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Thermodynamic Correlations, k – Exponents, Speed of Sound, and COP Data for Binary Refrigerant Mixtures

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Abstract

Our study covers thermodynamic performance quantities for binary refrigerant mixtures of R-32/R-134a with compositions of 20/80%, 30/70%, 40/60% by mass for a wide range of thermodynamic conditions (pressure: 0.2 - 3.0 MPa, temperature: 240 - 480 ^oK and saturated conditions). The primary thrust of the study is the calculation of coefficient of performance (COP) values for refrigeration systems. Additional attention is also given to speed of sound data and to isentropic process changes.

The relevant COPs are derived based on a simplified reference refrigeration cycle with one stage compression and throttling, saturated vapor and no liquid sub-cooling prior to the throttling valve. The COP values are given for various condensing and evaporating temperatures. For all calculations, a Peng – Robinson type equation of state is used to determine the necessary fluid properties. The enthalpy, entropy, and constant-pressure and constant-volume specific heats as well as the k-type isentropic change exponents are presented for all mixtures for the range of thermodynamics conditions listed above. Comparisons are made illustrating the influence of pressure and temperature on the k-type exponents $k_{p,v}$, $k_{T,v}$, and $k_{p,T}$, and on the ratio of specific heats k ($k = c_p/c_v$). Furthermore, graphs with speed of sound data for this extended range of conditions are also given.

Keywords: R-32/R-134a mixtures, enthalpy, entropy, constant-pressure and constant-volume specific heats, isentropic exponents, coefficient of performance, speed of sound.

1. Introduction

The binary refrigerant mixtures R-32/R-134a under consideration in this work are suggested as environmentally acceptable working fluid substitutes to the refrigerant $CHClF_2$ (HCFC–22 or R-22) in various applications. The development of alternative technologies requires a great deal of effort. Our work is a computational study of the properties and characteristics of blends based on the fundamentals of thermodynamics. The prediction of equilibrium state property values for saturated vapor and saturated liquid R-32/R-134a binary mixtures involves activity and fugacity coefficients (Reid et al., 1988; Stegou-Sagia and Damanakis, 1999). A Peng – Robinson type equation of state (Smith and Van Ness, 1975) is used to determine enthalpy, entropy, and real gas isentropic changes in terms of pressure, volume and temperature.

In previous publications (Kouremenos et al., 1985; Stegou-Sagia, 1997; Stegou-Sagia, 2000; Stegou-Sagia and Katsanos, 1996), equations for corresponding k-type exponents were introduced such that

$$k_{p,v} = -\frac{v}{p}\frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T \tag{1a}$$

$$k_{T,v} = 1 + \frac{v}{c_v}\left(\frac{\partial p}{\partial T}\right)_v \tag{1b}$$

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$$k_{p,T} = \frac{T\left(\frac{\partial p}{\partial T}\right)_v}{T\left(\frac{\partial p}{\partial T}\right)_v + p\left(\frac{c_v}{c_p} - 1\right)}$$

$$= \frac{\left(\frac{\partial s}{\partial T}\right)_p}{\left(\frac{\partial s}{\partial T}\right)_p + \frac{p}{T}\left(\frac{\partial s}{\partial p}\right)_T} \quad (1c)$$

It should be emphasized that the accuracy of the proposed property equations used in our calculations have been tested by comparisons between both experimental and computational property data (ASHRAE, 2001; Coolpack, 2001; Damanakis, 2001; Higashi, 1995; ICI, 1995; Nagel and Bier, 1995; NIST, 1998; Stegou-Sagia, 1997; Stegou-Sagia, 2000).

Binary mixtures of HFC–32 and HFC-134a with compositions of 20/80%, 30/70%, and 40/60% by mass were evaluated. The values of the above k-type exponents are plotted for each mixture as is the refrigeration capability (i.e. COP) of one-stage vapor compression systems. Moreover, our work also includes the speed of sound data calculated by Kouremenos et al. (1985), Smith and Van Ness (1975), and Stegou-Sagia (2000) using

$$a^2 = -v^2 \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T \quad (2)$$

2. Thermodynamic Properties

As we have already mentioned above, our computational algorithm uses the Peng-Robinson equation of state (Damanakis 2001, Higashi 1995, Nagel and Bier 1995, Smith and Van Ness 1975, Stegou-Sagia and Damanakis 1999) to determine the necessary expressions for the calculation of enthalpy and entropy as a function of temperature, pressure, and mass concentration. This equation of state is given by

