specified temperature and pressure is

$$\text{obtained from the ideal gas equation as } V = \frac{RT}{P}.$$

When the difference in pressure between two successive iterations becomes less than 0.0001 bars, the solution is assumed to be converged. The flow chart for the solution has been shown in the figure 1.

Based on this a computer code in FORTRAN having nine subroutines has been developed to get the thermodynamic properties of refrigerant R-134 for saturated as well as superheated vapour.

It may be noted that for this work, ASHRAE reference conditions have been used for the calculation of enthalpies and entropies of refrigerants. ASHRAE used 0°C as the reference temperature and stipulated that the saturated liquid enthalpy and the saturated liquid entropy at this temperature equal to 200 kJ/kg and 1 kJ/kg-K respectively.

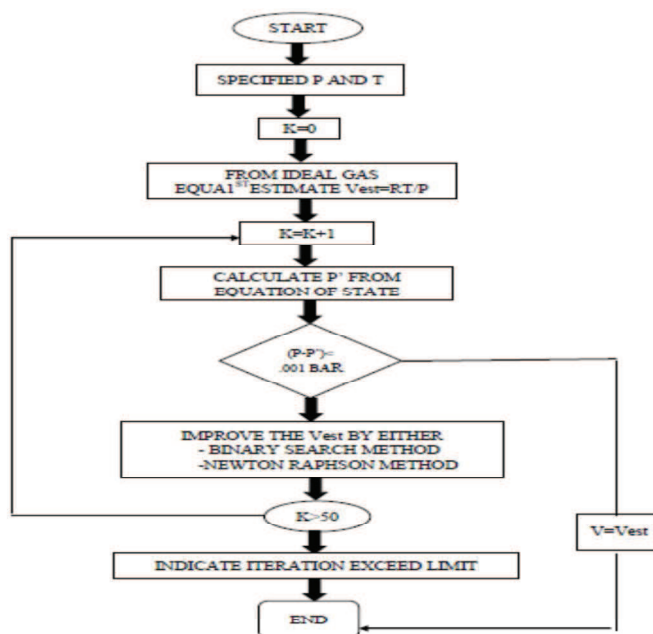


Fig. 1. Flow Chart of the Computer Program.

Results and discussion: The code is run to get the values of saturated thermodynamic properties of R-

134a. Output results of different properties are compared with the values given in ASHRAE

handbook [11]. Although the present values are not exactly matching with the hand book values, rather there are some differences. However, the errors are acceptable for quick and repeated calculations particularly for the normal operating temperature range. The error in enthalpy, entropy and other properties are calculated using the following expression:

$$\%error = \left| \frac{\text{Calculated Value} - \text{ASHRAE handbook data}}{\text{ASHRAE handbook data}} \right|$$

The deviation of the property values from the ASHRAE values can also be easily visualized from the figures presented after this. Fig 2 shows the variation of saturation pressure of the refrigerant with the increase in normal temperature within the operating temperature range. It shows a little difference in saturation pressure value from the ASHRAE value. It is also observed that the trend of curve of saturation pressure is almost same as the ASHRAE curve. The maximum error in the saturation pressure is found to be 1.823%.

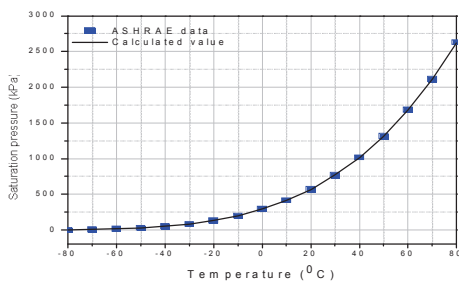


Fig. 2. Comparison graph of Saturation pressure Values with ASHRAE handbook data for R-134a

Fig. 3 represents the effect of increasing temperature on saturated liquid density within the operating temperature range from -80°C to 80°C. It shows similar trend of curve of saturation liquid density as ASHRAE data. It is observed that with the increase in temperature the saturated liquid density decreases. Error calculation is done with respect to ASHRAE value and the maximum percentage of error is found to be 0.341%. The variation of saturated vapour volume with temperatures has been shown in Fig. 4. It also shows similar curve of saturated vapour volume curve as ASHRAE presented. Curve shows that with the increase of temperature saturated vapour volume initially decreases in a rapid rate after some time it decreases at a slower rate. The maximum error is found to be more in this case and its value is approximately 4.62%.

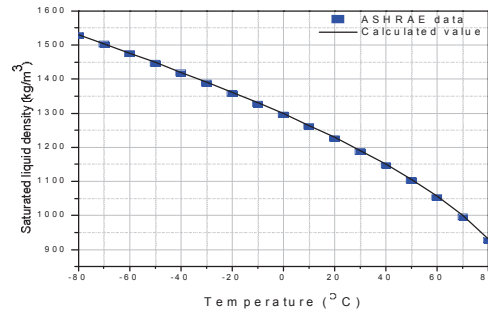


Fig. 3. Comparison of calculated values of saturated liquid density with ASHRAE data

Fig. 5 and Fig. 6 present the effect of increasing temperature on saturated enthalpy for liquid and vapour respectively within the operating temperature range. It shows that with the increase in temperature both saturated liquid enthalpy and saturated vapour enthalpy increase. The variations also follow the same trend of property values given by ASHRAE. Maximum error for saturated liquid enthalpy and saturated vapour enthalpy are found to be 4.851% and 3.83% respectively.

