J. King Saud Univ., Vol. 7, *Eng. Sci.* (2), pp. 247–265 (A.H. 1415/1995)

Determination of Thermodynamic Properties of New Refrigerants by a Simple Equation of State

Khalil Abu-Abdou and M.F. Zedan

Mechanical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

(Received 3/4/1993; Accepted for publication 11/5/1994)

Abstract. A simple extension of the Redlich-Kwong equation of state in which one of the original constants is replaced by a polynomial in powers of temperature is shown to accurately fit the p-v-T data of the new refrigerants: HCFC-123 and HFC-134a and the data of refrigerant HCFC-22. The two new refrigerants are developed to replace the thermally efficient but ozone-depleting refrigerants CFC-11 and CFC-12, respectively. The coefficients of the polynomial extension are determined by fitting known p-v-T properties at a number of selected base points. Based on this equation of state and a specific heat relation, a simple computational procedure is used to compute the enthalpy and entropy. With only 4 terms in the polynomial extension of the equation of state, the method is shown to produce highly accurate results over a wide range of pressures and temperatures for each of the three refrigerants.

List of Symbols

b	=	a constant in the Redlich-Kwong equation of state
C_p	=	constant-pressure specific heat, J/kg° K
h	=	enthalpy, J/kg
K_i	=	coefficients of the equation of state (eqn. (1))
N	=	number of terms retained in the equation of state
N^*	=	number of base points
p	=	pressure, Pa
p_c	=	critical pressure, Pa
R	=	gas constant, J/kg° K
s	=	entropy, J/kg° K
T	=	Temperature, °K
T_c	=	critical temperature, °K
υ	=	specific volume, m^3/kg

γ = a constant in the exponential term of the BWR-equation of state

In all equations, the basic SI unit is used for each quantity.

Introduction

Recent scientific investigations revealed that the phenomenon of atmospheric ozone depletion has now taken new alarming dimensions. This phenomenon is not confined to Antarctica anymore. In fact it has already spread to the middle and high latitudes of the stratosphere in both hemispheres and is persisting over the four seasons. Ozone depletion has been found to be related to the chlorine content of halogenated hydrocarbon compounds released to the atmosphere, primarily as refrigerants from air conditioning and refrigeration equipment. Refrigerants are classified into groups according to their molecular structure as CFC, HFC or HCFC compounds. Refrigerants in the first group, such as CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2), have the highest chlorine content (3 and 2 chlorine atoms respectively) and accordingly have the highest ozone depletion potential (ODP). On the other hand HCFC refrigerants such as HCFC-22 ($CHCl F_2$) (with only one chlorine atom) are far less harmful to the ozone layer.

The refrigeration industry has come under tremendous pressure to find replacement refrigerants that can be used in existing equipment with minor retrofits. Based on safety, ozone depletion potential, global warming potential, energy efficiency, and compatability with traditional lubricating oils, two new refrigerants: HCFC-123 ($CHCl_2 CF_3$) and HFC-134a (CH_2FCF_3) have emerged as clear candidates for low-pressure and medium pressure systems, respectively. The first is a balanced alternative refrigerant for machines that run on CFC-11 while the second is for machines that use CFC-12. For high pressure chillers, HCFC-22 continues to be a good choice until a replacement becomes available. Assigning an ODP of 1.0 to CFC-11, the candidate refrigerants HCFC-123, HFC-134a and HCFC-22 are found to have ODP values of 0.016, zero and 0.05 respectively [1]. In spite of their low ODP, HCFCs are currently planned to be phased out by the year 2020. However, it appears now that the phase-out of HCFC-123 may be extended or eliminated altogether due to the many advantages it has and its extremely low ODP. The industry has moved quickly to make these new refrigerants available by opening chemical plants specifically built to produce them in 1991 [1].

As with any other thermodynamic cycle, one has to know the working fluid properties at all salient points of the refrigeration cycle in order to be able to carry out thermodynamic analysis. Thermodynamic properties of the new refrigerants

have already been made available by the industry in the form of tables and/or charts. However, using charts is generally inaccurate, while using tables is cumbersome due to encountered interpolation. The main objective of the present paper is to provide a simple and accurate computerized procedure to determine properties of these refrigerants. The proposed procedure is simple enough to be used conveniently on small hand held computers. This work is also motivated by the trend towards greater computerization in the industry as a whole, which makes the present procedure highly desirable as a part of large analysis packages. The method used earlier by the authors [2] for CFC-12 is applied here for the new refrigerants.

In Ref. [2], the authors compared the performance of three equations of state; namely the Benedict-Webb-Rubin (BWR) equation, an extended van der Waals (EVDW) equation and an extended Redlich-Kwong (ERK) equation. In the last two equations which are originally two-constant equations, the authors replaced one of the two original constants by a polynomial in powers of temperature. The ERK equation with only 4 terms was found to give an accuracy comparable to that given by the full BWR equation for CFC-12. In the present work the ERK equation is again chosen as the preferred equation of state, and the BWR equation is still considered for comparison purposes. The enthalpy and entropy are calculated by a procedure based on general thermodynamic relations that utilizes the developed equation of state and a low-pressure specific heat relation. The accuracy of both the ERK and BWR equations is investigated for different numbers of terms.

Brief Description of the Method of Analysis

In this section we present a brief description of the method. For more details the reader is referred to Ref. [2]. The Redlich-Kwong and BWR equations of state (see, for example, [3, p. 250] for their original forms) are recast in the form

$$p - \frac{RT}{\upsilon - b} = \sum_{i=1}^{N} K_i \ \phi_i(T, \upsilon) \tag{1}$$

where $b = \left[\frac{(3\sqrt{2}-1)}{3} \cdot \frac{RT_c}{P_c}\right] = 0.08664 \ \frac{RT_c}{P_c}$ for ERK equation and zero for the BWR equation. The molar mass M, gas constant R, critical pressure P_c and critical temperature T_c are given in Table 1 for all the three refrigerants investigated.

Table 1. Molar masses and critical properties

Refrigerant	M (kg/kmol)	R (J/kg°K)	P_c(MPa)	T_c(°K)
HFC134a	102.03	81.478	4.0550	374.15
HCFC-123	152.93	54.367	3.7896	458.15
HCFC-22	86.47	96.154	4.9771	369.15

The number of terms N is 7 for the untruncated BWR equation and is arbitrary (up to this point) for the ERK equation. The functions ϕ_i for the BWR equation are as follows:

$$\phi_1 = RT/\upsilon^2,\ \phi_2 = -1/\upsilon^2,\ \phi_3 = -1/(T^2\upsilon^2)$$

$$\phi_4 = RT/\upsilon^3,\ \phi_5 = -1/\upsilon^3,\ \phi_6 = 1/\upsilon^6$$

$$\text{and}\quad \phi_7 = (1 + \gamma/\upsilon^2)e^{-\gamma/\upsilon^2} / (T^2\upsilon^3) \tag{2}$$

where γ is an additional constant assumed to be known in the linearized problem. For the ERK equation, functions ϕ_i are given by

$$\phi_i = T^{i-1} / [\sqrt{T}\,\upsilon(\upsilon + b)] \tag{3}$$

The coefficients K_i in both equations of state are determined by solving an overdetermined system of linear equations formed by applying eq. (1) at a number of base points $N^* > N$, using a least squares procedure [4, p. 534]. The properties p,υ and T must be known at these base points.