$$p = \frac{RT}{v - b_M} - \frac{\alpha_M}{v^2 + 2vb_M - b_M^2} \quad (3)$$

The mixture constants α_M and b_M used in equation (3) are derived using the following mixing rules (Perry and Green, 1984; Smith and Van Ness, 1975):

$$\alpha_M = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \alpha_{ij}$$

$$= x_1^2\alpha_{11} + x_2^2\alpha_{22} + 2\,x_1x_2\alpha_{12} \quad (4a)$$

$$b_M = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j b_{ij}$$

$$= x_1^2 b_{11} + x_2^2 b_{22} + 2\,x_1x_2 b_{12} \quad (4b)$$

where

$$\alpha_{12} = \alpha_{21} = \left(\alpha_{11}\alpha_{22}\right)^{0.5}\left(1 - k_{12}\right) \quad (5a)$$

$$b_{12} = b_{21} = \frac{\left(b_{11} + b_{22}\right)}{2}\left(1 - l_{12}\right) \quad (5b)$$

The interaction parameter l_{12} is kept constant and the quantity k_{12} is taken as a function of temperature from Hozumi et al. (1995), Perry and Green (1984), and Piao et al. (1995), i.e.

$$l_{12} = 0.02372 \quad (6a)$$

$$k_{12} = 0.003 - \left[0.00007\left(T - 273.15\right)\right] \quad (6b)$$

The constants α_{ii} and b_{ii} are calculated utilizing (Hozumi et al., 1995; Zhang et al., 1995)

$$\alpha_{ii} = 0.45724\frac{X_i R^2 T_{ci}^2}{p_{ci}} \quad (7a)$$

$$b_{ii} = 0.0778\frac{RT_{ci}}{p_{ci}} \quad (7b)$$

$$X_i = \Big[1 + \left(0.37464 + 1.54226\omega_i - 0.26992\omega_i^2\right)$$

$$\cdot\left(1 - \sqrt{T/T_{ci}}\right)\Big]^2 \quad (7c)$$

where i=1,2 refers to R-32 and R-134a, respectively. The acentric factor ω is given by (Perry and Green, 1984)

$$\omega = \Big[-\ln p_c - 5.92714 + 6.09648\,\theta^{-1}$$

$$+ 1.28862\ln\theta - 0.169347\,\theta^6\Big]$$

$$/\Big[15.2518 - 15.6875\,\theta^{-1}$$

$$-13.472\ln\theta + 0.43577\,\theta^6\Big] \quad (8)$$

with p_c in atm and $\theta = T_b/T_c$ (i.e. the ratio of the binary mixture temperature to the critical temperature). The critical values are tabulated in TABLE I.

TABLE I. CRITICAL CONSTANTS OF R-32 AND R-134A (ASHRAE, 2001; ICI, 1995; NIST, 1998).

	R-32	R-134a
Critical Temperature T_c in ^oK	351.55	474.16
Critical Pressure p_c in kPa	5830	4067
Critical Volume v_c in cm^3/mol	123.81	198.96

The main thermodynamic properties i.e. the entropy, the enthalpy and the specific heats c_v and c_p are given below as a function of temperature, pressure, and density:

$$s = s_0 + \left(A \ln T + BT + \frac{CT^2}{2} + \frac{DT^3}{3} \right) - \left(A \ln T_0 + BT_0 + \frac{CT_0^2}{2} + \frac{DT_0^3}{3} \right) + \frac{1}{1000\,M}\left[R \ln\rho - R \ln \frac{\rho}{1-\rho b_M} + \frac{\partial \alpha_M(T)}{\partial T} \cdot \frac{1}{b_M \sqrt{8}} \left(\ln\left| \frac{-b_M\rho + 1 - \sqrt{2}}{-b_M\rho + 1 + \sqrt{2}} \right| - \ln\left| \frac{1-\sqrt{2}}{1+\sqrt{2}} \right| \right) \right] \quad (9a)$$

$$h = u_0 + \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right) - \left(AT_0 + \frac{BT_0^2}{2} + \frac{CT_0^3}{3} + \frac{DT_0^4}{4} \right) - R\left(T - T_0\right) + \frac{p}{\rho 1000M} + \frac{1}{1000M} \frac{-\alpha_M(T) + T\frac{\partial \alpha_M(T)}{\partial T}}{b_M \sqrt{8}} \cdot \left(\ln\left| \frac{-b_M\rho + 1 - \sqrt{2}}{-b_M\rho + 1 + \sqrt{2}} \right| - \ln\left| \frac{1-\sqrt{2}}{1+\sqrt{2}} \right| \right) \quad (9b)$$

The mixture entropy s and enthalpy h calculated by equations (9) are in kJ/kg K and in kJ/kg, respect-tively. For each blend which we have, the proper coefficients α_M and b_M are used.

