International Journal of Thermophysics, Vol. 16, No. 1, 1995

Application of a New Selection Algorithm to the Development of a Wide-Range Equation of State for Refrigerant R134a[1]

K. B. Shubert[2] and J. F. Ely[2,3]

Refrigerant R134a (1,1,1,2-tetrafluoroethane) is a leading substitute for refrigerant R12. As such, there has been worldwide activity to develop accurate wide-range equations of state for this fluid. In this study, we have developed a new selection algorithm for determining high-accuracy equations of state in the Helmholtz representation. This method combines least-squares regression analysis with simulated annealing optimization. Simulated annealing, unlike stepwise regression, allows for the controlled acceptance of random increases in the objective function. Thus, this procedure produces a computationally efficient selection algorithm which is not susceptible to the function-space local-minima problems present in a purely stepwise regression approach. Two equations are presented in this work and compared against experimental data and other high-accuracy equations of state for R134a. One equation was produced strictly by using stepwise a regression algorithm, while the other was produced using the simulated-annealing selection algorithm. In both cases the temperature dependence of the equations was restricted to have no terms whose exponents were greater than five.

KEY WORDS: equation of state; R134a; refrigerants; simulated annealing; stepwise regression; thermodynamic properties.

1. INTRODUCTION

Refrigerant R134a (1,1,1,2-tetrafluoroethane) is currently the leading substitute for R12 (dichlorodifluoromethane) as a working fluid in refrigeration and heat-pump systems. Since the Montreal Protocol of 1987 [1],

---

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

[2] Department of Chemical Engineering and Petroleum Refining, Colorado School of Mines, Golden, Colorado 80401-1887, U.S.A.

[3] To whom correspondence should be addressed.

0195-928X/95/0100-0101$07.50/0

which dictated the gradual replacement of chlorofluorocarbons (CFCs) with substances less detrimental to the ozone layer, extensive data collection and modeling of thermophysical properties of potential replacements have been undertaken. The need for accurate representation of the thermodynamic behavior of these new refrigerants is particularly important to the refrigeration industry in order to optimize new equipment design using these compounds.

From a scientific perspective, the large quantity of high-accuracy R134a data has resulted in the compound's being one of the best measured fluids available and it is therefore an optimal choice for theoretical work in equation-of-state development. We also note that R134a is a good candidate for a reference fluid in corresponding states theory for ethane based refrigerants [2]. This use, however, places restrictions on the temperature dependence of the equation of state.

This particular study presents two equations of state developed for R134a from recent thermodynamic measurements. The first equation was developed by means of a new selection algorithm which is based on simulated-annealing optimization. This algorithm incorporates random exchange of potential equation-of-state terms to guard against minimization to a local optima. The second equation was developed using the more conventional stepwise-regression algorithm of Wagner [3] and de Reuck and Armstrong [4]. Both equations were restricted to have temperature-dependent terms whose exponents did not exceed five (i.e., $T^{\pm 5}$). The two equations are compared both with experimental data and with three other published equations of state.

2. EXPERIMENTAL DATA

Since 1989, the R134a data available in the literature have been increasing at a rapid rate. There are extensive pressure–volume–temperature (PVT) measurements, covering temperature–pressure ranges from 180 to 450 K and 0.1 to 70 MPa, both in single-phase regions and along the saturation boundary (see papers cited in Refs. 5 and 6). Single-phase sound velocity has been measured in both the vapor and the liquid regions [7, 8], as has the isobaric heat capacity [9, 10]. Second virial coefficient data have been derived from PVT measurements or sound velocity data [7, 11, 12], and Magee [13] reported measurements of isochoric heat capacity in the liquid region. More complete listings of R134a experimental data are published elsewhere in the literature [5, 6].

Table I lists those data sets which were used in this study. The data sets marked with an asterisk denote those sets used in developing the equations of state. Those without an asterisk were used for comparisons only.