To calculate h and s at an arbitrary state point, specified by the property pair (p,T), we start from a reference point r with known enthalpy h_r and entropy s_r and with a pressure p_r low enought to assume ideal gas behavior. Following a path along the isobaric p_r = constant from (p_r, T_r) to (p_r,T) and then along an isotherm T = constant from (p_r, T) to (p,T), we can write

$$h(p,T) = h_r + \Delta h_p + \Delta h_T \tag{4}$$

$$s(p,T) = s_r + \Delta s_p + \Delta s_T \tag{5}$$

where

$$\Delta h_p = \left(\int_{T_r}^{T} C_p \, dT \right)_{p_r} \tag{6}$$

$$\Delta s_p = \left(\int_{T_r}^{T} \frac{C_p}{T} dT \right)_{p_r} \tag{7}$$

$$\Delta h_T = \left\{ \int_{p_r}^{p} \left[\upsilon - T \left(\frac{\partial \upsilon}{\partial T} \right)_p \right] dp \right\}_T \tag{8}$$

and

$$\Delta s_T = \left[-\int_{p_r}^{p} \left(\frac{\partial \upsilon}{\partial T} \right)_p dp \right]_T \tag{9}$$

The evaluation of the integrals in eqs. (6) and (7) is fairly straight forward provided that we have an ideal gas approximation for C_p, *e.g.*,

$$C_p = b_0 + b_1 T + b_2 T^2 + b_3 T^3 \tag{10}$$

The evaluation of the integrals in eqs. (8) and (9) is somewhat tricky and needs manipulations making use of the thermodynamic relations and functions as given in [2]. The final results when using the ERK equation are

$$\Delta h_T = \frac{1}{b} \ln \frac{\upsilon}{\upsilon + b} \sum_{i=1}^{N} \left(i - \frac{5}{2} \right) K_i \, T^{i-(3/2)} + (p\upsilon - RT) \tag{11}$$

$$\Delta s_T = R \ln \frac{\upsilon - b}{\upsilon^*} + \frac{1}{b} \ln \frac{\upsilon}{\upsilon + b} \sum_{i=1}^{N} \left(i - \frac{3}{2} \right) K_i T^{i-(5/2)} \tag{12}$$

when using the BWR equation of state, we get

$$\Delta h_T = -K_2 \frac{1}{\upsilon} - K_3 \frac{3}{T^2 \upsilon} - K_5 \frac{1}{2\upsilon^2} + K_6 \frac{1}{5\upsilon^5} + K_7 \frac{3}{\gamma T^2} \left[1 - \left(1 + \frac{\gamma}{2\upsilon^2} \right) e^{-\gamma/\upsilon^2} \right] + (P\upsilon - RT) \tag{13}$$

$$\Delta s_T = R \ln\frac{\upsilon}{\upsilon^*} - K_1\frac{R}{\upsilon} - K_3\frac{2}{T^3\upsilon} - K_4\frac{R}{2\upsilon^2} + K_7\frac{2}{\gamma T^3}\left[1-\left(1+\frac{\gamma}{2\upsilon^2}\right)e^{-\gamma/\upsilon^2}\right] \quad (14)$$

where $\upsilon^* = \upsilon(p_r,T)$ is the specific volume at the low pressure p_r at which $C_p(T)$ is fitted, and the temperature T of the point at which solution is sought. The specific volumes υ^* and υ in equations (11) to (14) are obtained from the equation of state with already determined K_i-coefficients. However, since υ is an implicit function of p and T in either equation of state, υ has to be obtained iteratively for any given pair (p,T), *e.g.* by Newton's method, the regula-falsi method or any other standard root finding scheme. The properties h and s are then easily obtained by substituting from equations (6), (7) and (11) to (14) into equations (4) and (5), respectively.

Results and Discussion

The general procedure described in Ref. [2] and summarized in the previous section has been used to calculate the properties of Refrigerants 134a, 123 and 22. The base points used to determine the coefficients of the equations of state for these refrigerants are displayed on the pressure-enthalpy (p − h) charts in Figs 1 to 3. Also shown on these figures are the points at which the results of the procedure (υ, h and s) are checked against tabulated ("correct") values [5;6;7, p.70]. For HFC-134a, the base points cover a wide range to temperatures and pressures extending from T = − 50° C to 210°C and from p = 0.02 MPa to 4 MPa which is very close to the critical pressure. For HCFC-123, the range of available data [6] is more limited, however, it covers the working pressures and temperatures of vapor compression systems of most applications. The base and check points shown in Fig. 2 spread over the range covered by the tables: T ≈ − 17 to 65°C and p ≈ 0.014 to 0.23 MPa. The base points for HCFC-22 cover the range: T ≈ − 60 to 200°C and p = 0.02 to 2.8 MPa. In the three cases a number of base points are located on the saturation line. The checking points are scattered within the range covered by the base points for all refrigerants. The ranges for HFC-134a and HCFC-22 are much larger than the working ranges in which these refrigerants might be used.

The input to the present procedure are the base points discussed above and an ideal-gas specific heat relation $C_p(T)$. For HFC-134a, we used

