Thermochimica Acta, 82 (1984) 263–275
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMPARISON OF BENEDICT–WEBB–RUBIN AND BACK EQUATIONS OF STATE FOR USE IN *P–V–T* CALCULATIONS

P.P. CHANDNANI, A. CHAKMA and J. LIELMEZS

Department of Chemical Engineering, The University of British Columbia, Vancouver, B.C. V6T 1W5 (Canada)

(Received 25 June 1984)

ABSTRACT

By means of the available experimental gas and liquid state volumetric data, the relative predictive accuracy of the Benedict–Webb–Rubin and BACK equations was compared at the low, intermediate and critical state range of temperatures and pressures for methane, ethane and ethylene.

The average absolute volumetric deviation percent values calculated over the $T-P$ range studied, showed that for both the BACK equation and the simpler Benedict–Webb–Rubin equation their accuracy levels increase when both pressure and temperature decrease; but the BACK equation proves superior for calculations performed at the critical and in the liquid states.

INTRODUCTION

The need for accurate prediction of volumetric properties of industrially important fluids is increasing rapidly in process analysis. Equations describing these properties range from simple one- or two-constant expressions to complex equations with more than 50 constants. Even if the complex polynomials represent a more precise description of $P-V-T$ data, their application can require difficult and time consuming iterative procedures. Shorter equations, on the other hand, may be less accurate but are simpler to use thus consuming less calculation time.

The Benedict–Webb–Rubin equation [1–6] is one of the intermediate, noncubic in density, equations of state which are used for high-precision work, and which has proved to be highly successful in providing a good description of the thermodynamic behavior of real fluids for both vapor and liquid phases [7–12,21].

On the other hand, the more complex BACK (Boublik–Alder–Chen–Kreglewski) equation of state has been found capable of accurately describing the phase equilibria of some selected pure fluids and their mixtures [13–19].

0040-6031/84/$03.00

In this work we have comparatively studied the performance of the Benedict–Webb–Rubin equation versus the more complex BACK equation in fluid property estimation in terms of the predictive accuracy of the state equation and the relative computer time (CPU seconds) needed to complete the programmed iterative processes.

EQUATIONS OF STATE

Benedict–Webb–Rubin (BWR) equation

The BWR equation of state is [1–12,21]

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^2}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \tag{1}$$

As a modification of the Beattie–Bridgeman equation, the BWR equation was obtained empirically by curve-fitting the isometrics of the $(P - RT\rho)/\rho^2$ vs. T plot. The BWR equation has a sufficient number of constants to allow accurate correlations [1–12,21]. As a matter of fact, for systems for which the constants and interaction coefficients needed are available, the BWR equation is highly reliable [1–12,21]. It is interesting to note that the findings of this work indirectly confirm assertions made by Lielmezs and co-workers

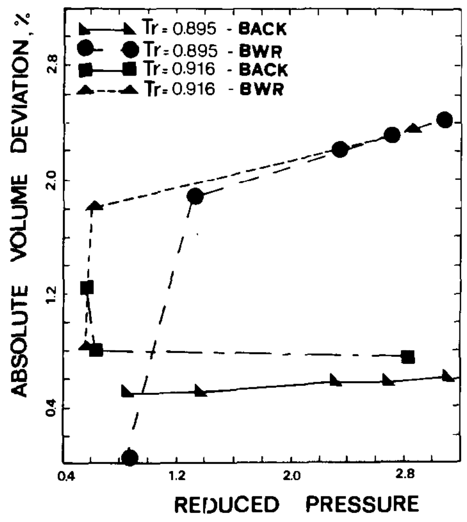

Fig. 1. Comparison of absolute volume deviation percent of BACK and BWR equations for methane at close to critical state temperatures and supercritical state pressures.

[21] that the overall accuracy of the BWR equation may be improved if more reliable constant sets are generated, and that in terms of the available constants, the BWR equation of state is found less reliable in the critical region (see also Table 2, Figs. 1–5).

