International Journal of Thermophysics, Vol. 16, No. 3, 1995

The Selection of International Standards for the Thermodynamic Properties of HFC-134a and HCFC-123[1]

S. G. Penoncello,[2,3] R. T Jacobsen,[2] K. M. de Reuck,[4] A. E. Elhassan,[4] R. C. Williams,[2] and E. W. Lemmon[2]

The objectives and activities of the International Energy Agency—Annex 18 are summarized. One of the goals of the Annex was to determine the formulations that best represent the thermodynamic properties of HFC-134a and HCFC-123. The formulations selected were those which accurately represented the experimental data and simultaneously exhibited thermodynamic consistency. Methods of comparison include analysis of the experimental data, statistical comparisons of values calculated from the property formulations to experimental values, and graphical analyses of the thermodynamic surface. The analytical methods used are summarized in this paper. The equations of state reviewed in these comparisons represented the most accurate formulations available in December 1992. Four equations of state were reviewed for HFC-134a and three equations of state were considered for HCFC-123. These equations represented the work of independent researchers in Germany, Japan, and the United States. The formulations selected as international standards are presented.

KEY WORDS: environmentally acceptable refrigerants; equation of state; thermodynamic properties; international standards.

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Center for Applied Thermodynamic Studies, University of Idaho, Moscow, Idaho 83844-1011, U.S.A.

[3] To whom correspondence should be addressed.

[4] IUPAC Thermodynamic Tables Project Centre, Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology, and Medicine, London SW7 2BY, United Kingdom.

1. INTRODUCTION

Annex 18 of the International Energy Agency (IEA) Heat Pump Programme was established to determine international standards for the thermophysical properties of environmentally acceptable refrigerants. The idea for this Annex was suggested at the "IEA Seminar on the CFC Problem," held in Rome, Italy, in May 1988. Researchers from the United States prepared and submitted several proposals for the establishment of the Annex to the IEA from 1988 to 1989. Preliminary approval of the Annex was given by the IEA in December 1989, and final approval was granted in March 1990. The Annex was approved for 3 years. The United States was appointed as operating agent. Other members countries that participate in the Annex are Austria, Canada, Germany, Japan, Norway, Sweden, and the United Kingdom.

One goal of the Annex is to determine property formulations that can be considered as international standards for the environmentally acceptable refrigerants. To meet this end, two surveys were conducted by the Annex to assess the current research being done in the areas of experimental measurement and correlation. Researchers from 15 countries, representing 61 research groups, responding. Information on current and planned experimental and analytical work for many refrigerants and refrigerant mixtures were collected. A report of the first survey was published in June 1991 [1]. An update to this survey was undertaken in late 1992, with a report to be published in late 1994.

Given the importance of HCFC-123 and, especially, HFC-134a, it is not surprising that a large quantity of property data has become available in a very short time. These data have, in turn, given rise to a number of equations of state for each of these fluids. The Annex participants decided to select an existing equation of state as a standard formulation for each fluid rather than attempt to develop a new one. The comparisons and evaluations of the available equations of state were assigned to two independent groups or "evaluators" in the United States and the United Kingdom. The evaluators presented their preliminary findings at the July 1992 meeting of Annex 18. At that meeting, the Annex made recommendations for further comparisons and evaluations and also decided to allow revisions to the equations and additions to the data sets reviewed, subject to a submission deadline of December 1992. Four equations of state for HFC-134a and three equations of state for HCFC-123 were evaluated. The final recommendations of the evaluators were presented at the April 1993 meeting of the Annex. "Scientific papers" published in the *Journal of Physical and Chemical Reference Data* detail the selected equations of state: that of Tillner-Roth and Baehr [2] for HFC-134a and the equation of Younglove and McLinden [3] for HCFC-123. These equations of state are to form the basis for international properties bulletins to be published by the International Institute of Refrigeration.

This paper summarizes the procedure used in selecting the equations of state. Thermodynamic properties calculated using candidate equations of state compared with existing experimental data are summarized in statistical form.