The constant volume and pressure specific heats c_v and c_p are expressed in kJ/kg K by

$$c_v = A + BT + CT^2 + DT^3 - R + \frac{T}{1000M} \cdot \frac{\partial^2 \alpha_M(T)}{\partial T^2} \frac{1}{b_M \sqrt{8}} \left(\ln\left| \frac{-b_M\rho + 1 - \sqrt{2}}{-b_M\rho + 1 + \sqrt{2}} \right| - \ln\left| \frac{1-\sqrt{2}}{1+\sqrt{2}} \right| \right) \quad (10a)$$

and

$$c_p = c_v - \frac{T}{1000M} \left(\frac{R}{v - b_M} - \frac{\frac{\partial \alpha_M(T)}{\partial T}}{v^2 + 2vb_M - b_M^2} \right)^2 \cdot \left(-\frac{RT}{(v - b_M)^2} + \frac{\alpha_M(T)(2v + 2b_M)}{\left(v^2 + 2vb_M - b_M^2\right)^2} \right)^{-1} \quad (10b)$$

The quantities p_0, T_0, s_0, and u_0 (i.e. thermo-physical properties at the reference state) and the coefficients A, B, C, and D are tabulated in TABLE II.

TABLE II. VALUES OF p_0 (kPa), T_0 (K), s_0 (kJ/kg K), AND u_0 (kJ/kg) AND THE COEFFICIENTS A, B, C, AND D (DAMANAKIS, 2001; HIGASHI, 1995; NAGEL AND BIER, 1995).

	R-32/R-134a		
	20/80%	30/70%	40/60%
p_0	251.325	251.325	251.325
T_0	273.15	273.15	273.15
s_0	1.111	1.188	1.264
u_0	262.50	276.50	290.63
A	0.1408	0.1746	0.1988
B	$2.76\ 10^{-3}$	$2.626\ 10^{-3}$	$2.529\ 10^{-3}$
C	$-1.766\ 10^{-6}$	$-1.578\ 10^{-6}$	$-1.456\ 10^{-6}$
D	$4.064\ 10^{-10}$	$3.578\ 10^{-10}$	$3.100\ 10^{-10}$

3. k-Exponents, COP Values and Speed of Sound

The three real gas k-type exponents can be expressed as

$$k_{p,v} = -\frac{v}{p}\frac{c_p}{c_v} \left(\frac{-RT}{(v - b_M)^2} + \frac{\alpha_M(T)\left(2v + 2b_M\right)}{\left(v^2 + 2vb_M - b_M^2\right)^2} \right) \quad (11a)$$

$$k_{T,v} = 1 + \frac{v}{c_v} \left(\frac{R}{v - b_M} - \frac{\frac{\partial \alpha_M(T)}{\partial T}}{v^2 + 2vb_M - b_M^2} \right) \quad (11b)$$

$$k_{p,T} = T\left(\frac{R}{v - b_M} - \frac{\frac{\partial \alpha_M(T)}{\partial T}}{v^2 + 2vb_M - b_M^2} \right) \Big/ \left[T\left(\frac{R}{v - b_M} - \frac{\frac{\partial \alpha_M(T)}{\partial T}}{v^2 + 2\,vb_M - b_M^2} \right) + p\left(\frac{c_v}{c_p} - 1 \right) \right] \quad (11c)$$

The related correlation for the speed of sound is given by (Smith and Van Ness, 1975; Stegou-Sagia, 2000; Stegou-Sagia and Katsanos, 1996)

$$a^2 = -v^2 \frac{c_p}{c_v}\left(\frac{-RT}{\left(v-b_M\right)^2} + \frac{\alpha_M(T)\left(2v+2b_M\right)}{\left(v^2+2vb_M-b_M^2\right)^2} \right) \quad (12)$$

Vapor – compression refrigeration systems are the most common refrigeration units in use today. The COP for any refrigeration cycle is defined as the ratio of the refrigeration effect to the net work input required to achieve that effect (Smith and Van Ness 1975). Using equations (3) to (8) and (9), a computer algorithm for the pressure, enthalpy and entropy needed to make COP calculations has been developed. Special care has been taken with respect to the phase equilibrium conditions, as the behavior of mixtures is clearly different from that of pure materials. Furthermore, as already mentioned above, there is no vapor superheating prior to the compressor and no sub-cooling prior to the throttling device. The results presented below give a limit on refrigeration system performance.