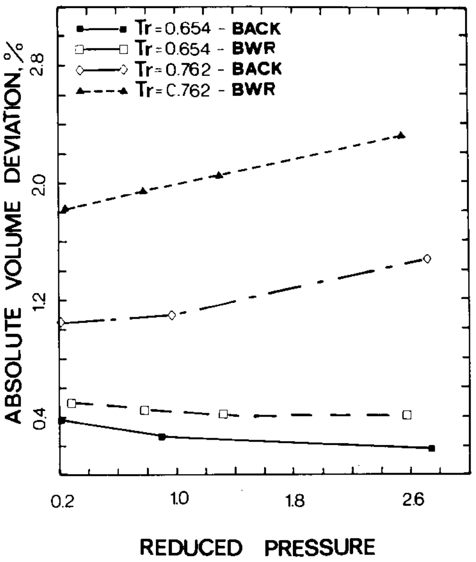

Fig. 2. Comparison of absolute volume deviation percent of BACK and BWR equations for methane at intermediate range temperatures over a wide range of pressures.

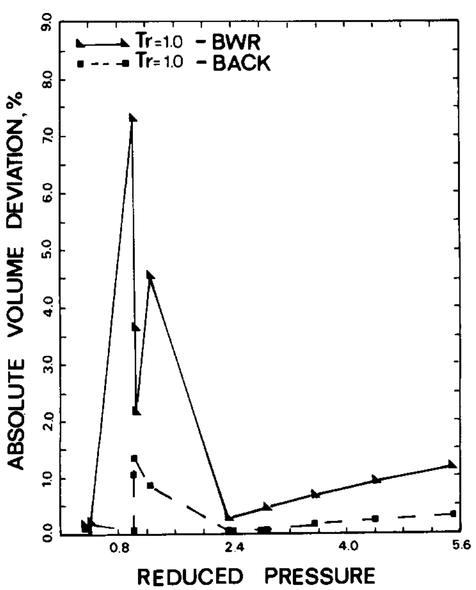

Fig. 3. Comparison of absolute volume deviation percent of BACK and BWR equations for ethylene at critical state temperatures over a wide range of pressures.

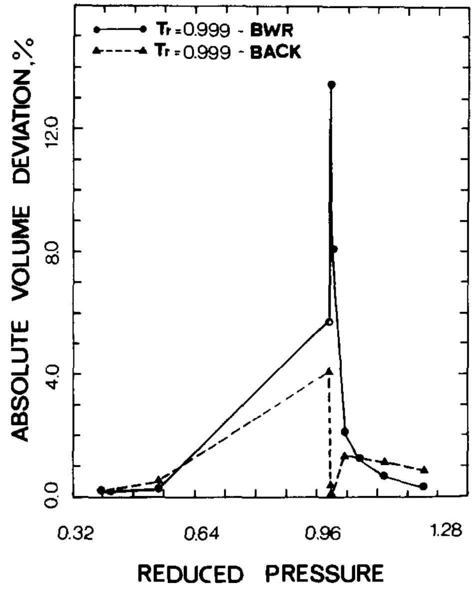

Fig. 4. Comparison of absolute volume deviation percent of BACK and BWR equations for ethylene at close to critical state temperatures and low and critical state vicinity pressures.

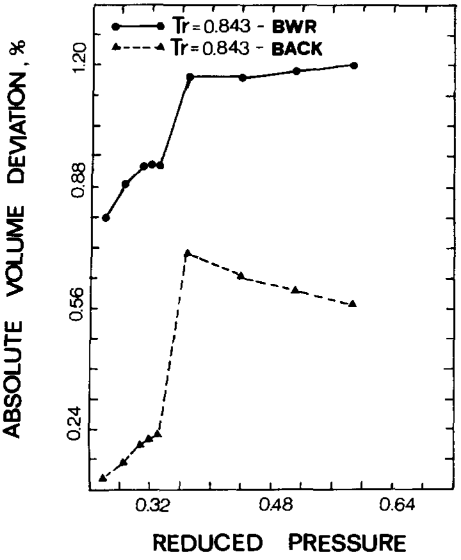

Fig. 5. Comparison of absolute volume deviations of BACK and BWR equations for ethylene at intermediate range temperatures and low pressures.