2. ANALYSIS OF EXPERIMENTAL DATA AND EQUATIONS OF STATE

A summary of the experimental data for HFC-134a and HCFC-123 is given in Table I. The sources reporting these data were reviewed and estimated uncertainties in the measurements were used to establish data quality. The equations of state considered are listed in Table II along with their critical properties. All experimental data, for each type of property, were compared with values calculated from each candidate equation of state. The selections of the equation of state that gave the best representation of the highest quality experimental data were based on the two final reports [9, 10] presented at the Annex meeting in April 1993. These contained detailed graphical comparisons for each equation of state with each set of experimental data. In addition, for each equation of state, graphs showing isobars on C_v–T (isochoric heat capacity), C_p–T (isobaric heat capacity), and w–T (speed of sound) plots were given as well as isotherms on μ–P (Joule–Thomson coefficient) and k–P (isentropic expansion coefficient) plots. Examples of these plots are given in Figs. 1 and 2 for the equations of state selected in this study. Plots of this type allow for the examination of the thermodynamic surface computed from each equation of state for discontinuities or anomalous behavior. Statistical comparisons were also made using the absolute average deviation (AAD), the bias (BIAS), the standard deviation (SDV), and the root-mean square deviation (RMS). The results of these statistical comparisons are summarized in Table III (HFC-134a) and Table IV (HCFC-123). The definitions of the statistics are based on the percentage deviation for any property, X,

$$\%\Delta X = 100\left(\frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}}\right) \tag{1}$$

Using this definition, the statistics above are defined as,

$$\text{AAD} = \frac{1}{n}\sum_{i=1}^{n} |\%\Delta X_i| \tag{2}$$

$$\text{BIAS} = \frac{1}{n}\sum_{i=1}^{n} (\%\Delta X_i) \tag{3}$$

Table I. Experimental Data for HFC-134a and HCFC-123

Data type	No. of points	Range of data		
		P (MPa)	T (K)	ρ (mol · dm^{-3})
	HFC-134a			
P-ρ-T	2235	0.09-70.9	180–453	0.02-15.7
C_P-P-T	271	0.04–30	253-523	—
C_V-ρ-T	150	—	187-343	11.0-15.2
w-P-T	626	0.01-75	179–420	—
Second virial coefficient	51	—	260–453	—
Joule-Thomson coefficient	108	0.3-20	333–423	—
Vapor pressure	452	—	211-374	—
Saturated liquid density	143	—	180-374	—
Saturated vapor density	57	—	294-374	—
Saturated liquid heat capacity	170	—	172-356	—
	HCFC-123			
P-ρ-T	657	0.12-34.5	176-523	0.05-11.5
C_P-P-T	145	0.50-3.2	276–440	—
C_V-ρ-T	79	—	196-340	9.3-11.2
w-P-T	243	0.05-75.7	283-373	—
Second virial coefficient	12	—	260–453	—
Vapor pressure	406	—	160–457	—
Saturated liquid density	196	—	174–457	—
Saturated vapor density	70	—	293–457	—
Saturated liquid heat capacity	92	—	160-304	—

Table II. Equations of State and Corresponding Critical Properties Considered in this Study

Ref.	Maximum pressure (MPa)	Temperature range (K)	T_c (K)^a	P_c (MPa)	ρ_c (kg · m^{-3})
		HFC-134a			
Piao et al. [4]	15	240–480	374.27	4.0635	508
Huber & McLinden [5]	70	172–450	374.179	4.056	513
Huber & Ely [6]	70	172–450	374.179	4.059	513
Tillner-Roth & Bahr [2]	70	172–455	374.18	—^{b}	508
		HCFC-123			
Piao et al. [7]	15	270-550	456.86	3.6655	556
Younglove & McLinden [3]	40	166-600	456.831	3.6618	550
JAR^c [8]	40	270-523	456.86	3.666	555

[a] Temperatures are reported on the ITS-90.

[b] Not available.

[c] Japanese Association of Refrigeration.

