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COMPARISON OF BENEDICT–WEBB–RUBIN, STARLING AND LEE–KESLER EQUATIONS OF STATE FOR USE IN *P–V–T* CALCULATIONS

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ABSTRACT

By means of the available experimental gas compressibility data, the predictive accuracy of the Benedict–Webb–Rubin, Starling and Lee–Kesler equations was tested over wide temperature and pressure ranges for the following commonly used industrial gases: CH_4, C_2H_6, C_3H_8, CO_2, Ar, He, H_2 and N_2.

The root mean square (RMS) percent errors ($\mathrm{RMS}=[\sum_{i=1}^{n}(\%\ \mathrm{error})^2/n]^{1/2}$, where % error $= [(Z_{\mathrm{calculated}} - Z_{\mathrm{experimental}})/Z_{\mathrm{experimental}}] \times 100$ calculated over the *T–P* range investigated for all compounds, showed a degree of superiority and ease of use of the Lee–Kesler equation over the Benedict–Webb–Rubin and Starling equations.

In order to treat quantal fluids H_2 and He, the Benedict–Webb–Rubin equation was modified by making constant B_0 temperature dependent, while the Starling and Lee–Kesler equations were rewritten through inclusion of quantum effect corrected pseudo-critical state parameters.

INTRODUCTION

The need for accurate volumetric properties of industrially important fluids is increasing rapidly in process analysis. The Benedict–Webb–Rubin equation [1–6,28] and its recent modifications, the Starling [39–43] and Lee–Kesler [21] equations form a family of one of the more elaborate equations of state that have proved to be highly useful for process industries in predicting the behavior of phase equilibria. This study, however, has analyzed the predictive accuracy of each of these equations of state through the use of the available compressibility data (including data near the critical point and in the liquid state) calculating the *P–V–T* properties for the following relatively small, ranging from inert, non-polar to slightly polar, polar and quantal common industrial compounds: Ar, CH_4, C_2H_6, C_3H_8, CO_2, He, H_2 and N_2. Computer programs were set-up to calculate for each of these three equations the compressibility factors, and the corresponding volumes and densities.

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TABLE 1

Summary of data

Compound	Critical properties [a]		Physical properties	
	T_c (K)	P_c (atm)	Acentric factor [a] ω	Molecular or atomic weight
H_2	$43.6/(1+\frac{21.8}{2.016\,T})$ [c]	$20.2/(1+\frac{44.2}{2.016\,T})$ [c]	−0.22	2.016
He	$10.47/(1+\frac{21.8}{4.003\,T})$ [c]	$6.67/(1+\frac{44.2}{4.003\,T})$ [c]	−0.387	4.003
Ar	150.8	48.1	−0.004	39.948
N_2	126.2	33.5	0.040	28.013
CO_2	304.2	72.8	0.225	44.01
CH_4	190.6	45.4	0.008	16.043
C_2H_6	305.4	48.2	0.098	30.07
C_3H_8	369.8	41.9	0.152	44.097

Experimental data [b]

Compound	No. of data points	Reduced pressure range, P_r	Reduced temperature range, T_r	Average compressibility factor $Z_{av}=(1/n)\sum_i^n Z_i$	Compressibility factor range, Z
H_2	26	1.17 −31.65	0.45– 15.1	1.103	0.27–1.66
He	32	0.88 −88.0	3.85–130	1.119	0.99–1.62
Ar	31	0.04 – 4.10	0.66– 3.32	0.8166	0.07–1.05
N_2	37	0.06 – 2.95	0.79– 3.17	0.6505	0.10–1.04
CO_2	39	0.01 – 1.90	0.95– 1.87	0.5796	0.13–1.00
CH_4	27	0.04 – 1.52	0.52– 2.62	0.8159	0.07–1.00
C_2H_6	21	0.04 – 2.04	0.65– 2.05	0.7734	0.34–0.99
C_3H_8	30	0.016– 7.30	0.84– 1.30	0.6833	0.24–0.98

[a] Taken from Reid et al. [36] unless indicated otherwise.

[b] All compressibility data taken from Vargaftik [45] and crosschecked against the data of Din [15] and Reamer et al. [35] (see discussion on experimental data used, this work).

[c] Compare with Table 4. See also footnote **, p. 22.