In a similar way, the entropy values for saturated liquid and saturated vapour have been compared and present in figures 7 and 8 respectively. The maximum errors are calculated for the above two properties and are found to be 5.32% and 1.34% respectively. In comparison to data base refrigerant property code, this method is not so good as far as maximum error is concerned. But it will take less computer access time than the data base system. Even fitting polynomials to the accurate data of refrigerant property tables will carry less error. But the problem with this is that different sets of polynomials have to be fitted at different pressure and temperature zones.

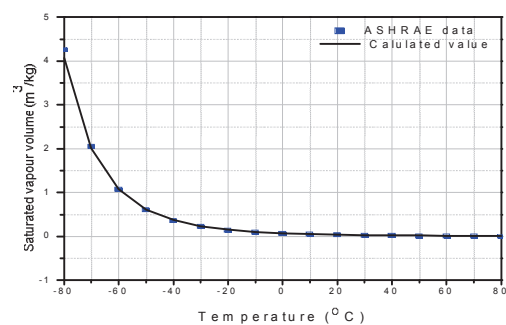


Fig. 4. Comparison of calculated values of saturated vapour volume with ASHRAE data

Conclusion: This work presents a procedure for the evaluation of the thermodynamic properties of refrigerants R-134a which has replaced R-12 in the refrigeration industries. Accordingly, a FORTRAN code has been developed and the output has been compared with the thermodynamic property values

given in ASHRAE handbook. The computed values from the code are close to the actual values, although there are some differences in some of the properties. The error is relative less in case of saturated pressure

and specific volume and more in case of liquid enthalpy and liquid entropy. This code can be used as subroutine for the analysis of any R-134a based refrigeration system.

Fig. 5. Comparison of calculated values of saturated liquid enthalpy with ASHRAE data

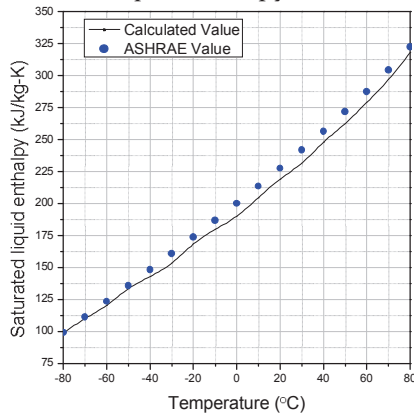


Fig. 6. Comparison of calculated values of saturated vapour enthalpy with ASHRAE data

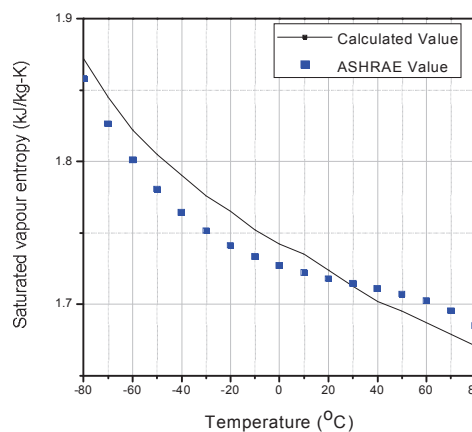
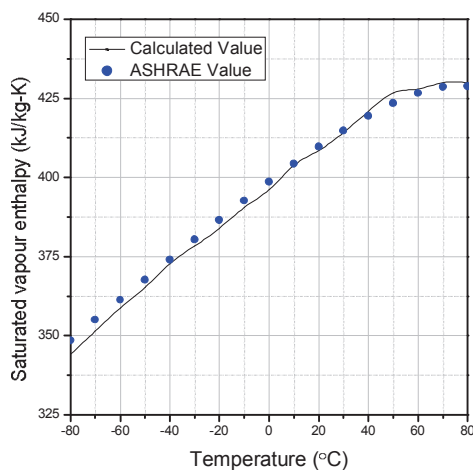
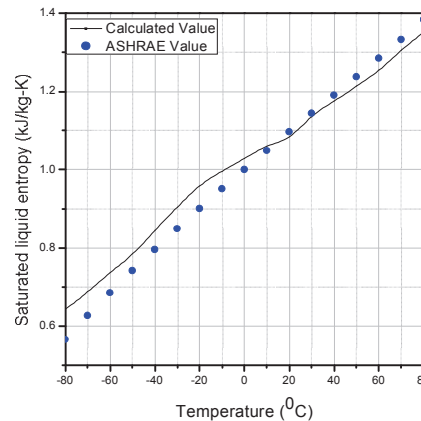


Fig. 7. Comparison of calculated values of saturated liquid entropy with ASHRAE data

Fig. 8. Comparison of calculated values of saturated vapour entropy with ASHRAE data

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