Results

Emphasis was place on the choice of equation of state and the relevant thermodynamic properties (enthalpy, entropy, specific heats c_V , c_P). As already mentioned, detailed comparisons were carried out with available sources from the literature and a minimal maximum deviation of approximately 1.5% was observed. Results for the k-exponents, COP and the speed of sound for a wide range of pressure and temperature follow.

Figures 1 to 4, 5 to 9 and 10 to 14 show the real gas behavior and the speed of sound for R-32/R-134a mixtures with compositions of 20/80%, 30/70% and 40/60% by mass. The k-type exponents ($k_{p,v}$, $k_{T,v}$, $k_{p,T}$) are illustrated on these graphs as well as the ideal gas isentropic k-exponent (i.e. ratio of specific heats).

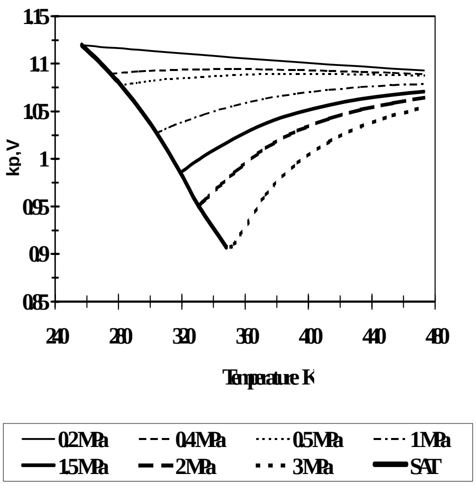

Figure 1. The exponent $k_{p,v}$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 20/80% by mass.

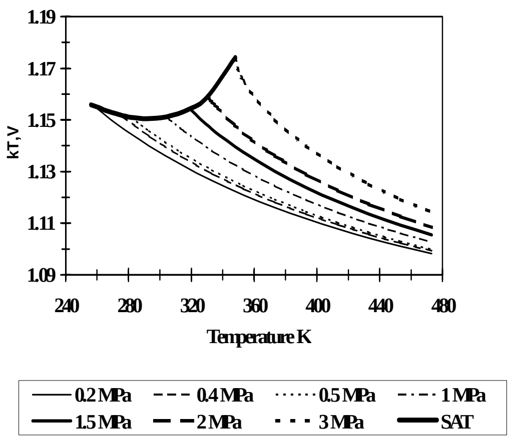

Figure 2. The exponent $k_{T,v}$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 20/80% by mass.

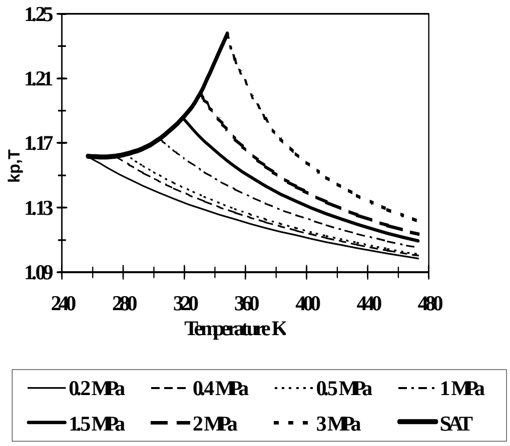

Figure 3. The exponent $k_{p,T}$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 20/80% by mass.

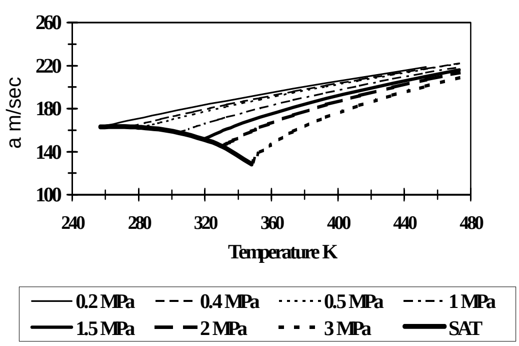

Figure 4. Speed of sound in m/sec versus temperature in K for various pressures for a R-32/R-134a mixture with a composition of 20/80% by mass.

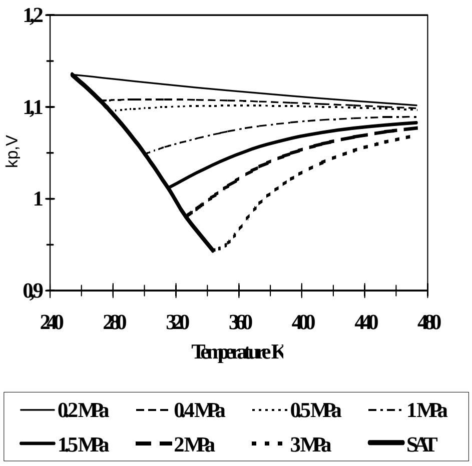

Figure 5. The exponent $k_{p,v}$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 30/70% by mass.