The calculated compressibility factors were then evaluated against the experimental data *. The evaluation was done for each experimental data point in terms of the root mean square (RMS) percent error defined as

$$\mathrm{RMS}=\left[\frac{\sum_{i=1}^{n}(\%\ \mathrm{error})^2}{n}\right]^{1/2} \tag{1}$$

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* It is felt that a P–V–T property representation of pure compound will indicate how the particular equation of state will handle various mixtures involving the same pure compound. Indeed if an equation of state handles effectively the P–V–T properties of compounds, it should also handle well mixtures containing the same compound and provided we have acceptable mixing rules. (see work by McFee et al. [26]).

in which

$$\% \text{ error} = \left[\frac{Z_{\text{calculated}} - Z_{\text{experimental}}}{Z_{\text{experimental}}} \right] \times 100 \qquad (2)$$

The "best" equation of state or the "best" set of constants is found by noting which calculation yields the lowest RMS percent error for the same set of experimental data. Table 1 presents the summary of data used. It also contains parameter Z_{AV} *. Low Z_{AV} value indicates the presence of the more difficult to curve-fit critical ** and liquid state data points in given data set. Tables 2 and 3 present constants and derived entities for the Benedict–Webb–Rubin equation.

For constant B_0 (Benedict–Webb–Rubin equation, Table 2) for He, we have introduced the following temperature dependent correction

$$B_{0,\text{He}} = 0.0154393 - 0.0000851708\ RT \qquad (4)$$

to be used when $T > 70$ K.

In the case of the Starling [eqns. (6)–(17)] and Lee–Kesler [eqns. (18)–(23)] equations, we have included quantum effect corrected (for H_2 and He) pseudo-critical state parameters (Tables 1 and 4).

Tables 4–6 pertain to the use of the Starling equation including several corrected constant values. Table 7 gives the constants to be used in the Lee–Kesler equation. Table 8 presents the conversion factors used; while Table 9 summarizes the results obtained–the calculated RMS-percent errors (eqn. 1) by the equations of state and the compounds selected.

The results obtained (Table 9) provide an idea of the magnitude and nature of errors found in terms of the compound involved and point out the need for generating reliable specific constant sets (for instance, Benedict–Webb–Rubin equation, Tables 2 and 3) through the use of proper calculating methods.

In this work the multiproperty regression method proved to be the most successful, even if, in general, this method is time consuming and not always in itself assures success.

However, the results also show (Table 9) that the simpler, less time consuming generalized methods can be used to advantage. Of these generalized methods, the Lee–Kesler method (based on a combination of the modified Benedict–Webb–Rubin equation and Pitzer's [29–32] macroscopic theorem of corresponding states) appeared to have an edge of superiority (Table 9). However, it did appear that in cases where necessary state parameters and constants are reliable, the Benedict–Webb–Rubin equation may still give better results.

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* Z_{AV} is defined as

$$Z_{AV} = (1/n) \sum_{i=1}^{n} Z_i \qquad (3)$$

where Z is the ith ($i = 1, 2, \ldots, n$) compressibility factor.

** In the critical region, as a rule, the values of compressibility factor are low.

TABLE 2

Recommended constants[a] for Benedict–Webb–Rubin correlation[c] (eqn. 5).

Compound	Regression data	A	A_0	B	B_0	C
CO_2	PVT, VP	0.24204855	1.8367101	0.00625361	0.03201493	19008.12
N_2	PVT	0.0312319	0.872086	0.0032351	0.0281066	547.364
Ar	PVT	0.0288333	0.8233675	0.00215277	0.02228195	798.1743
H_2	PVT	0.0005028	0.20988	$0.000511 + 0.0010061/RT$	0.0236092	2.81141
He	PVT	−0.00057339	0.040962	−0.00000019727	0.023661[b]	−0.00552
CH_4	PVT, VP	0.04940	1.8550	0.00338004	0.04260	2545.00
C_2H_6	PVT, VP	0.34516	4.15556	0.011122	0.0627724	32767.0
C_3H_8	PVT, VP	0.93265688	5.9995798	0.0242286	0.073771408	111873.64