$$C_p = 0.3270633 + 1.706384 \times 10^{-3}\,T \quad (15)$$

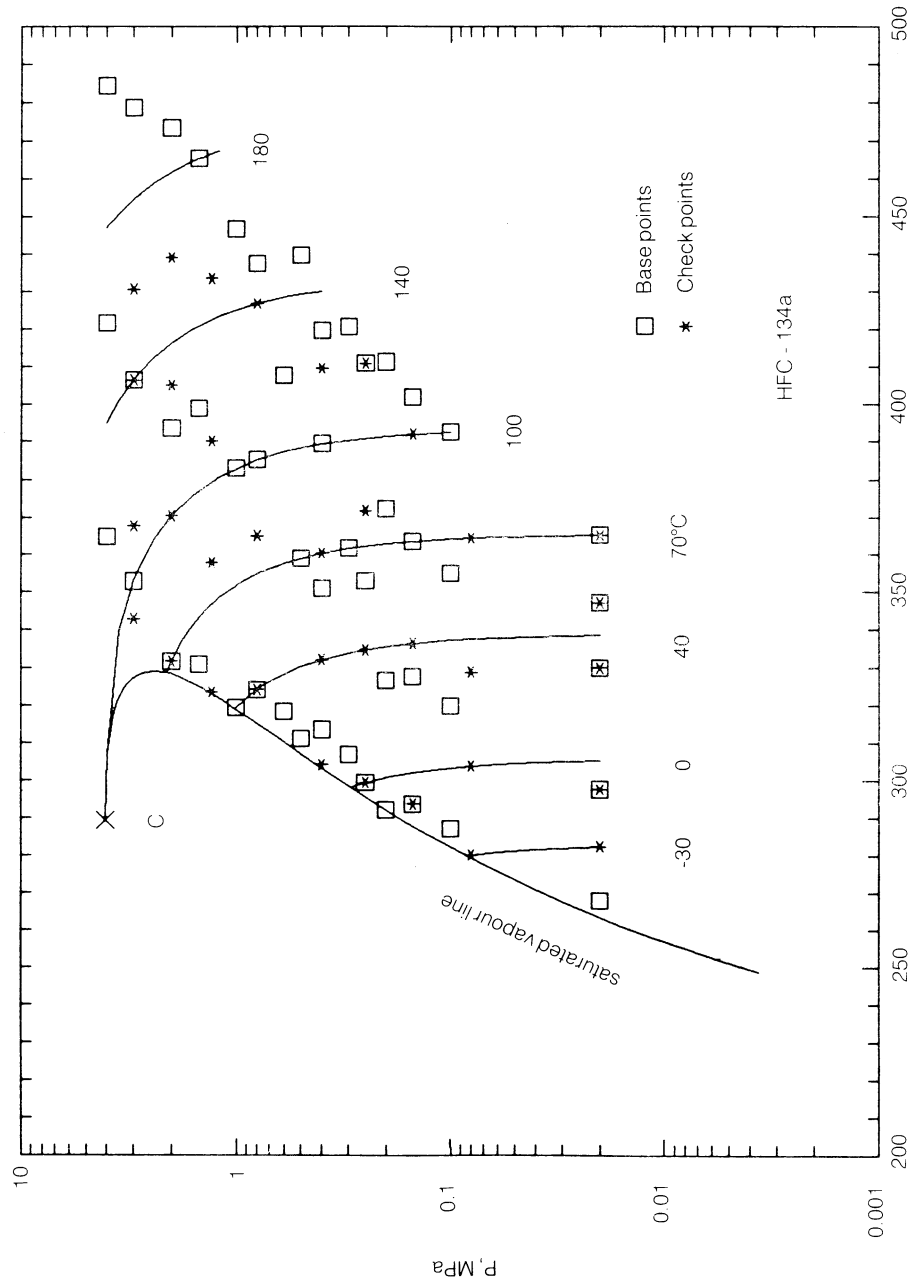

Fig. 1. Base and check points for Refrigerant 134a.

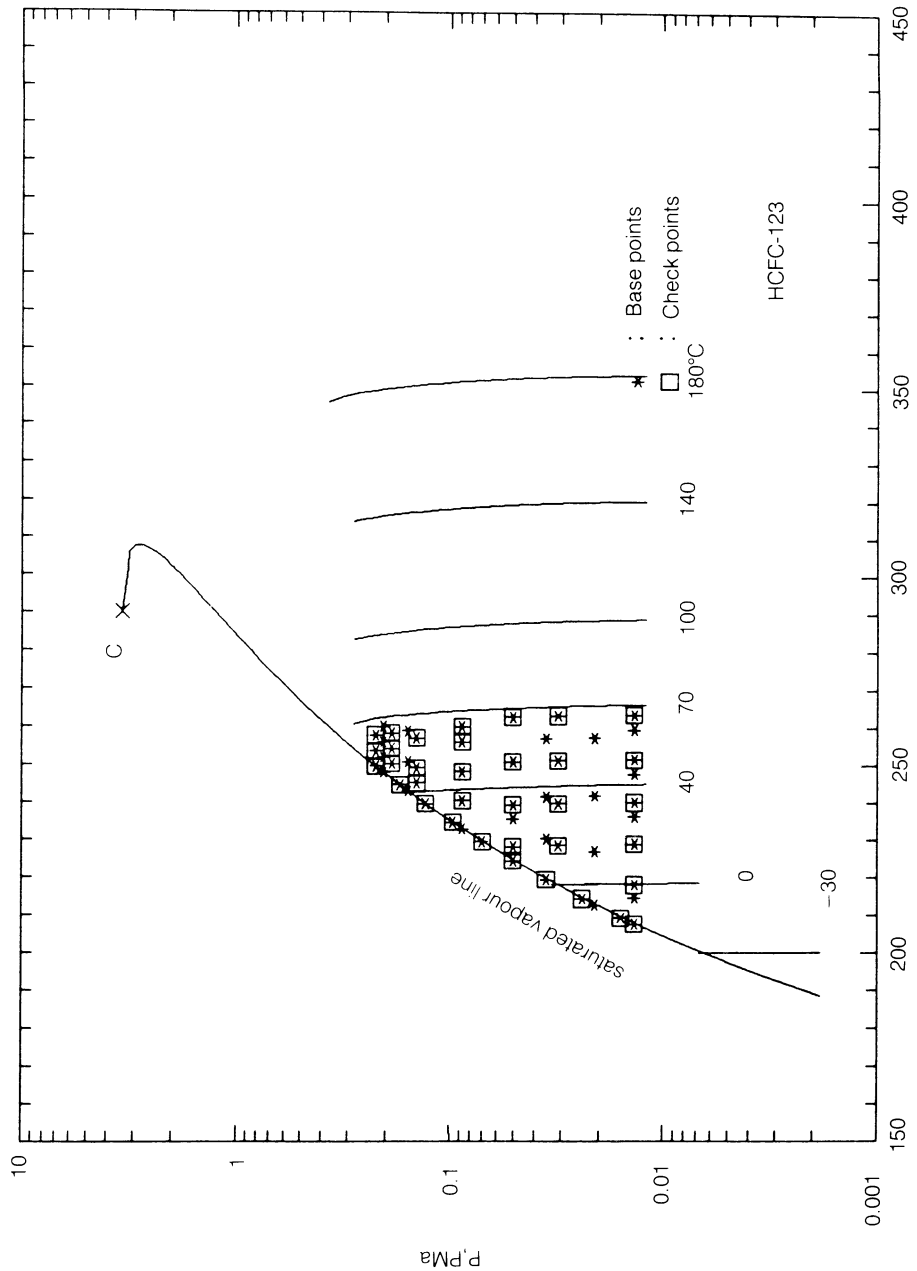

Fig. 2. Base and check points for Refrigerant 123.