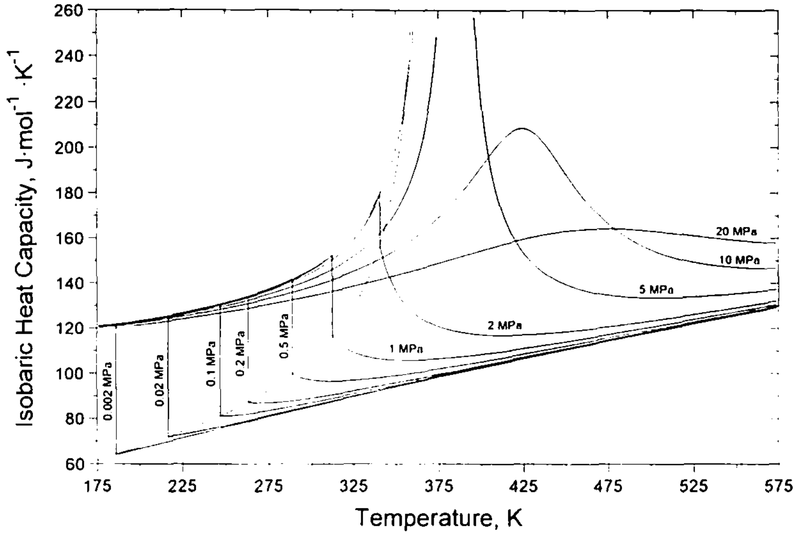

Fig. 1. Isobaric heat capacity vs temperature (C_p-T) plot computed using the fundamental equation of Tillner-Roth and Baehr [2] for HFC-134a showing the saturation curve (dashed line) and several isobars.

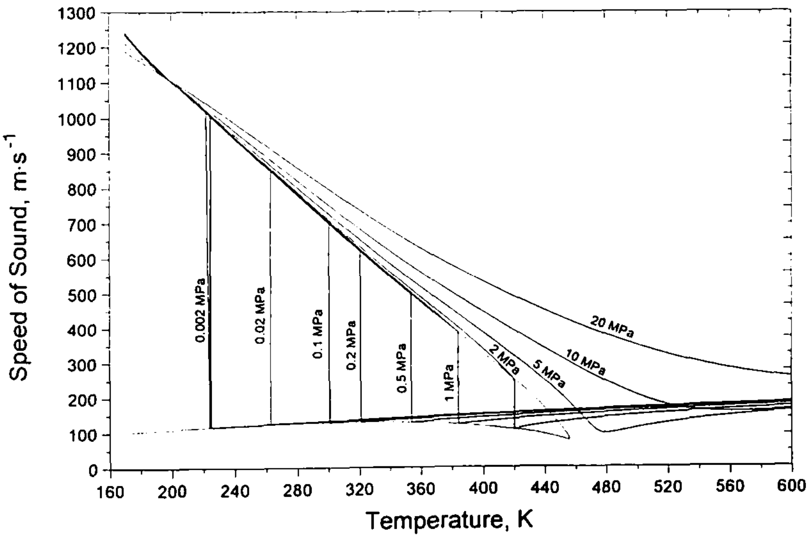

Fig. 2. Speed of sound vs temperature (w-T) plot computed using the equation of state of Younglove and McLinden [3] for HCFC-123 showing the saturation curve (dashed line) and several isobars.

Table III. Statistical Comparisons of Properties Calculated Using Candidate Equations of State to Experimental Data for HFC-134a