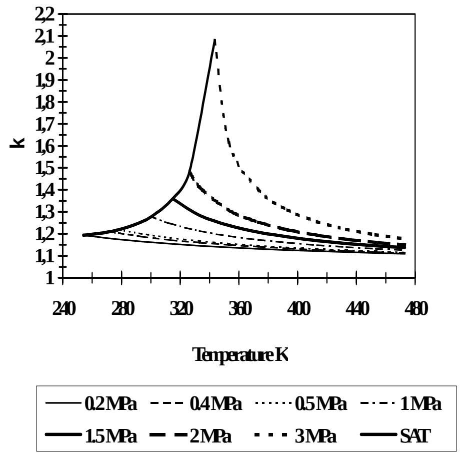

Figure 8. The exponent $k = c_p / c_v$ for various pressures and temperature for a R-32/R-134a mixture with a composition of 30/70% by mass.

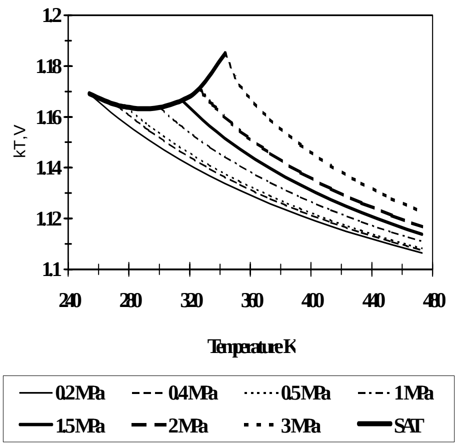

Figure 6. The exponent $k_{T,v}$ for various pressures and temperature for a R-32/R-134a mixture with a composition of 30/70% by mass.

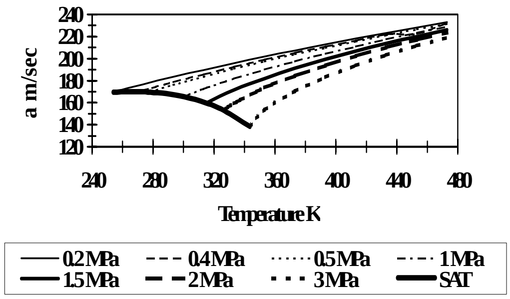

Figure 9. The speed of sound versus temperature for various pressures for a R-32/R-134a mixture with a composition of 30/70% by mass.

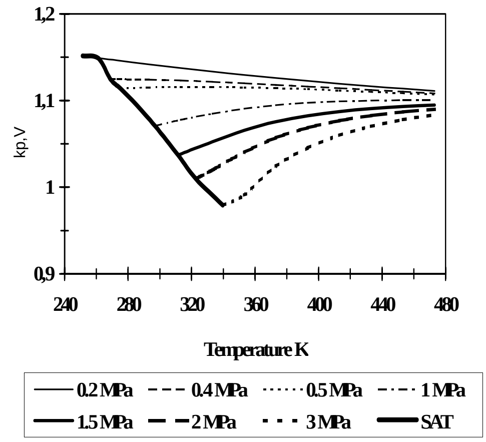

Figure 10. The exponent $k_{p,v}$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 40/60% by mass.

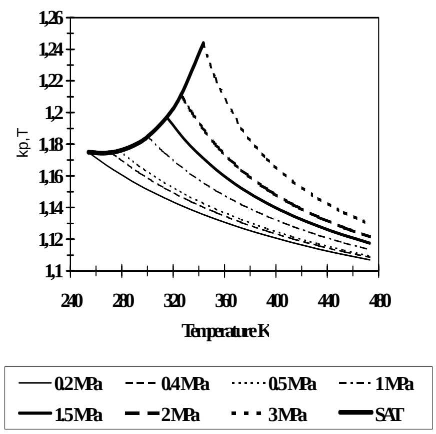

Figure 7. The exponent $k_{p,T}$ for various pressures and temperature for a R-32/R-134a mixture with a composition of 30/70% by mass.

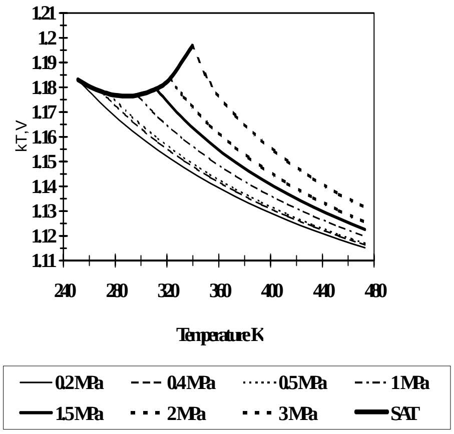

Figure 11. The exponent $k_{T,v}$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 40/60% by mass.