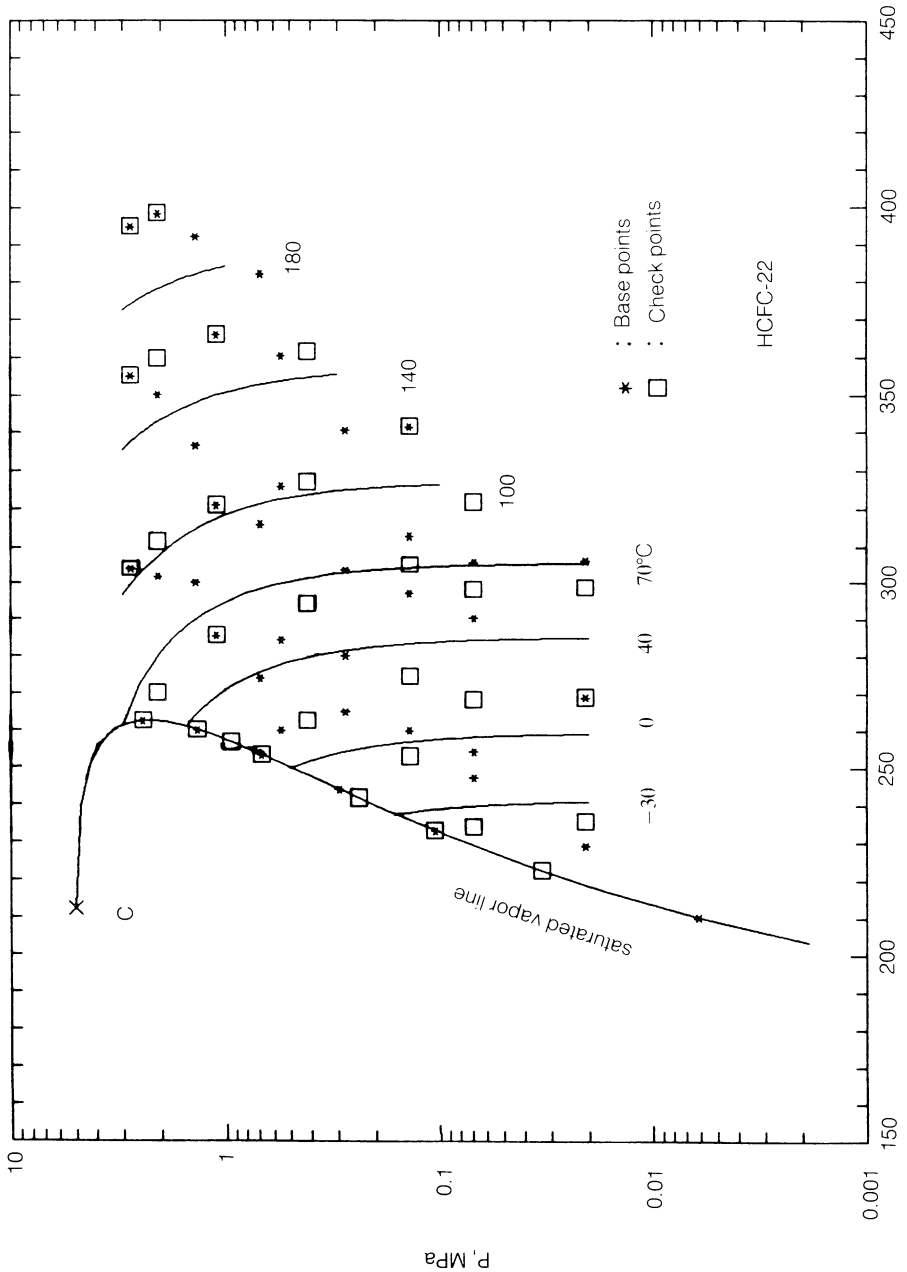

Fig. 3. Base and check points for Refrigerant 22.

where T is in °K and C_p in kJ/kg° K. This expression for C_p was obtained by fitting the enthalpy at p = 0.02 MPa, which is the lowest pressure found in the tables [5], by a polynomial in powers of temperature. The degree of the polynomial was increased so long there was significant decrease in the variance [4]. C_p was then found simply as the derivative of the polynomial with respect to temperature, $(\frac{\partial h}{\partial T})_p$.

Using a similar procedure, we obtained expressions for the specific heats of the other two refrigerants. These are:

$$C_p = 0.3080039 + 1.216815 \times 10^{-3} T \tag{16}$$

for HCFC-123 obtained by fitting the enthalpy at a pressure of 0.01365 MPa, and

$$C_p = 0.2975566 + 1.200945 \times 10^{-3} T - 8.67371 \times 10^{-8} T^2 \tag{17}$$

for HCFC-22 obtained by fitting enthalpy at a pressure of 0.020684 MPa.

The procedure was run using each of the ERK and the BWR equations of state. Results were obtained when different numbers of terms are retained in these equations. Of course the full BWR equation has 7 terms only as mentioned before. The accuracy of the results is assessed by evaluating the root mean square (rms) of the percentage errors (in υ,h and s) at the checking points shown in Figs 1,2 and 3. The root mean square percentage error is defined, for υ as an example, as follows:

$$\text{rms error} = \left[\frac{1}{N_{pts}} \sum_{1}^{N_{pts}} \left(\frac{\upsilon_{tab} - \upsilon_c}{\upsilon_{tab}} \times 100 \right)^2 \right]^{\frac{1}{2}} \tag{18}$$

where N_{pts} is the number of checking points, υ_{tab} is the tabulated specific volume and υ_c is the calculated specific volume.