Compound	C_0	$\alpha \times 10^5$	$\gamma \times 10^3$	RMS (eqn. 1)	Z_{av} (eqn. 3)	Reference
CO_2	176028.05	4.878407	4.280822	0.77	0.5796	8
N_2	7813.75	7.09232	4.5	2.15	0.6505	13 (47, 12)
Ar	13140.25	3.55889	2.33813	3.40	0.8166	48 (47)
H_2	51.1509	21.1294	3.5072	2.21	1.013	19 (47)
He	−0.16227	−0.72673	0.77942	1.35	1.119	25 (47, 12, 36)
CH_4	22570.0	12.4359	6.0	0.63	0.8159	1 (12, 36, 47)
C_2H_6	179592.0	24.339	11.80	1.26	0.7734	1 (12, 36, 47)
C_3H_8	508243.7	48.67309	18.911758	0.66	0.6833	8

[a] All constants calculated by means of multiproperty regression analysis.

[b] Suggested B_0-temperature correction: $B_{0,He} = 0.0154393 - 0.0000851708\ RT$ for $T > 70$ K (this work, eqn. 4).

[c] All calculated data within the experimental error. PVT= *PVT* data. VP= Vapour pressure data.

TABLE 3

Constants for Benedict–Webb–Rubin correlation (eqn. 5)

Compound	Regression data	A	A_0	B	B_0	C
CO_2	VP	0.136814	2.51606	0.0041239	0.0448849	14918.0
	VP	0.136814	2.73742	0.0041239 [a]	0.0499101	14918.0
	PVT	0.2091177	1.534841	0.0060337	0.0206380 [a]	15828.1
	PVT	0.2117938	1.506609	0.006150275	0.02034075	14353.9
N_2	NA	0.025102	1.053642	0.0023277	0.0407426	728.41
	VP, PVT	0.0149	1.19250	0.00198154	0.04580	548.064
	VP	0.01536841	0.5719747	0.002012855	0.04618903	551.33
H_2	VP	−0.001974672	0.2063201	0.0003595485	0.018497	10.04429
	PVT	0.00163211	0.155156	$0.0003383 + 0.0032658/RT$	0.020846	7.27093
CH_4	VP, PVT	0.069198	1.8712416	0.00397874	0.04320305	3017.9295
	VP	0.06661414	1.589113	0.004363266	0.04335035	2551.919
	PVT	0.043520	1.79894	0.00252033	0.0454625	3587.8
	PVT	−0.003985562	1.92441	0.0002279009	0.04356982	−593.5488
	VP	0.049396	1.854904	0.0033799	0.0425989	2544.808
C_2H_6	VP, PVT	0.42861571	3.3640857	0.01261194	0.04804813	35935.46
	NA	0.750559	2.190065	0.0195532	0.0210804	49486.7
	VP	0.345135	4.15534	0.0111215	0.062771	32764.53
C_3H_8	NA	0.8583692	6.23558	0.02237136 [a]	0.07963844	111186.6
	PVT	1.026809	4.29138	0.02764357	0.03625513	90710.4
	PVT, VP	0.94770	6.87225	0.0225	0.097313	129090.0
	VP	0.6855057	6.245638	0.02353479	0.08182161	65830.77

Compound	C_0	α	γ	RMS (eqn. 1)	Z_{av} (eqn. 3)	Reference
CO_2	147 443.0	0.0000847	0.005394	1.08 [b]	0.5796	14, 47, 12
	138 567.0	0.0000847	0.005394	1.14 [b]		14, 47, 12, 36
	174 221.6	0.00004352	0.0039018	2.95 [b]		37, 47, 12
	205 752.5 [1]	0.00003782074	0.00330265	3.04 [b]		24, 47
N_2	8 059.0	0.0001272	0.0053	2.97	0.6505	18, 47, 12, 36
	5 889.07	0.000291545	0.0075	8.28		44
	106.4597 [2]	0.00028903 [a]	0.007606	13.48		1, 24
H_2	11.33076 [4]	−0.0000562403 [a]	0.006058854	3.56	1.013	24
	360.921	0.000116552	[3]	8.34		27, 47
CH_4	23 500.139	0.000096836	0.0057118	1.24	0.8159	8
	2 143.107 [5]	0.000122851 [a]	0.0064268	3.82		24, 47
	31 838.2	0.00033	0.0105	4.46		16, 47, 12, 36
	1 399.04 [a]	0.001000637	0.005708053	5.89		10, 47
	1 359.059	0.0001243	0.006	v. high		34, 47
C_2H_6	213 406.11	0.0002103529	0.011003275	1.71	0.7735	8
	258 836.6	0.00015377	0.01	1.9		46.47
	3 833.70	0.0002434	0.0118	v. high		34, 47
C_3H_8	501 164.1	0.0005648831	0.02093228	0.69	0.6833	1, 47
	233 154.4 [6]	0.0004155765	0.0178694	1.13		24, 47, 12, 36
	508 256.0	0.000607475	0.022	1.43		24, 47
	28 032.37 [7,a]	0.000524958 [a]	0.02048722	2.09		