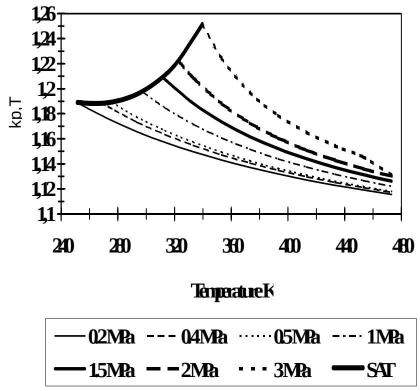

Figure 12. The exponent $k_{p,T}$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 40/60% by mass.

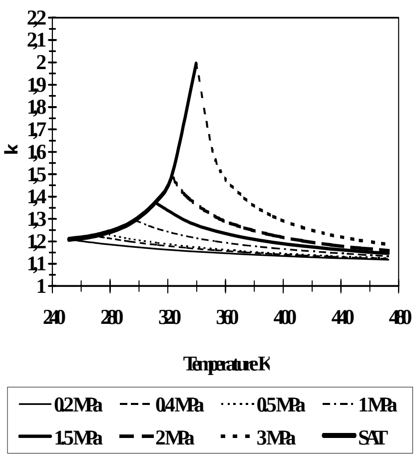

Figure 13. The exponent $k = c_p / c_v$ as a function of pressure and temperature for a R-32/R-134a mixture with a composition of 40/60% by mass..

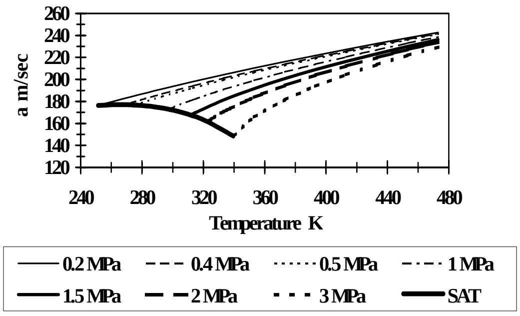

Figure 14. The speed of sound versus temperature for various pressures for a R-32/R-134a mixture with a composition of 40/60% by mass.

Comparisons between R-32/R-134a mixtures with compositions of 20/80%, 30/70% and 40/60% by mass are presented in Figures 15 to 18. With the aid of these graphs it is obvious that the 40/60% R-32/R-134a blend has the highest values of the real gas k-exponents at a pressure of 1 MPa.

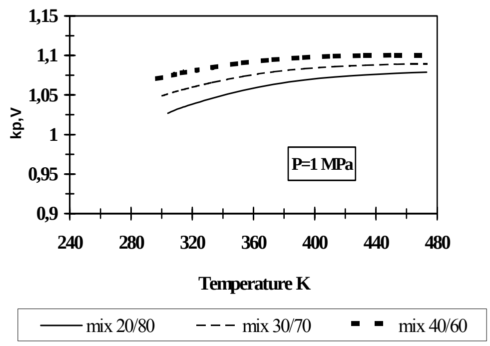

Figure 15. The exponent $k_{p,v}$ versus temperature at p=1MPa for the R-32/R-134a mixtures (compositions of 20/80%, 30/70% and 40/60% by mass).

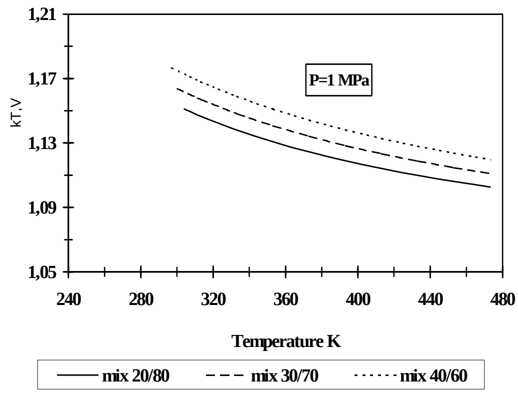

Figure 16. The coefficient $k_{T,v}$ versus temperature at p=1MPa for the R-32/R-134a mixtures (compositions of 20/80%, 30/70% and 40/60% by mass).