The Boublik–Alder–Chen–Kreglewski (BACK) equation

The BACK equation of state [12–19] is an inverted-square-well potential (Fig. 6) equation of the form

$$\frac{P\tilde{V}}{RT} = Z = Z^{\mathrm{h}} + Z^{\mathrm{a}} \tag{2}$$

where Z^{h} denotes the repulsive force contributions while Z^{a} represents the attractive force effects.

Following Boublik [18] and Chen and Kreglewski [13–17] we express the Z^{h} term as

$$Z^{\mathrm{h}} = \frac{1 + (3\alpha - 2)\zeta + (3\alpha^2 - 3\alpha + 1)\zeta^2 - \alpha^2\zeta^3}{(1-\zeta)^3} \tag{3}$$

For Z^{a} term we use the polynomial expansion of Alder et al. [19] as given by Kreglewski and Chen [14–16]

$$Z^{\mathrm{a}} = \sum_{N}^{4}\sum_{M}^{9} MD_{NM}\left(\frac{U_{\mathrm{m}}}{kT}\right)^{N}\left(\frac{\tilde{V}^0}{\tilde{V}}\right)^{M} \tag{4}$$

where U_{m}/k is the minimum value of the intermolecular energy, $U(r)$, for

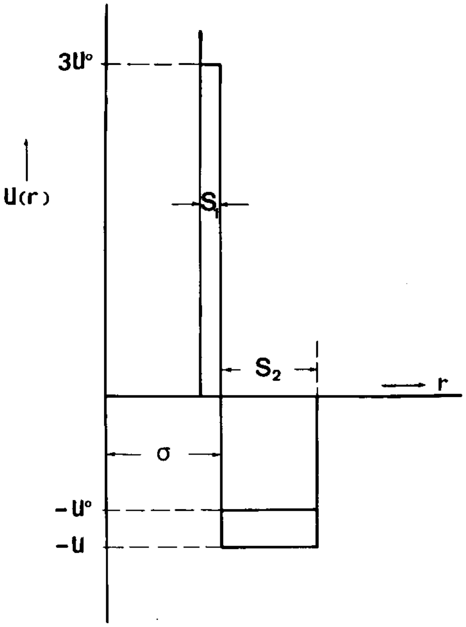

Fig. 6. The inverted-square-well potential with $U(r) = \infty$ for $0 < r < (\sigma - S_1)$ and $U(r) = 3U^0$ from $r = (\sigma - S_1)$ to $r = \sigma$.

the inverse-square-well potential (Fig. 6). We can write [14–20]

$$\zeta = 0.74048\frac{\tilde{V}^0}{\tilde{V}} = \tfrac{1}{6}\pi N_0\frac{\sigma^3}{\tilde{V}} \qquad (5)$$

$$\tilde{V}^0 = \tilde{V}^{00}\left[1 - C\exp\left(\frac{-3U^0}{kT}\right)\right]^3 \qquad (6)$$

$$\frac{U}{k} = \frac{U^0}{k}\left(1 + \frac{\eta}{kT}\right) \qquad (7)$$

where $\tilde{V}$ is the molar volume of the system; $\tilde{V}^0$ is the close-packed molar volume; N_0 is the Avogadro number; σ is the collision diameter; and $U(r)$ is the inverted-square-well potential energy.

The characteristic constants of fluids are as follows.

(1) α = characteristic constant of substance depending on the shape (non-sphericity) of the molecule. For small spherical molecules, $\alpha = 1$, and eqn. (3) reduces to the Carnahan–Starling hard-sphere equation [20]. If $\alpha > 1.0$, then the shape is something other than a convex spherical body.

To obtain initial α values, we used a relation between α and Pitzer's acentric factor, ω, as proposed by Chen and Kreglewski [13–16]

$$\alpha = 1 + 0.3\omega \qquad (8)$$

(2) $\tilde{V}^0$ = close-packed volume of the molecular hard cores, with $\tilde{V}^{00}$ being the $\tilde{V}^0$ value extrapolated to 0 K. $\tilde{V}^{00}$ can be related to the critical volume, $\tilde{V}_c$, of a compound as follows [13–16]

$$\tilde{V}^{00} = \frac{\tilde{V}_c}{4.6} \qquad (9)$$

(3) C = substance characteristic constant, representing the ratio of S_1, to σ in the inverted-square-well potential model (Fig. 6). The numerical value of C has been found to be 0.12 for most of the compounds [13–16]. For associated compounds the value may differ.