Table I. Thermophysical Experimental Data Used in Fitting and Comparing Equations of State for R134a

Author(s)	Year	No. pts.	Pressure range (MPa)	Temperature range (K)	Density range ($mol \cdot dm^{-3}$)
Single-Phase PVT data					
Hou et al. [24]	1990	429	0.75–70.9	180–380	6.45–15.7
Klomfar et al. [25]	1993	66	1.05–56.3	205–310	12.3–15.7
Magee [13]	1992	150	2.58–34.9	187–343	11.1–15.2
*Morrison and Ward [22]	1991	131	0.70–5.78	279–367	8.26–12.7
*Tillner-Roth and Baehr [11]	1992	411	0.09–16.4	293–453	0.02–9.94
*Tillner-Roth and Baehr [23]	1993	432	0.73–15.8	243–413	1.13–14.0
*Weber [12]	1989	69	0.22–5.33	321–423	0.07–2.33
Virial data					
*Goodwin and Moldover [7]	1990	15		235–440	
*Tillner-Roth and Baehr [23]	1992	9		293–453	
*Weber [12]	1989	11		323–423	
Heat capacity (C_v)					
*Magee [13]	1992	150		187–343	
Heat capacity (C_p)					
Nakagawa et al. [9]	1990	47	0.04–30	253–523	
Saitoh et al. [10]	1990	31	1.0–3.0	276–356	
Sound velocity					
*Goodwin and Moldover [7]	1990	94	0.01–0.6	233–340	
*Guedes and Zollweg [8]	1992	206	0.13–70	179–380	

Ideal-gas heat capacities were obtained from the correlation developed by McLinden et al. [14], based on the sound velocity data of Goodwin and Moldover [7].

3. EQUATIONS OF STATE

In this work, the two equations of state presented are developed from a stochastic selection algorithm (SAEOS) and from the stepwise regression technique of Wagner [3], modified by de Reuck and Armstrong [4] (STWEOS). These results are compared against three equations of state: the Tillner-Roth and Baehr (TRB94) scientific formulation [6], the Huber and Ely (HE92) Schmidt–Wagner [15] equation [7], and the Huber and McLinden (HM92) modified Benedict–Webb–Rubin [17] equation [18]. All of these equations are wide-ranging and are applicable in both the liquid and the vapor regions.

As with the HE92 and TRB94, the STWEOS and SAEOS represent the R134a thermodynamic surface in terms of the Helmholtz free energy as a function of dimensionless temperature and density. An advantage of the Helmholtz formulation over the pressure formulation is that it allows representation of other thermodynamic properties by differentiation. For the new equations, the dimensionless molar Helmholtz free energy is expressed as the sum of ideal and residual terms:

$$\frac{A(\rho, T)}{RT} = \Phi^{\text{ideal}}(\delta, \tau) + \Phi^{\text{r}}(\delta, \tau) \tag{1}$$

where $\delta = \rho/\rho_c$, $\tau = T_c/T$, and $R = 0.08314471\ \text{bar} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is the ideal gas constant. The assumed functional representation of the dimensionless residual Helmholtz free energy is

$$\Phi^{\text{r}}(\delta, \tau) = \sum_{n=1}^{N} a_n \tau^{i_n} \delta^{j_n} \exp(-\delta^{k_n}) \tag{2}$$

where N is the total number of terms in the expression. The ideal contribution Φ^{ideal} is calculated from the McLinden et al. heat capacity correlation [14] and the ideal-gas law.

The equations of state determined in this work (SAEOS and STWEOS) were developed by a weighted, linear least-squares regression and multiproperty fit of the asterisked data sets in Table I. The critical point used was $T_c = 374.18$ K, $\rho_c = 4.9798\ \text{mol} \cdot \text{dm}^{-3}$, and $P_c = 40.56$ bar. All temperatures are on the IPTS-90 temperature scale. Fitting was accomplished by minimizing the weighted sum of squares and constraining the regression to the critical point. Additionally, the term bank of 138 terms was restricted to temperature powers whose magnitudes were no greater than five to force a simpler and more physically realistic regression result. The selection methods were initiated from the normal equations, as in a traditional linear least-squares fit.