Data type	Equation of state	AAD	BIAS	SDV	RMS
P-ρ-T	Piao et al. [4]	0.275	−0.049	0.681	0.683
density deviations	Huber & McLinden [5]	0.234	−0.071	0.586	0.590
	Huber & Ely [6]	0.304	0.035	0.853	0.853
	Tillner-Roth & Baehr [2]	0.181	−0.097	0.512	0.521
P-ρ-T	Piao et al. [4]	0.435	0.293	0.756	0.809
pressure deviations	Huber & McLinden [5]	0.437	0.354	0.765	0.841
(critical region)	Huber & Ely [6]	0.470	0.181	0.783	0.802
	Tillner-Roth & Baehr [2]	0.335	0.277	0.741	0.789
C_v-ρ-T	Piao et al. [4]	0.381	−0.124	0.439	0.455
isochoric heat	Huber & McLinden [5]	0.367	0.179	0.399	0.436
capacity deviations	Huber & Ely [6]	0.305	0.035	0.382	0.383
	Tillner-Roth & Baehr [2]	0.403	0.281	0.430	0.512
C_p-P-T	Piao et al. [4]	0.880	0.536	1.549	1.636
isobaric heat	Huber & McLinden [5]	0.868	0.739	1.070	1.299
capacity deviations	Huber & Ely [6]	1.083	0.929	1.693	1.929
	Tillner-Roth & Baehr [2]	0.617	0.414	0.905	0.994
w-P-T	Piao et al. [4]	0.586	0.226	0.977	1.002
speed of sound	Huber & McLinden [5]	0.226	−01344	0.369	0.392
deviations	Huber & Ely [6]	0.194	−0.092	0.261	0.277
	Tillner-Roth & Baehr [2]	0.246	−0.188	0.418	0.458
Second virial	Piao et al. [4]	3.656	−3.045	2.929	4.206
coefficient	Huber & McLinden [5]	0.762	0.326	1.232	1.263
differences[a]	Huber & Ely [6]	0.802	0.390	1.684	1.714
	Tillner-Roth & Baehr [2]	1.047	0.238	1.836	1.834
μ-P-T	Piao et al. [4]	1.947	−1.122	2.361	2.604
Joule-Thomson	Huber & McLinden [5]	1.977	−1.082	2.587	2.792
coefficient	Huber & Ely [6]	2.042	−1.096	2.595	2.806
deviations	Tillner-Roth & Baehr [2]	1.810	−0.702	2.487	2.573
Vapor pressure	Piao et al. [4]	0.176	0.057	0.342	0.346
deviations	Huber & McLinden [5]	0.165	0.064	0.333	0.339
	Huber & Ely [6]	0.237	−0.012	0.358	0.358
	Tillner-Roth & Baehr [2]	0.165	0.052	0.337	0.341
Saturated liquid	Piao et al. [4]	0.433	−0.121	1.140	1.143
density deviations	Huber & McLinden [5]	0.313	0.077	0.989	0.989
	Huber & Ely [6]	0.410	0.186	1.046	1.059
	Tillner-Roth & Baehr [2]	0.276	−0.046	0.914	0.912
Saturated vapor	Piao et al. [4]	2.238	2.008	2.637	3.294
density deviations	Huber & McLinden [5]	1.296	0.443	2.266	2.288
	Huber & Ely [6]	1.288	0.242	2.265	2.257
	Tillner-Roth & Baehr [2]	1.265	0.763	2.112	2.227
Saturated liquid	Piao et al. [4]	0.983	0.226	1.247	1.264
heat capacity	Huber & McLinden [5]	0.679	−0.115	0.777	0.783
deviations	Huber & Ely [6]	0.791	−0.517	0.869	1.009
	Tillner-Roth & Baehr [2]	0.565	−0.306	0.877	0.926

[a] Second virial coefficient comparisons are based on differences ($dm^3 \cdot mol^{-1}$).

Table IV. Statistical Comparisons of Properties Calculated Using Candidate Equations of State to Experimental Data for HCFC-123