(4) η/k = substance characteristic constant which considers the temperature dependency of the inverted-square-well potential. According to Kreglewski and Chen [14–16], it does not significantly influence the P–V–T behavior of the system but affects the residual internal energy values.

Kreglewski and Chen [14–16] proposed the following expression for the η/k term

$$\eta/k = 0.6\omega T_c \qquad (10)$$

(5) U^0/k = characteristic constant of fluid representing the hard sphere interaction energy. For smaller molecules for which $\tilde{V}^{00}$ is $\lesssim 22$ cm^3 g^{-1} mol^{-1} (i.e., argon, methane), this term has been found [13–16] to be equal to the critical temperature, T_c, of the compound. For larger molecules Chen and Kreglewski [13] proposed as a good initial estimate value that obtained

from the following expression

$$U^0/k = T_c\left(1 + \frac{\eta}{2.5kT_c}\right)^{-1} \tag{11}$$

D_{NM} represents an array of 24 universal constants originally stemming from the work of Alder et al. [19]. In this work however we used the set of D_{NM} values first determined by means of curve-fitting by Chen and Kreglewski [13–16].

EXPERIMENTAL DATA USED AND COMPUTER PROGRAMMING

The summary of experimental data used, along with their temperature and pressure ranges, is given in Tables 1 and 2. The experimental P–V–T data sets were taken from the work of Douslin and Harrison [23,24]. Then these data were cross-checked for accuracy against the values of Vargaftik [25], Din [26] and McFee et al. [21]. At this point we considered these data to be sufficiently reliable and did not make any further study to re-evaluate their accuracy. Hence, the data set used for this study is only a representative one.

The computer program consisting of a main program and six subroutines, was set-up to curve-fit, by means of non-linear regression methods, the five characteristic constants, U^0/k, $\tilde{V}^{00}$, α, η/k and C, of the BACK equation, then to calculate the P–V–T and phase equilibria parameters required, in both gaseous and liquid states.

The main program initializes the values of the universal constant set D_{NM} for the BACK equation. It also reads in the experimental data needed for the compound in question, the number of constants to be fitted, the number of sets to be used in the strategy to regress the objective function by means of a modified complex Box method [27], the type of weighting to be given, and the conversion factors for any parameter values, if needed. The main program controls the transfer of the various subroutines (see the following discussion) and controls the iterative process of computation.

Subroutines

ESTIM. This subroutine reads in the initial values of constants, or generates their values from the critical properties and relations as specified. It generates approximate values of the saturated vapor volume by means of the Rackett equation [22].

EVAL. This subroutine performs calculations regarding the data fitting. For a given thermodynamic state point, subroutine EVAL takes as its input a test set of BACK equation constants (characteristic constants only since the universal constants D_{NM} have been taken from Chen and Kreglewski [13–16] and are fixed) and evaluates the volume, V, at given experimental P and T;

TABLE 1

Summary of data used

Compound	Critical properties [a]			Physical properties [a]	
	P_c (bar)	T_c (K)	V_c (m^3 kmol^{-1})	Pitzer's acentric factor, ω	Molecular weight
CH_4	46.04	190.58	0.099	0.008	16.043
C_2H_6	48.717	305.33	0.14556	0.098	30.07
C_2H_4	50.419	282.35	0.13098	0.085	28.054

BWR state equation constants [b]

	a	A_0	b	B_0	c	C_0	$\alpha \times 10^5$	$\gamma \times 10^3$
CH_4	0.04940	1.8550	0.00338004	0.04260	2545.00	22570.0	12.4359	6.0
C_2H_6	0.34516	4.15556	0.011122	0.0627724	32767.0	179592.0	24.339	11.80
C_2H_4 [c]	0.259	3.33958	8.6×10^{-3}	0.0556833	21120.0	131140.0	17.8	9.23

Characteristic constants of fluids for the BACK equation [d]

	U^0/k	$\tilde{V}^{00}$	α	η/k	C [e]
CH_4	190.3546	0.0215196	1.00326	1.257828	0.12
C_2H_6	296.7784	0.0315467	1.03056	18.13660	0.12
C_2H_4	275.1571	0.0282145	1.02590	15.07696	0.12

[a] Taken from Reid et al. [22] unless otherwise indicated.