For HFC-134a, Fig. 4 shows the rms of the percentage errors in computed υ,h and s using both equations of state against the number of terms retained in these equations. The results indicate that when using the BWR equation, the errors drop as the number of terms N is increased to 5, then stay roughly constant as N is increased to 7 terms (full equation). When using the ERK equation of state, the errors drop as N increases up to 4 then stay roughly constant thereafter except for a slight increase around N = 7. Using either equation of state with N = 4 gives roughly the same rms error in h and the same rms error in s. Such errors are only slightly higher than the

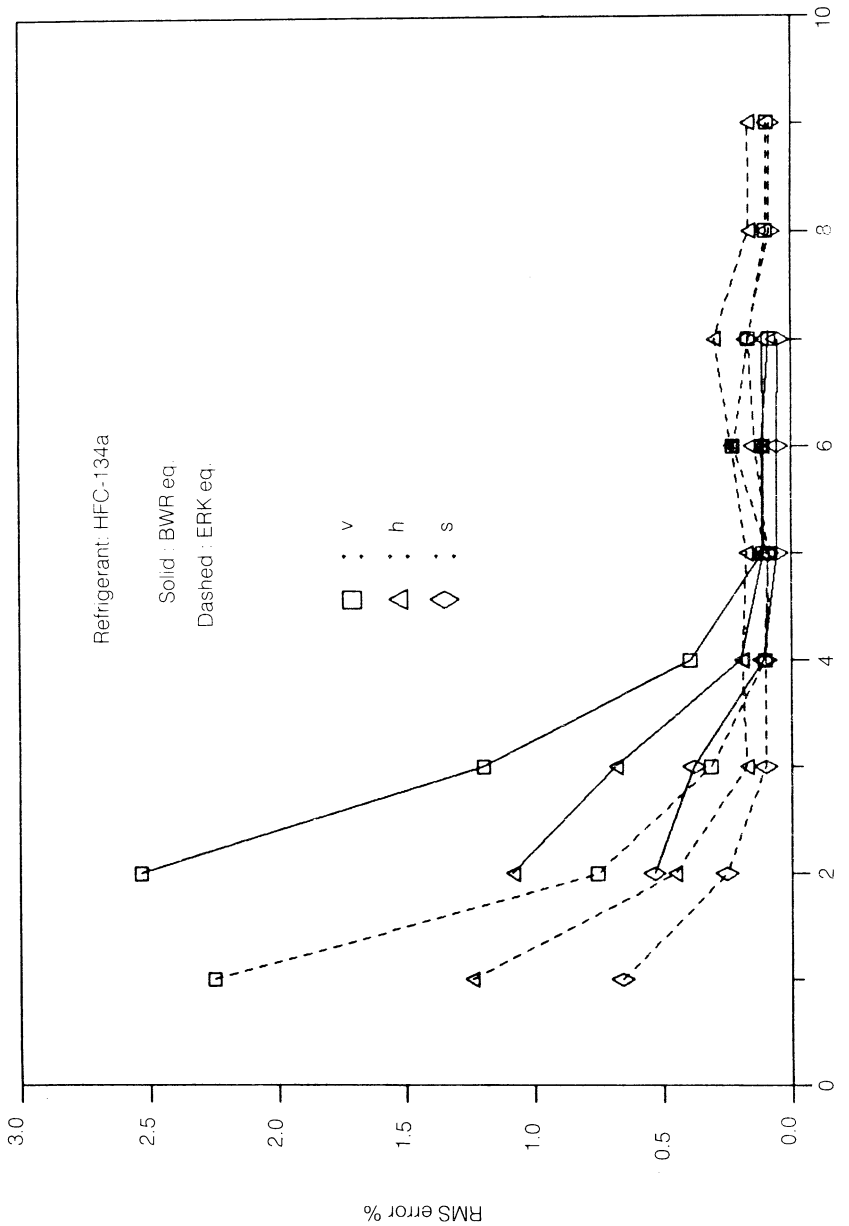

Fig. 4. Effect of the number of terms retained in the equation of state on the root mean square errors in the calculated properties of Refrigerant-134a.

minimum errors which are obtained when using the full BWR equation. It is worth noting that using the ERK equation with $N \leq 4$ gives substantially more accurate results than using the truncated BWR equation, especially for υ. In Fig. 5, the percentage errors in υ, h and s obtained by using the ERK equation with 4 terms are shown on the p-h chart at a number of selected points. The maximum errors in υ, h and s are about 0.223%, 0.289% and 0.161%, respectively. Because these values as well as the rms errors reported earlier are extremely low, we feel that the ERK equation of state is an excellent alternative to more complicated equations of state. The coefficients K_1 to K_4 computed for this equation are given in Table 2. Ref. [8] gives the following complicated equation

$$p = \frac{RT}{\upsilon - B} + \sum_{i=1}^{4} \frac{(A_i + B_i T + C_i \exp(-KT)}{(\upsilon - B)^{i+1}} \tag{19}$$

to represent the p-v-T behavior of HFC-134a. Since the errors obtained here when using the ERK equation with 4 coefficients are within the uncertainty of the values in the tables [5], we strongly recommend this simple equation in conjunction with the current computational procedure to calculate the properties of HFC-134a.

Table 2. Computed coefficients of the ERK equation of state

i	K_i		
	HFC-134a	**HCFC-123**	**HCFC-22**
1	−11993.38234111341	61726.56092475343	−7169.275575756461
2	66.62041228150454	−639.9733053854964	32.22209613419979
3	−0.1486540955412096	2.132141649121004	−6.916131872636901D-02
4	1.134020436840702D-04	−2.354521544495022D-03	5.15191799349599D-05

Figure 6 shows the rms error results versus the number of terms in the equation of state for HCFC-123. We observe that the errors in υ,h and s are generally smaller than corresponding errors for HFC-134a in Fig. 4. This may be attributed partly to the small range of pressures and temperatures of the base and check points used for HCFC-123. We further observe that errors do not change as drastically with increasing N as for HFC-134a. The best results for h and s are obtained with only 2 coefficients in the equation of state while the accuracy of υ improves slightly at higher N. Similar to the previous case we list the coefficients of the equation of state obtained with N = 4 in Table 2.