In the stepwise-regression algorithm used to produce STWEOS, the terms with the highest correlation to the dependent variable are added to the equation one at a time. The statistical significance of each term and of the equation as a whole is measured after each permutation of the regression equation. Similarly, terms of the least significance are removed from the equation, or term exchanges may take place. The result is a selection algorithm which balances minimizing the sum of squares with statistical analysis of equation significance. The minimization is considered complete when the sum of squares cannot be significantly improved by adding or exchanging any terms.

The stochastic selection algorithm incorporated was adapted from the simulated annealing method developed by Kirkpatrick et al. [19] and independently by Cerny [20]. Simulated annealing has strong appeal as a Monte Carlo method of optimization due to its simple nature and its success in such areas as network design and biology. The essence of simulated annealing is the Metropolis algorithm [21], which describes the probability of success, $P\{r\}$, for a proposed change in energy state with the Boltzmann distribution:

$$P\{r\} \propto \exp\left(\frac{-\Delta E}{kT}\right) \tag{3}$$

where ΔE is the change in energy between two states, k is Boltzmann's constant, and T is the "annealing temperature," which decreases with time in an annealing situation. The principle of the algorithm is that if ΔE is less than zero, the state change is automatically accepted. If ΔE is greater than zero, the state change is accepted with the above probability. The result of the algorithm is a Boltzmann distribution of the total energy of the system. In a combinatorial optimization problem, ΔE is replaced by the difference between two configurations of the objective function and T is replaced by a control parameter, subject to an annealing schedule.

Table II. SAEOS and STWEOS Terms and Coefficients

	SAEOS				STWEOS			
No.	a_n	i_n	j_n	k_n	a_n	i_n	j_n	k_n
1	6.9039853 E−1	0	1	0	8.7008031 E−1	0	1	0
2	−1.6405351 E+0	1.5	1	0	−1.5873026 E+0	1.5	1	0
3	−1.1941330 E−2	1.5	2	0	−2.8826680 E−2	−1	2	0
4	1.6890082 E−2	0	4	0	1.2562965 E−2	−1	3	0
5	1.7473678 E−4	1	7	0	1.2770479 E−3	0	6	0
6	−8.2963189 E−2	4	1	1	5.7580805 E−5	2	7	0
7	−1.7060781 E−1	0	1	2	−6.2671873 E−7	5	7	0
8	−1.4933930 E−1	5	1	2	−3.7667774 E−1	0	1	1
9	7.1277622 E−1	0	2	2	−1.3389008 E−1	4	1	1
10	−1.3722043 E+0	1	2	2	−7.2323198 E−1	1	2	1
11	2.4430200 E+0	3.5	2	2	3.2882140 E−2	3	2	1
12	−1.7255335 E+0	4.5	2	2	−1.2479886 E−1	2	4	1
13	−1.4123652 E−1	2	3	2	1.8035927 E+0	5	1	2
14	−7.5690611 E−4	3	8	2	−1.7009306 E+0	4.5	2	2
15	1.2659876 E−4	0	11	2	−6.5134228 E−2	5	2	2
16	1.6002802 E−4	3	11	2	2.5956210 E−2	2	3	2
17	−3.1140163 E−1	3	0	2	2.1963997 E−4	4	5	2
18	4.0580402 E−2	4	0	2	1.4469705 E−4	2	9	2
19	1.4007341 E−1	3	2	1	−2.3262905 E−3	3	11	2
20	2.0237533 E−1	1	0	2	4.5489573 E−1	0	2	4

In our particular application, simulated annealing was incorporated by presetting the number of terms in the regression equation, then allowing the annealing process to accept or reject term exchanges as described above. The weighted sum of squares was the objective function and different terms in the equation of state represented different configurations. The proposed exchange was selected at random, and the annealing schedule was controlled by proportionally decreasing the control parameter every 100 attempted exchanges. The two resulting forms of the dimensionless Helmholtz free energy for SAEOS and STWEOS are presented in Table II, respectively, where a_n, i_n, j_n, and k_n are defined in Eq. (2).