[b] Taken from McFee et al. [21] unless otherwise indicated.

[c] Taken from Reid et al. [22].

[d] Calculated, this work, unless otherwise indicated.

[e] Taken from Chen and Kreglewski [13–16].

or again, evaluates P at experimental T and V values according to the type of objective function needing to be used. This subroutine also evaluates the error function at the input set of BACK equation constants and returns this error estimate to the main program.

PPD. This subroutine takes T and V as its input and returns, through the use of the BACK equation, the value of P and the partial derivative $(\partial P/\partial V)_T$ as its output.

FUDV. This subroutine takes T and V as its input and through the BACK equation returns the value of $\ln \phi$ and the partial derivative $(\partial \ln \phi/\partial V)_T$ as its output.

MAX. This subroutine determines extreme values amongst a set of values.

NEWCON. This subroutine determines a new set of constants that are to be fitted to any given function by using the values of constants in the other available sets and the additional knowledge of which these sets is the worst.

RESULTS AND DISCUSSION

Although both of the equations selected for the study, the BWR and the BACK equations of state, provide a good description of real fluid behavior in two-phase, gas and compressed-liquid regions, nevertheless, it is still desirable to know the differences in the levels of predictive accuracy in terms of CPU seconds demanded by the iteration process. This is especially true in cases where series of repetitive calculations for the density of the system are required.

The levels of predictive accuracy were established on a relative basis by means of percent average absolute deviation (AAD%) defined as

$$AAD\% = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{\Pi_{\text{expt}} - \pi_{\text{calc}}}{\Pi_{\text{expt}}} \right| \times 100 \qquad (12)$$

TABLE 2

Experimental data used [a] and comparison of results

Compound	Number of data points	Reduced pressure (P_r) range	Reduced temperature (T_r) range	Average absolute volume deviation (%) [b]	
				BWR [c]	BACK [c]
CH_4	14	0.213 -3.101	0.651 -1.000	1.73	0.52
C_2H_6	12	0.9976-0.9994	0.999	30.72	3.11
C_2H_4	29	0.260 -5.475	0.8435-1.000	2.20	0.63

[a] The experimental data point values have been taken from the work of Douslin and Harrison [23,24].

[b] These average absolute volume deviation values should be compared with the absolute volume deviation plots for CH_4, C_2H_6 and C_2H_4 taken at several reduced isotherms in terms of reduced pressures (Figs. 1–5).

[c] Average CPU time (s) to calculate density in the given state: for BWR equation, 0.2 s; for BACK equation, 0.267 s; machine, AMDAHL 470.

where $i = i$th data point; N = total number of data points; expt and calc refer to the experimental and calculated values of the data point, respectively; and Π is a general property, i.e., density, volume.

The relative calculation time effect was introduced through a CPU time ratio, R, defined as

$$R = \frac{\mathrm{CPU_{BACK}}}{\mathrm{CPU_{BWR}}} \tag{13}$$

where $\mathrm{CPU_{BACK,BWR}}$ were determined by averaging the CPUs used to calculate the pressure of each state for all the states prescribed at fixed state and machine operating conditions for the same computer.

Tables 1 and 2 contain the physical properties and experimental data used, and calculated results obtained, for comparing the relative performance of the Benedict–Webb–Rubin (BWR) and BACK equations of state. Table 1 contains the set of constants for the BWR equation suggested by McFee et al. [21] as the most accurate for P–V–T calculations for the substances given.