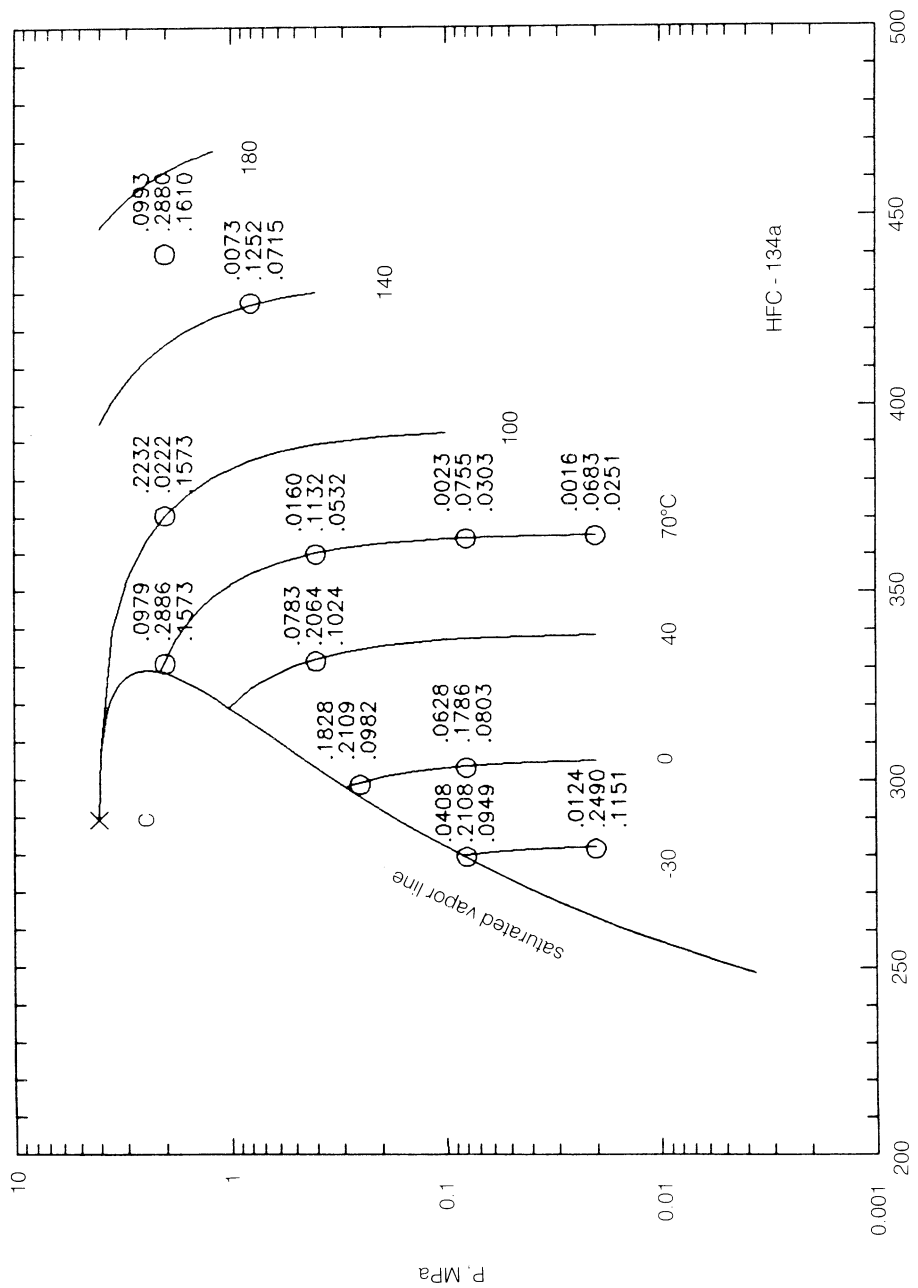

Fig. 5. Errors in properties calculated at selected points in the superheat region of Refrigerant-134a, using the ERK equation of state with 4 polynomial terms.

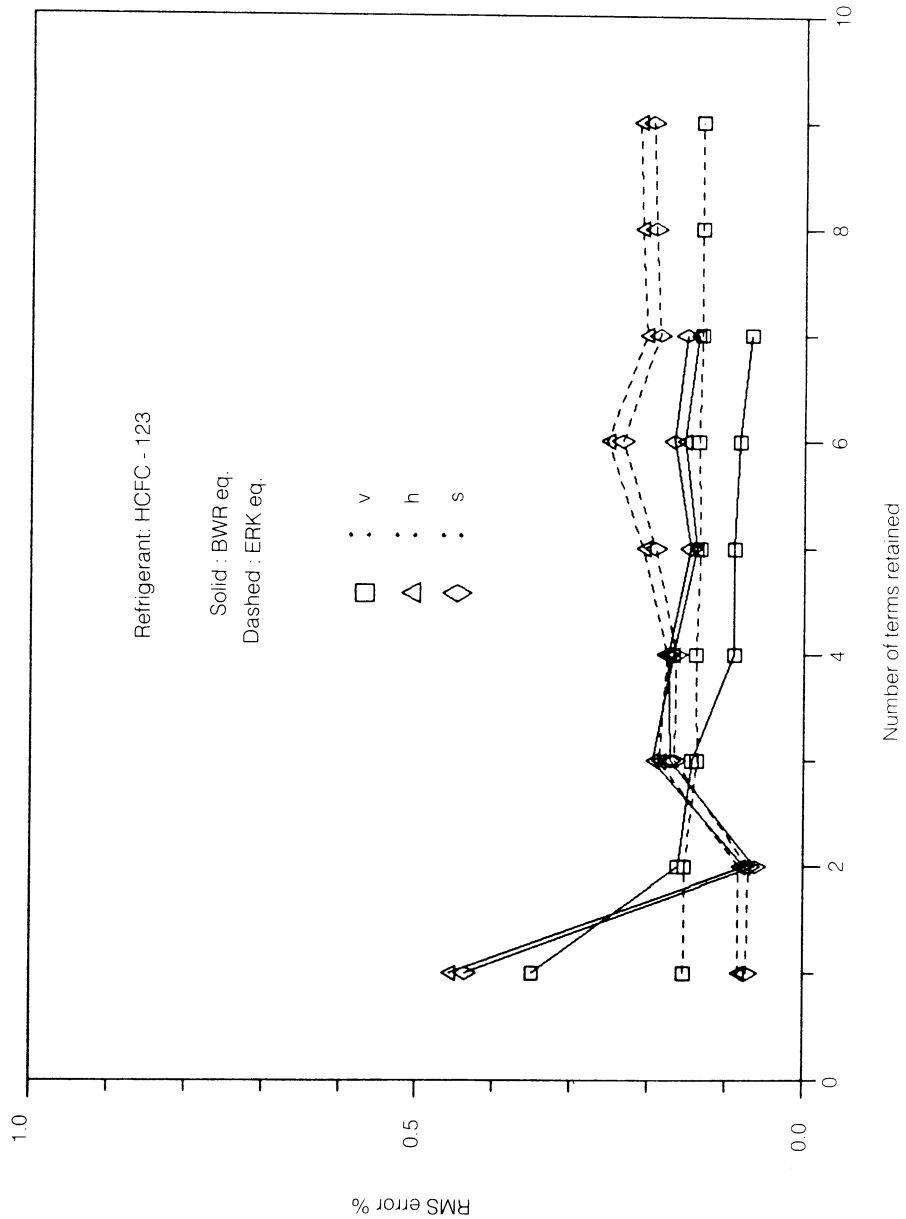

Fig. 6. Effect of the number of terms retained in the equation of state on the root mean square errors in the calculated properties of Refrigerant - 123.