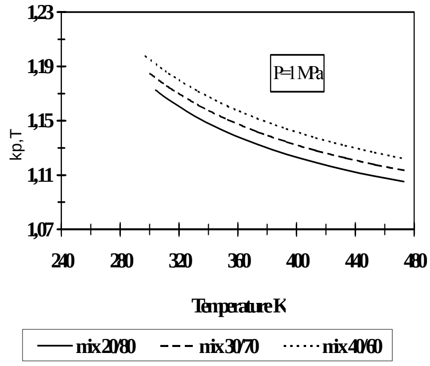

Figure 17. The exponent $k_{p,T}$ versus temperature at p=1MPa for the R-32/R-134a mixtures (compositions of 20/80%, 30/70%, 40/60% by mass).

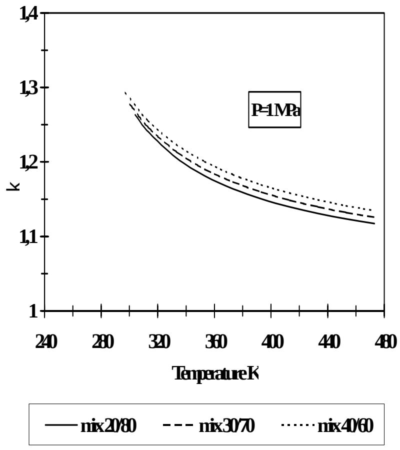

Figure 18. The exponent $k = c_p / c_v$ versus temperature for R-32/R-134a mixtures (compositions of 20/80%, 30/70% and 40/60% by mass).

Figures 19-21 illustrate fundamental performance trends for refrigerant systems operating with R-32/R-134a mixtures. The diagrams have been plotted for a wide range of condensing and evaporating temperatures. The effect of irreversible compression has been taken into account by using an isentropic compressor efficiency of $\eta_{is} = 0.9$.

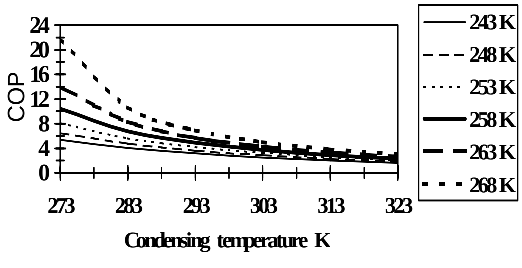

Figure 19. COP values as a function of condensing temperature for different evaporating temperatures for a R-32/R-134a mixture with a composition of 20/80% by mass (isentropic compressor efficiency of 0.9).

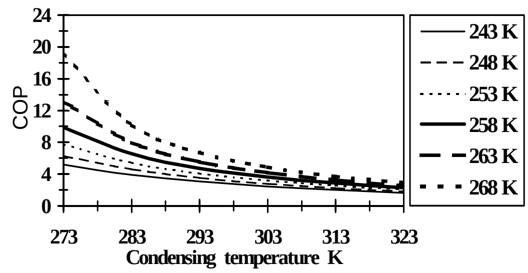

Figure 20. COP versus condensing temperature for various evaporating temperatures for a R-32/R-134a mixture with a composition of 30/70% by mass (isentropic compressor efficiency of 0.9).

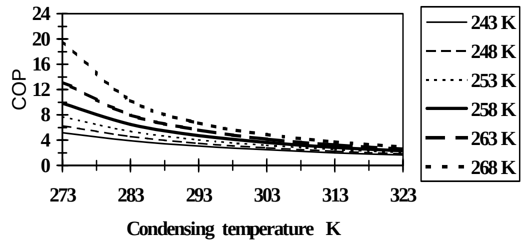

Figure 21. COP values versus condensing temperature for various evaporating temperatures for a R-32/R-134a mixture with a composition of 40/60% by mass (isentropic compressor efficiency of 0.9).

Conclusions

For the first time, an extended analysis on the characteristics of R-32/R-134a mixtures as they relate to refrigeration systems has been presented The information given is intended as an aid to the design of vapor compression refrigeration systems utilizing various compositions of this alternative refrigerant mixture R-32/R-134a. The figures clearly detail the real gas behavior of this working medium. In addition, the equations and figures may be used to calculate a number of other quantities, including refrigerant blowby rates in the compressor. Results for these quantities will be generated in a forthcoming project.