4. RESULTS

4.1. Ancillary Equations

In order to ensure accurate representation of the saturation boundary, fitting of the saturation vapor and liquid densities and of the vapor pressure was accomplished outside of the multiproperty regression by correlating available saturation data to functions of temperature. These correlations were then used to create data sets of temperature, vapor pressure, and liquid and vapor densities, and these values were used in the regression matrix. The forms of these saturation equations are as follows.

Saturation pressure, P_σ:

$$\ln(P_\sigma) = g_1(1-\tau)^{1.9} + g_2 + \frac{g_3}{\tau} + g_4\tau + g_5\tau^2 + g_6\tau^3 \tag{4}$$

Saturated liquid density, ρ_{σ_L}:

$$\rho_{\sigma_\mathrm{L}} = \rho_\mathrm{c}\left(1 + \frac{g_1(1-\tau)^{0.35} + g_3(1-\tau)^2 + g_4(1-\tau)^3}{1 + g_2(1-\tau)^{0.65}}\right) \tag{5}$$

Table III. Coefficients for Ancillary Saturation Equations

Property	P_σ, Eq. (4)	ρ_{σ_L}, Eq. (5)	ρ_{σ_V}, Eq. (6)
g_1	1.3666083 E+1	2.1566052 E+0	2.8926695 E+1
g_2	1.3070610 E+1	−3.2735034 E−1	−9.4576921 E+1
g_3	−1.1067436 E+1	−5.8559510 E−1	1.0579216 E+2
g_4	2.3146704 E+0	5.5860169 E−1	−4.0973758 E+1
g_5	4.0365344 E+0		
g_6	−4.6509393 E+0		

Saturated vapor density, $\rho_{\sigma v}$:

$$\rho_{\sigma v} = \frac{P_\sigma}{RT}\Bigg(1 + \tau(z_c - 1)\left(\frac{P_\sigma}{P_c}\right) \times \Bigg(1 + \left(1 - \frac{1}{\tau}\right)^{0.35}\left(g_1 + \frac{g_2}{\tau} + \frac{g_3}{\tau^2} + \frac{g_4}{\tau^3}\right)\Bigg)\Bigg)^{-1} \tag{6}$$

The constants for these equations are given in Table III.

4.2. Sound Velocity

Experimental sound velocity, which is typically of a very high accuracy, is nonlinear in the equation-of-state parameters. It was included in the regression matrix by using a previously fit equation of state to create a series of pressure derivative data with respect to density $(\partial P/\partial \rho)_T$ from the measured sound velocity data and calculated heat capacity ratio. This linearization procedure gave a $(\partial P/\partial \rho)_T$ data set, which was then incorporated into the fitting routine. Iteration between the $(\partial P/\partial \rho)_T$ data file and the regression equation coefficients is done until there is good agreement (convergence) between sequential $(\partial P/\partial \rho)_T$ data files. Isobaric heat capacity, which also has a nonlinear relationship to the equation-of-state parameters, was not used in fitting due to its lower experimental accuracy.

4.3. Comparisons

Statistical comparisons were made between each equation of state and each data set using percentage deviations, Γ, calculated in terms of the experimental data:

$$\Gamma = 100\,\% \left(\frac{\Pi(\mathrm{EOS}) - \Pi(\mathrm{EXP})}{\Pi(\mathrm{EXP})}\right) \tag{7}$$

where Π represents a given property and (EOS) and (EXP) refer to equation-of-state and experimental values, respectively. The statistics calculated from these deviations are the average absolute deviation (AAD), the average deviation (BIAS), and the root-mean-square (RMS) deviation.

Table IV presents the statistical results found for the SAEOS and STWEOS along with those for the three previous equations of state: TRB94, HE92, and HM92. The first group of entries in Table IV represents those PVT data sets which were used in the regression analysis. The second group is composed of those data sets which are presented for comparison.