Table 1 also contains the characteristic constants calculated (this work, except constant C which was suggested by Chen and Kreglewski [14]) for use in the BACK equation. As the compounds involved (Tables 1 and 2) consist of relatively small and simple molecules and the temperature range used was between the limits $0.651 < T_r < 1.000$, we used the universal constant, D_{NM}, set values * as originally proposed by Chen and Kreglewski [14].

Table 2 contains the average absolute deviations of equation of state predictions of volume for the given substance, the number of data points entered, and the temperature and pressure ranges used including the values of CPU seconds (Table 2, footnote c) showing the average iteration time needed for BWR and BACK equations at fixed thermodynamic state and the same computing conditions. The results obtained for the BWR equation (Table 2, Figs. 1–5) confirm in general what in terms of accuracy should be expected from this type of non-cubic in density state equation for both vapor and liquid phases, including the large errors (up to 48%) shown along the critical isotherm (Figs. 3 and 4). This, especially for ethane, illustrates the inadequacy of the BWR equation in describing the volumetric behavior of the dense (liquid) phase near the critical region (Fig. 3). The average CPU time for the BWR equation needed to complete the iteration process at a given thermodynamic state was found to be CPU = 0.2 s (Table 2). On the other hand, the more complex BACK equation [13–16] as expected, proved to be highly accurate in fitting the P–V–T behavior for the given substances

---

* The first original set consists of 24 values of the universal constants, D_{NM}, valid down to $T_r = 0.55$, the triple point of argon. The second set, not considered in this work, consists of 20 universal constants, D_{NM} (given by Chen and Kreglewski [15]) and may be used to a value of $T_r = 0.296$, the liquid state of ethane.

(Table 2, Figs. 1–5). The largest error up to 12% occurred along the critical isotherm of ethane (Fig. 3) except the error seemed to decrease as the pressure approached the critical pressure. At this point the BACK equation did show the opposite behavior of the BWR equation (Fig. 3). The average CPU time for the BACK equation for the length of the iteration process at a given thermodynamic state was determined to be $\mathrm{CPU}_{\mathrm{BACK}} = 0.267$ s (Table 2). For a single iterative process for a given thermodynamic state, the BACK equation requires more CPU time than the BWR equation in a ratio of 1.34 : 1 (eqn. 14, Table 2, footnote c). As shown by Table 2 and Figs. 1–5, the accuracy level of the BACK equation for the dense (liquid) phase and in the critical state region is much higher than that of the BWR equation. For low pressures and all temperatures both equations show increased accuracy levels. For the compounds studied (Tables 1 and 2, Figs. 1–5) it appears that for both equations their accuracy levels increase when both pressure and temperature decrease.

If CPU times needed and the error level of the state equations obtained are compared, decisions can be made as to which equation of state should be considered for use, and in what fluid state ranges. As a general consideration, the complex equations are used for highly accurate calculations of P–V–T and simple thermodynamic property values, but are least desirable for the thermodynamic property calculations of mixtures such as activity coefficients of mixture components or multi-component vapor–liquid equilibrium ratios which involve an excessive need of computer storage facilities.

The successful use of equations of state presupposes the ready availability of accurate and well-tested constants (both universal and characteristic). A careful use of P–V–T and vapor pressure data do not necessarily ensure accurate prediction of density and enthalpy, for instance. As a matter of fact, not all constant sets for a given substance will describe equally well the P–V–T, enthalpy and vapor pressure behavior of the system at the same time.

McFee et al. [21] recently showed that significant errors can be introduced if constant sets obtained by means of inappropriate methods are used. Hence, the original BWR equation might be applicable with greater accuracy than thought possible, provided the input parameters are reliable. For the BWR equation this is achieved through newer calculation methods of constants; for instance, multiproperty regression analysis, although time consuming, yields very encouraging results [7–12].

In case of equations of state derived from statistical mechanics through various approximations, e.g., the BACK equation, the constants (both, characteristic and universal) of these equations are related to the intermolecular force potential. Since molecular properties are not known with any great certainty, the parameters by necessity are obtained by means of curve-fitted empirical relations using experimental data (see eqns. 4–12).

These data, which are correlated to molecular properties, are P–V–T state parameters (particularly the saturated and critical states) and thermal properties and vapor–liquid measurements for pure substances and/or mixtures.