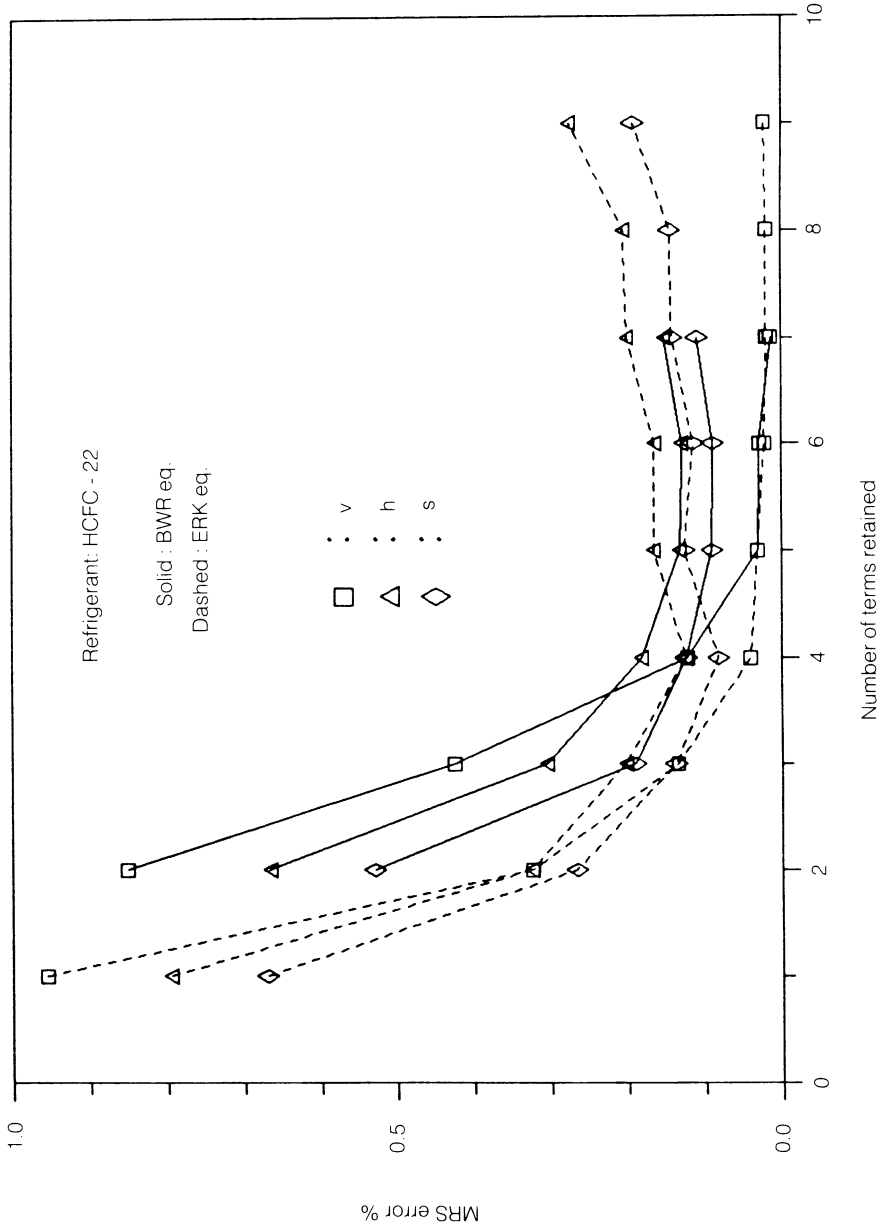

Fig. 7. Effect of the number of terms retained in the equation of state on the root mean square errors in the calculated properties of Refrigerant-22.

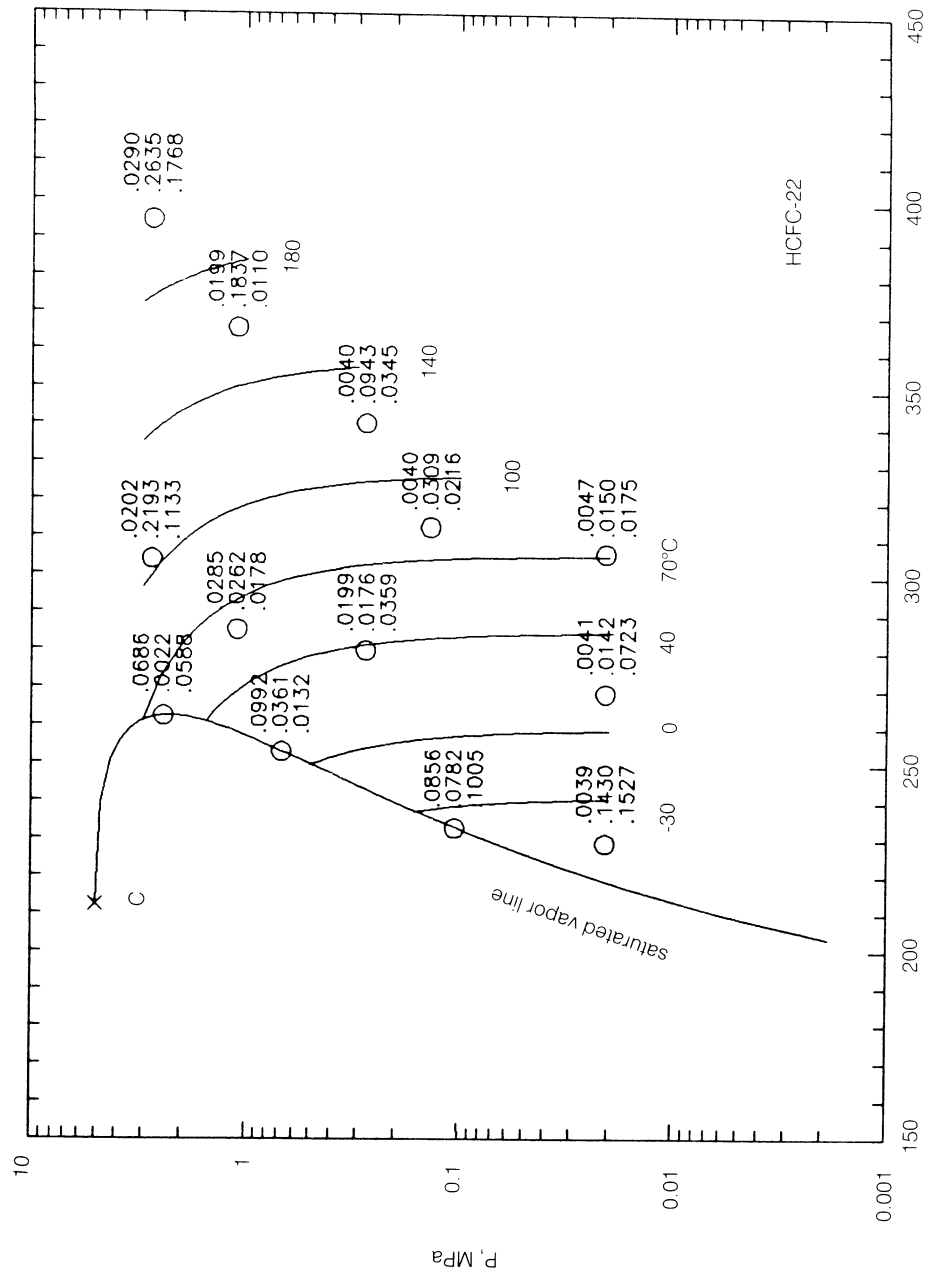

Fig. 8. Errors in properties calculated at selected points in the superheat region of Refrigerant-22, using the ERK equation of state with 4 polynomial terms.