Table IV. Statistical Comparison of the Equations of State to Experimental Data

Data type	STWEOS			SAEOS			TRB94			HM92			HE92		
	AAD	Bias	RMS	AAD	Bias	RMS	AAD	Bias	RMS	AAD	Bias	RMS	AAD	Bias	RMS
Primary PVT															
M&W [22]	0.071	0.034	0.116	0.072	0.031	0.119	0.076	0.044	0.119	0.061	0.008	0.120	0.063	−0.003	0.135
TRB92 [11]	0.054	0.010	0.145	0.038	−0.003	0.081	0.028	−0.008	0.091	0.086	0.000	0.227	0.125	−0.028	0.542
TRB93 [23]	0.067	−0.010	0.210	0.055	−0.007	0.194	0.043	−0.015	0.138	0.190	−0.088	0.362	0.452	−0.391	1.965
WEB [12]	0.092	0.080	0.075	0.065	0.049	0.070	0.085	0.080	0.079	0.076	0.042	0.093	0.169	0.127	0.177
Secondary PVT															
HOU [24]	0.183	0.183	0.160	0.175	0.175	0.161	0.183	0.183	0.160	0.134	0.099	0.158	0.113	−0.057	0.140
KLOM [25]	0.057	−0.057	0.032	0.063	−0.063	0.038	0.063	−0.063	0.038	0.193	−0.193	0.065	0.198	−0.198	0.072
MAG [13]	0.102	0.101	0.037	0.100	0.100	0.036	0.106	0.106	0.037	0.071	−0.007	0.083	0.075	−0.004	0.087
PVT—all	0.097	0.058	0.175	0.087	0.052	0.159	0.085	0.054	0.149	0.126	−0.004	0.246	0.206	−0.004	0.246
Saturation properties															
P_σ	0.089	−0.017	0.147	0.207	0.131	0.313	0.108	0.068	0.218	0.041	−0.004	0.070	0.120	−0.039	0.146
ρ_{σ_L}	0.047	−0.012	0.168	0.058	−0.025	0.267	0.019	−0.011	0.059	0.019	−0.018	0.068	0.067	0.065	0.248
ρ_{σ_V}	0.178	−0.085	0.258	0.340	0.078	0.516	0.196	−0.012	0.316	0.179	−0.052	0.237	0.554	0.330	0.545
Other data types															
2nd Virial	0.350	0.014		0.376	0.012		1.341	1.025		0.448	−0.059		0.330	0.036	
C_v	0.485	−0.377	0.403	0.538	−0.415	0.426	0.359	−0.238	0.384	0.367	−0.179	0.398	0.305	−0.034	0.381
C_p	0.567	−0.552	0.299	0.573	−0.554	0.367	0.621	−0.611	0.280	0.674	−0.655	0.412	0.680	−0.611	0.504
Sound	0.112	0.030	0.333	0.179	0.068	0.395	0.169	0.046	0.424	0.200	0.010	0.380	0.158	−0.046	0.245

The other two groups of data are saturation properties, compared against correlations presented in Eqs. (4)–(6), and second virial coefficient, heat capacity, and sound velocity statistics.

Both the STWEOS and the SAEOS have comparable fits in PVT to any of the other equations of state, particularly with regard to data sets [22] and [12]. TRB94 does a superb job of fitting PVT data sets [23] and [11], but STWEOS and, particularly, SAEOS do well compared to HE92 and HM92. In general, SAEOS does a better job of representing PVT data than STWEOS, especially for those data sets used in the fitting routine. In the PVT data sets [24], [25], and [13], which were used for comparisons only, STWEOS and SAEOS have comparable statistics to TRB94, and overall perform equally well as the HM92 and HE92 equations. SAEOS's major strength is in the PVT results.

As mentioned previously, the SAEOS equation was produced using simulated annealing, and it is evident that there were improvements over STWEOS in the PVT fits. This did, however, give rise to sacrifices in the representation of other properties. As a result, the equation resulting from stepwise regression is a better overall equation, and further discussion of comparisons will emphasize STWEOS.

With regard to the saturation pressure and vapor density, STWEOS does comparably or better than any of the other equations. It is in the neighborhood of the other equations in saturated liquid density—well within the experimental uncertainty of the data. STWEOS is comparable to HE92 and HM92 in the second virial coefficient, and is superior to TRB94. Isochoric heat capacity is not quite as good as the other equations, but the predicted isobaric heat capacity is slightly better. The sound velocity fit for STWEOS is superior to that obtained with any of the other models.