As in the multiproperty regression analysis for the BWR equation [7,8], the parameters needed for the BACK equation are obtained through unique optimization procedures (see preceding discussion on experimental data used and computer programming). The accuracy of the BACK equation in terms of the relations proposed in this work (eqns. 2–12) is best for fluids consisting of globular molecules, but less good for long-chain molecules.

LIST OF SYMBOLS

A_0, B_0, C_0, a, b, c, α, γ	Benedict–Webb–Rubin equation constants
k	Boltzmann constant
P	pressure
R	universal gas constant
T	temperature
V	volume
Z	compressibility factor
ρ	density
ω	acentric factor

Superscript

0	reference, ideal

Subscripts

c	critical state
r	reduced state (with respect to the vapor–liquid critical state)

ACKNOWLEDGMENT

The financial support of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1 M. Benedict, G.B. Webb and L.C. Rubin, J. Chem. Phys., 8 (1940) 334.
2 M. Benedict, G.B. Webb and L.C. Rubin, J. Chem. Phys., 10 (1940) 747.
3 M. Benedict, G.B. Webb and L.C. Rubin, Chem. Eng. Prog., 47 (1951) 419.

4 M. Benedict, G.B. Webb and L.C. Rubin, Chem. Eng. Prog., 47 (1951) 449.
5 M. Benedict, G.B. Webb, L.C. Rubin and L. Friend, Chem. Eng. Prog., 47 (1951) 571.
6 M. Benedict, G.B. Webb, L.C. Rubin and L. Friend, Chem. Eng. Prog., 47 (1951) 609.
7 C.J. Lin, Y.C. Kwok and K.E. Starling, Can. J. Chem. Eng., 50 (1970) 644.
8 K.W. Cox, J.L. Bono, Y.C. Kwok and K.E. Starling, Ind. Eng. Chem. Fundam., 10 (1971) 245.
9 P.R. Bishnoi and D.B. Robinson, Can. J. Chem. Eng., 49 (1971) 462.
10 P.R. Bishnoi and D.B. Robinson, Can. J. Chem. Eng., 50 (1972) 101.
11 K.C. Chao and R.L. Robinson, Adv. Chem. Ser., (1979) 182.
12 H. Nishiumi, J. Chem. Eng. Jpn., 13 (1980) 72.
13 S.S. Chen and A. Kreglewski, Report of Investigation, Thermodynamic Research Centre, Texas A & M University, College Station, TX, 1977.
14 S.S. Chen and A. Kreglewski, Ber. Bunsenges. Phys. Chem., 81 (1977) 1048.
15 A. Kreglewski and S.S. Chen, J. Chim. Phys., 75 (1978) 347.
16 A. Kreglewski, J. Chim. Phys., 77 (1980) 441.
17 A. Kreglewski, R.C. Wilhoit and B.J. Zwolinski, J. Chem. Eng. Data, 18 (1973) 432.
18 T. Boublik, J. Chem. Phys., 63 (1975) 4048.
19 B.J. Alder, D.A. Young and M.A. Mark, J. Chem. Phys., 56 (1972) 3013.
20 N.F. Carnahan and K.E. Starling, J. Chem. Phys., 51 (1969) 1184.
21 D.G. McFee, K.H. Mueller and J. Lielmezs, Thermochim. Acta, 54 (1982) 9.
22 R.C. Reid, J.M. Prausnitz and T.K. Sherwood, The Properties of Gases and Liquids, McGraw-Hill, New York, 3rd edn., 1977.
23 D.R. Douslin and R.H. Harrison, J. Chem. Thermodyn., 5 (1973) 491.
24 D.R. Douslin and R.H. Harrison, J. Chem. Thermodyn., 8 (1976) 301.
25 N.B. Vargaftik, Tables on the Thermophysical Properties of Liquids and Gases, Wiley, New York, 2nd edn., 1975.
26 F. Din, Thermodynamic Functions of Gases, London, Vols. 1–3, Butterworth, 1956.
27 S.S. Rao, Optimization, Theory and Application, Wiley-Eastern, New Delhi, 1978.