Nomenclature

a	Speed of sound [m/sec]
b_M	Mixture constant in equation (3) [cm^3/mol]
c_P	Constant pressure specific heat [kJ/(kg K)]
c_v	Constant volume specific heat [kJ/(kg K)]
h	Enthalpy [kJ/kg]
k	Ideal gas isentropic exponent
$k_{p,T}$	Isentropic exponent corresponding to the properties p, T

$k_{p,v}$ Isentropic exponent corresponding to the properties p, v
$k_{T,v}$ Isentropic exponent corresponding to the properties v, T
M Molecular weight
p Pressure [kPa]
R Gas constant [kPa cm^3/(mol K)]
s Entropy [kJ/(kg K)]
T Temperature [K]
v Molar volume [cm^3/mol]

Greek Symbols

α_M Mixture constant in equation (3) [kPa cm^6/mol^2]
ρ Molar density [mol/cm^3]
ω Acentric factor

Subscripts

1 R-32
2 R-134a
M mixture R-32/R-134a

References

ASHRAE, 2001, *Fundamentals Handbook*, ASHRAE, New York

Coolpack, 2001, *Coolpack Software*, Denmark Technical University, Department of Mechanical Engineering.

Damanakis, M., 2001, "Condensation of R-32/R-134a Mixtures on Horizontal Integral Fin Tubes" PhD. Thesis, National Technical University of Athens, School of Mechanical Engineering.

Higashi, Y., 1995, "Vapor – Liquid Equilibrium, Coexistence Curve and Critical Locus for Binary R-32/R-125 Mixture", *Proceedings of the 19th International Congress of Refrigeration*, Hague Netherlands, International Institute of Refrigeration, Vol. IVa, Theme 4, pp. 297-304.

Hozumi, T., Sato, H., Watanabe, K., 1995, "Second Virial Coefficients for R-32/R-134a Based on the Sound Velocity Measurements", *Proceedings of the 19th International Congress of Refrigeration*, Hague Netherlands, International Institute of Refrigeration, Vol. IVa, Theme 4, pp. 321-328.

ICI, 1995, *ICI Chemicals and Polymers*, Engineer’s Tables, Cheshire England: Runcorn.

Kouremenos, D. A., Antonopoulos, K. A., Kakastios, X. K., 1985, "Numerical Evaluation and Generalization of the Isentropic Change of Real Gas", *Proceedings of the 4th International Conference on Numerical Methods in Thermal Problems*, Swansea U.K., Pineridge Press, pp.1330-1341.

Nagel, M., Bier, K., 1995, "Vapor – Liquid Equilibrium of Ternary Mixtures of the Refrigerants R32, R125 and R134a", *Int. Journal of Refrigeration*, Vol. 18, pp.534-543.

NIST, 1998, *Refrigerant Properties Database 23, REFPROP*, Version 6.01, National Institute of Standards and Technology, USA.

Perry, R. H., Green, D. W., 1984, *Perry’s Chemical Engineer’s Handbook*, Chemical Engineering Series 6th ed, Mc-Graw-Hill International Editions, Singapore.

Piao, C. C., Iwata, I., Fujiwara, K., Noguchi, M., 1995, "A Study of Thermodynamic Properties of HFC-32/125/134a Ternary Mixture", *Proceedings of the 19th International Congress of Refrigeration*, Hague, Netherlands, International Institute of Refrigeration, Vol. IVa, Theme 4, pp.488-495.

Reid, R. C., Prausnitz, J. M., Poling, B. E., 1988, *The Properties of Gases and Liquids*, Mc-Graw Hill Book Company, 4th ed., Singapore.

Smith, J. M., Van Ness, H. C., 1975, *Introduction to Chemical Engineering Thermodynamics*, Mc Graw-Hill 3rd ed, Chemical Engineering Series.

Stegou-Sagia, A., 1997, "Thermodynamic property formulations and heat transfer aspects for replacements refrigerants; R-123, R-134a", *Int. J. of Energy Research* , Vol.21, pp.871-884.

Stegou-Sagia, A., 2000, "R-12, R-134a, R-502, R-407a. Generalized compressibility charts with isentropic exponents. Thermodynamic efficiency of refrigerating cycles, *Proceedings of ECOS’2000 Conference*, Hirs, G.G., ed., Universiteit Twente, Netherlands, Part 2, pp.889-897.

Stegou-Sagia, A., Damanakis, M., 1999, "Thermophysical property formulations for R32/R134a mixtures", *Int. J. Applied Thermodynamics*, Vol.2, No.3, pp.139-143.

Stegou-Sagia, A., Katsanos, D., 1996, "On isentropic changes of alternative refrigerants (R-123, R-134a, R-500, R-503)", *Energy-The Int. Journal*, Vol..21 No 12, pp.1071-1077.

Zhang, H. L., Sato, H., Watanabe, K., 1995, "Second Virial Coefficients for R-32, R-125, R-134a, R-143a R-152a and their Binary Mixtures", *Proceedings of the 19th International Congress of Refrigeration*, Hague Netherlands, International Institute of Refrigeration, Vol. IVa, Theme 4, pp.622-629.