Data type	Equation of state	AAD	BIAS	SDV	RMS
P ρ T density deviations	Piao et al. [7]	0.570	−0.173	1.345	1.355
	Younglove & McLinden [3]	0.318	0.103	1.061	1.065
	JAR [8]	0.489	0.167	1.226	1.237
P ρ-T pressure deviations (critical region)	Piao et al. [7]	0.385	−0.235	0.546	0.590
	Younglove & McLinden [3]	0.271	−0.217	0.397	0.450
	JAR [8]	0.372	−0.199	0.438	0.478
C_v ρ T isochoric heat capacity deviations	Piao et al. [7]	5.563	−4.404	4.031	5.925
	Younglove & McLinden [3]	0.947	0.744	0.817	1.101
	JAR [8]	5.833	5.833	2.029	6.164
C_p P-T isobaric heat capacity deviations	Piao et al. [7]	2.546	1.926	2.330	3.017
	Younglove & McLinden [3]	0.814	0.811	0.349	0.882
	JAR [8]	3.101	3.101	1.773	3.569
w P-T speed of sound deviations	Piao et al. [7]	4.335	3.669	4.062	5.467
	Younglove & McLinden [3]	1.100	0.694	1.205	1.388
	JAR [8]	0.982	0.326	1.259	1.298
Second virial coefficient differences[a]	Piao et al. [7]	1.302	−1.124	1.106	1.537
	Younglove & McLinden [3]	3.222	−0.680	4.161	4.041
	JAR [8]	34.115	34.115	23.927	41.040
Vapor pressure deviations	Piao et al. [7]	0.575	−0.119	0.932	0.939
	Younglove & McLinden [3]	0.406	0.089	1.003	1.006
	JAR [8]	0.379	−0.123	0.706	0.716
Saturated liquid density deviations	Piao et al. [7]	0.455	−0.173	1.010	1.022
	Younglove & McLinden [3]	0.270	0.036	0.631	0.631
	JAR [8]	0.289	−0.011	0.863	0.861
Saturated vapor density deviations	Piao et al. [7]	1.366	0.536	2.081	2.134
	Younglove & McLinden [3]	0.949	−0.613	1.450	1.564
	JAR [8]	1.044	0.084	1.534	1.524
Saturated liquid heat capacity deviations	Piao et al. [7]	—[b]	—[b]	[b]	—[b]
	Younglove & McLinden [3]	0.888	−0.614	1.328	1.457
	JAR [8]	33.43	33.43	26.64	42.65

[a] Second virial coefficient comparisons are based on differences ($dm^3 \cdot mol^{-1}$).

[b] Deviations below 240 K exceed 100%.

$$\mathrm{SDV} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\%\Delta X_i - \mathrm{BIAS})^2} \tag{4}$$

$$\mathrm{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\%\Delta X_i)^2} \tag{5}$$

3. SELECTED EQUATIONS OF STATE

Based on the evaluation of the data and the graphical and statistical analyses of the equations of state outlined in the previous section, the equations of state selected as international standards were those by Tillner-Roth and Baehr [2] for HFC-134a and that by Younglove and McLinden [3] for HCFC-123.

The equation of state for HFC-134a developed by Tillner-Roth and Baehr [2] is explicit in dimensionless Helmholtz energy and is given as

$$\Phi(\delta, \tau) = \frac{A}{RT} = \Phi^0(\delta, \tau) + \Phi^r(\delta, \tau) \tag{6}$$

where $\delta = \rho/\rho_c$ and $\tau = T_c/T$. Φ^0 is the ideal gas contribution to the dimensionless Helmholtz energy and Φ^r is the residual part. The ideal gas portion is derived from the thermodynamic relation

$$A^o = \mathrm{U}^o - \mathrm{TS}^o \tag{7}$$

To write Eq. (7), an expression for the ideal gas heat capacity is required.

The residual portion of the dimensionless Helmholtz energy is given as

$$\Phi^r(\delta, \tau) = \sum_{k=1}^{21} a_k \delta^{i_k} \tau^{j_k} \exp(-\gamma \delta^{l_k}) \tag{8}$$

where a_k are constant coefficients determined by fitting experimental data. All thermodynamic properties can be found from this type of equation by differentiation. For example, pressure (P) and enthalpy (H) can be expressed as

$$\frac{P}{P_c} = \frac{\delta}{\tau Z_c} \left[1 + \delta \left(\frac{\partial \Phi^r}{\partial \delta} \right)_\tau \right] \tag{9}$$

and

$$\frac{H}{RT} = \tau \left[\left(\frac{\partial \Phi^o}{\partial \tau} \right)_\delta + \left(\frac{\partial \Phi^r}{\partial \tau} \right)_\delta \right] + \delta \left(\frac{\partial \Phi^r}{\partial \delta} \right)_\tau + 1 \tag{10}$$

Details of the development of this equation of state by Tillner-Roth and Baehr [2].