The corresponding results for HCFC-22 are shown in Figs 7 and 8. The behavior of the rms of the percentage errors in υ,h and s with the number of terms retained in the ERK and BWR equation of state is similar to that reported earlier for HFC-134a. It appears that an ERK equation with 4 terms produces results with errors in υ,h and s comparable to the minimum errors obtained by using the BWR equation with larger number of terms. The percentage errors at sample points are displayed on the p - h chart in Fig. 8. Based on these results, we may expect a maximum error of 0.1% in υ, 0.26% in h and 0.18% in s in the range covered in Fig. 3. Again such errors are very small and are within the uncertainty of the values in the Table, [7]. Therefore, we also recommend the ERK equation with 4 terms and the present procedure to calculate the properties of HCFC-22. For the range considered, the coefficients of this equation are given in Table 2.

Summary and Conclusion

Because of their adverse effects on the ozone layer protecting the earth from harmful ultraviolet solar radiation, CFC refrigerants such as CFC-11 and CFC-12 will be phased out in the near future. HCFC refrigerants such as HCFC-22 are found to have much less ozone depletion potential and therefore they will not be phased out before the year 2020. Concerted effort by the industry produced two viable alternative refrigerants; HCFC-123 to replace CFC-11 and HFC-134a to replace CFC-12.

A computerized procedure developed earlier by the authors was adapted for the two new refrigerants HFC-134a and HCFC-123, and for HCFC-22. Starting from the tabulated p-v-T data at a number of base points, the coefficients of an equation of state are obtained. With the equation of state and a C_p relation, the enthalpy and entropy are calculated at any general point in the range covered by the base points. Two equations of state were investigated. The first is a simple extension of the Redlich-Kwong equation, proposed previously by the authors, in which one of the constants is replaced by a polynomial in powers of temperature. The second equation is the well known BWR equation. Maximum errors in computed υ,h and s around 0.3% or less should be expected over a wide range of pressures and temperatures covering possible working ranges of vapor compression systems employing these refrigerants. The present computer-based procedure is very convenient in thermal design or performance analysis saving effort and time and eliminating human error in interpolating tables and charts. The procedure can be built in on-line flow and thermal power measuring devices by utilizing digital technology.

Acknowledgement. The authors would like to express their thanks to Mr. Larry Butz

of the TRANE Co., La Crosse, Wisconsin, for kindly providing the ICI and DUPONT property data brochures and charts for the new refrigerants 123 and 134a, Refs. [5;6;8].

References

[1] Smithhart, E.L. *CFC's: Today There Are Answers.* La Crosse, Wisconsin: The Trane Co., July 1992.

[2] Abu-Abdou, K. and Zedan, M.F. "Comparative Study of some Equations of State for Computing Properties of Refrigerant-12." *Applied Energy,* 45, No. 4 (1993), 355-370.

[3] Black, W.Z. and Hartley, J.G. *Thermodynamics.* New York: Harper & Row Publishers, 1985.

[4] Gerald, C.F. and Wheatley, P.O. *Applied Numerical Analysis.* Reading, Massachusetts: Addison Wesley, 1984.

[5] ICI Chemicals & Polymers, Ltd. *Thermodynamic Properties of KLEA 134a, Brochure No. CP/25115/3 Ed/1191.* U.K., Cheshire: ICI Chemicals & Polymers, Ltd., Jan. 1992.

[6] TRANE Co. *R-123 Properties.* La Crosse, Wisconsin: Private communication, TRANE Co., 1993.

[7] Boltz, R.E. and Tuve, G.L. (Eds) *CRC Handbook of Tables for Applied Engineering Science,* 2nd ed. Roca Raton, Florida: CRC Press, 1973.

[8] ICI Chemicals & Polymers Ltd. *Physical Property Data KLEA 134a,* U.K., Cheshire: ICI Chemicals & Polymers Ltd., Jan. 1992.

إيجاد الخواص الديناميكيّة الحراريّة لوسائط التبريد الجديدة باستخدام معادلة حالة بسيطة

خليل أبو عبده و محمد فؤاد زيدان

قسم الهندسة الميكانيكيّة، كلية الهندسة، جامعة الملك سعود، ص.ب ٨٠٠، الرياض ١١٤٢١، المملكة العربية السعودية

(استلم في ١٩٩٣/٤/٣م ؛ قبل للنشر في ١٩٩٤/٥/١١م)

ملخص البحث. يُبْرز هذا البحث المقدرة الفائقة لصيغة معدّلة من معادلة ردليش ـ كوونج للحالة، والتي استبدلت فيها كثيرة حدود مؤلفة من قوى درجة الحرارة مكان أحد ثابتي معادلة الحالة الأصليّة، على التعبير بدقة عن العلاقة بين الضغط (p) ودرجة الحرارة (T) والحجم النوعي (υ) لكل من وَسيطي التبريد الجديدين HCFC-123 ، و HFC-134a ، ووسيط التبريد HCFC-22 . وهذان الوسيطان الجديدان هما البديلان اللذان جرى تطويرهما ليحلا على الترتيب محل وسيطي التبريد CFC-11 ، و CFC-12 المعروفين بكفاءتهما الحراريّة المرتفعة، ولكن أيضًا بمساهمتهما في تآكل طبقة الأوزون الجوي. وقد تّم تحديد معاملات كثيرة حدود الصيغة المعدّلة بدلالة الخواص الثلاثة ((P, υ, T)) عند عدد من النقاط المختارة تعرف بنقاط «القاعدة». واستنادًا إلى معادلة الحالة هذه بمعاملات معلومة وإلى علاقة معطاة للحرارة النوعيّة جرى تطوير طريقة منهجيّة حاسوبيّة لحساب خاصيتي الانثالبي والانتروبي. وقد أمكن بأربعة حدود فقط في كثيرة حدود معادلة الحالة المعدّلة تحقيق دقة عالية في نطاق واسع من قيم الضغط ودرجة الحرارة لوسائط التبريد الثلاثة التي تضمنتها الدراسة.