5. CONCLUSIONS

The coefficients resulting from two different selection algorithms for a multiproperty fit of experimental PVT, saturation properties, sound velocity, second virial coefficient, and isochoric heat capacity are presented. New coefficients for the ancillary for saturated liquid density are also presented. Comparisons with experimental data and with three other equations of state are also given. The two new equations are in the residual, dimensionless Helmholtz free energy representation and have been restricted to have temperature-dependent terms whose exponents did not exceed five (i.e., $T^{\pm 5}$). The simulated-annealing selection algorithm seems to have potential as a regression technique, but in this particular application, its major success was in realizing very accurate PVT fits, accompanied by a small sacrifice in the accuracy of the derived properties. Other weighting schemes may minimize this effect.

ACKNOWLEDGMENTS

The authors acknowledge Drs. Tillner-Roth and Baehr for making their scientific equation-of-state formulation available for comparison prior to publication. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DE-FG02-92-ER14294.

REFERENCES

1. Montreal Protocol on Substances that Deplete the Ozone Layer: Final Act, UNEP (1987).
2. M. L. Huber and J. F. Ely, *Int. J. Refrig.* **18**:1 (1994).
3. W. Wagner, A New Correlation Method for Thermodynamic Data Applied to the Vapour-Pressure Curve of Argon, Nitrogen and Water, *Fortschr.-Ber. VDI-Z*, Reihe 3, Nr. 39 (1977).
4. K. M. de Reuck and B. Armstrong, *Cryogenics* **19**:505 (1979).
5. S. G. Penoncello, R. T. Jacobsen, R. C. Williams, and E. W. Lemmon, IEA-Annex 18: Equation of State Comparisons for HFC-134a and HCFC-123 (1993).
6. R. Tillner-Roth and H. D. Baehr, *J. Phys. Chem. Ref. Data* (in press).
7. A. R. H. Goodwin and M. R. Moldover, *J. Chem. Phys.* **93**:2741 (1990).
8. H. J. R. Guedes and J. A. Zollweg, *Int. J. Refrig.* **15**:381 (1992).
9. S. Nakagawa, H. Sato, and K. Watanabe, *27th Natl. Heat Transfer Symp., Japan* (1990), p. 421.
10. A. Saitoh, S. Nakagawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **35**:107 (1990).
11. R. Tillner-Roth and H. D. Baehr, *J. Chem. Thermodyn.* **24**:413 (1992).
12. L. A. Weber, *Int. J. Thermophys.* **10**:617 (1989).
13. J. W. Magee, *Int. J. Refrig.* **15**:372 (1992).
14. M. O. McLinden, J. S. Gallagher, L. A. Weber, G. Morrison, D. Ward, A. R. H. Goodwin, M. R. Moldover, J. W. Schmidt, H. B. Chae, T. J. Bruno, J. F. Ely, and M. L. Huber, *ASHRAE Trans.* **95**:263 (1989).
15. R. Schmidt and W. Wagner, *Fluid Phase Equil.* **19**:175 (1985).
16. M. L. Huber and J. F. Ely, *Int. J. Refrig.* **15**:393 (1992).
17. R. T. Jacobsen and R. B. Stewart, *J. Phys. Chem. Ref. Data* **2**:757 (1973).
18. M. L. Huber and M. O. McLinden, *Proc. Int. Refrig. Conf.*, Purdue University (1992), pp. 453–462.
19. S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, *Science* **220**:671 (1983).
20. V. Cerny, *J. Opt. Theory Appl.* **45**:41 (1985).
21. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, and A. H. Teller, *J. Chem. Phys.* **21**:1087 (1953).
22. G. Morrison and D. K. Ward, *Fluid Phase Equil.* **62**:65 (1991).
23. R. Tillner-Roth and H. D. Baehr, *J. Chem. Thermodyn.* **25**:277 (1993).
24. H. Hou, B. H. Gammon, K. N. Marsh, and J. C. Holste, *Int. J. Refrig.* **15**:365 (1990).
25. J. Klomfar, J. Hruby, and O. Sifner, *Int. J. Thermophys.* **14**:727 (1993).