Younglove and McLinden [3] selected a 32-term modified Benedict–Webb–Rubin (MBWR) form to represent the thermodynamic properties of HCFC-123. The equation of state is given as

$$P = \sum_{n=1}^{9} a_n \rho^n + \exp(-\delta^2) \sum_{n=10}^{15} a_n \rho^{2n-17} \tag{11}$$

where $\delta = \rho/\rho_c$. The pressure (P) is given in bars and the density (ρ) is given in $\text{mol} \cdot \text{dm}^{-3}$. The a_n "coefficients" are temperature polynomials. In total, there are 32 constants in this equation of state. The a_n polynomials are given as

$$\begin{aligned}
a_1 &= RT \\
a_2 &= b_1 T + b_2 T^{1/2} + b_3 + b_4 T^{-1} + b_5 T^{-2} \\
a_3 &= b_3 T + b_7 + b_8 T^{-1} + b_9 T^{-2} \\
a_4 &= b_{10} T + b_{11} + b_{12} T^{-1} \\
a_5 &= b_{13} \\
a_6 &= b_{14} T^{-1} + b_{15} T^{-2} \\
a_7 &= b_{16} T^{-1} \\
a_8 &= b_{17} T^{-1} + b_{18} T^{-2} \\
a_9 &= b_{19} T^{-2} \\
a_{10} &= b_{20} T^{-2} + b_{21} T^{-3} \\
a_{11} &= b_{22} T^{-2} + b_{23} T^{-4} \\
a_{12} &= b_{24} T^{-2} + b_{25} T^{-3} \\
a_{13} &= b_{26} T^{-2} + b_{27} T^{-4} \\
a_{14} &= b_{28} T^{-2} + b_{29} T^{-3} \\
a_{15} &= b_{30} T^{-2} + b_{31} T^{-3} + b_{23} T^{-4}
\end{aligned} \tag{12}$$

The temperature (T) is given in kelvins. The details of the development of this equation of state are given in Younglove and McLinden [3].

4. CONCLUSIONS

The activities of the Annex have included surveys of research and compilations of property data for alternative refrigerants. An impartial evaluation of equations of state for HFC-134a and HCFC-123 has resulted in the selection of formulations for these fluids which are expected to become internationally accepted standards.

The equations of state by Tillner-Roth and Baehr [2] and Younglove and McLinden [3] are published in the journal cited. Slight modifications have been made to the versions of the equations of state used in this paper. The changes in the HFC-134a equation of state are to correct the low-pressure vapor heat capacity behavior based on a suggestion from the IEA Annex 18. The changes in the HCFC-123 equation of state are to fit recently measured vapor pressure data by Goodwin et al. [11] from 300 K to the critical point. These slight modifications in the equations of state are not expected to affect significantly the statistics presented in this paper.

REFERENCES

1. M. O. McLinden, W. M. Haynes, J. T. R. Watson, and K. Watanabe, *National Institute of Standards and Technology*, NISTIR 3969 (1991).
2. R. Tillner-Roth and H. D. Baehr, *J. Phys. Chem. Ref. Data* **23**(5):657 (1994).
3. B. A. Younglove and M. O. McLinden, *J. Phys. Chem. Ref. Data* **23**(5):731 (1994).
4. C.-C. Piao, M. Noguchi, H. Sato, and K. Watanabe, personal communication (1992).
5. M. L. Huber and M. O. McLinden, *Proceedings International Refrigeration Conference* (Purdue University, 1992).
6. M. L. Huber and J. F. Ely, *Int. J. Refrig.* **15**(6):393 (1992).
7. C.-C. Piao, H. Sato, and K. Watanabe, *Fluid Phase Equil.* **80**:87 (1992).
8. Japanese Association of Refrigeration, *Thermophysical Properties of Environmentally Acceptable Fluorocarbons—HFC-134a and HCFC-123* (1990).
9. S. G. Penoncello, R. T. Jacobsen, R. C. Williams, and E. W. Lemmon, *Equation of State Comparisons for HFC-134a and HCFC-123* (University of Idaho, Moscow, 1993).
10. A. E. Elhassan, R. J. B. Craven, and K. M. de Reuck, *Comparisons of Equations of State with Experimental Data for R134a and R123*, IUPAC Thermodynamic Tables Project Centre, London, England (1993).
11. A. R. H. Goodwin, D. R. Defibaugh G. Morrison, and L. A. Weber, *Int. J. Thermophys.* **13**:9 (1992).