VP, Vapour pressure data; NA, reference article not available; PVT, PVT data.

[a] Mistake made in reference article,

[b] Excludes occasional poor point near critical state. In general CO_2 is difficult to curve-fit in critical region even if method works elsewhere (compare with results of Table 2).

[1] C_0/T^2 becomes $C_0/T^{2.037402}$. [2] C_0/T^2 becomes $C_0/T^{0.9725759}$. [3] $\gamma=0.0026308$, $T<89.27$; $\gamma=0.003277$, $T>255.4$. [4] C_0/T^2 becomes $C_0/T^{1.380643}$. [5] C_o/T^2 becomes $C_0/T^{1.484483}$. [6] C_0/T^2 becomes $C_0/T^{1.872571}$. [7] C_0/T^2 becomes $C_0/T^{1.533527}$.

TABLE 4

Physical properties for use with the Starling correlation [a] (eqns. 6–17)

Compound	Critical temperature (K)	Critical density (g mole l^{-1})	Acentric factor
CH_4	190.69	10.101 [b]	0.008 [b]
C_2H_6	305.39	6.7569	0.1018
C_3H_8	369.89	4.9996	0.152 [b]
N_2	126.15	11.0997	0.035
CO_2	304.15	10.6384	0.225 [b]
Ar	150.8	13.3511	−0.004
H_2 [c]	43.6	19.4175	−0.22 [b]
He [c]	10.47	26.667	−0.387 [b]

[a] Starling [39–42] in his original paper states that only his suggested T_c, P_c and ω values should be used as these were employed when he back calculated for the generalized method from the experimental data. However, in this work we tried several sets of T_c, P and ω values. The T_c, P_c and ω values which appear in Table 4 are those values which gave the best RMS (eqn. 1) results. As seen they include the original Starling values as well as those specified by Reid et al. [36].

[b] These values differ from the original Starling value set, and have been taken from Reid et al. [36].

[c] Although Prausnitz and Chueh [33] specified the following quantum corrections for use in the Redlich–Kwong equation, we believe that the same type of corrections may be extended to the Starling and Lee–Kesler equations (see Table 1, also footnote h, this work)

$$T_c = \frac{T_c^0}{1+(21.8/mT)};\ P_c = \frac{P_c^0}{1+(44.2/mT)};\ V_c = \frac{V_c^0}{1-(9.91/mT)}$$

TABLE 5

Values of parameters A_j and B_j for use with the Starling generalized equation of state [36]

Parameter subscript (j)	Parameter value A_j	B_j
1	0.443690	0.115449
2	1.28438	−0.920731
3	0.356306	1.70871
4	0.544979	−0.270896
5	0.528629	0.349261
6	0.484011	0.754130
7	0.0705233	−0.044448
8	0.504087	1.32245
9	0.0307452	0.179433
10	0.0732828	0.463492
11	0.006450	−0.022143

TABLE 6

Starling constants (eqns. 6–17)

Constant	Methane		Ethane		Propane		Nitrogen
	I[a]	II[a]	III[a]	I[a]	I[a]	III[a]	I[a]
A	0.045561	0.042622	0.04162	0.286946	0.92425	0.79957	0.0152462
A_0	1.86476	1.99413	1.8549	4.0000	5.84227	5.64626	1.12572
B	0.0033564	0.003606	0.00338	0.0105046	0.024808	0.0225[b]	0.00218
B_0	0.0434893	0.04515[b]	0.0425989	0.058701	0.0718457	0.073038	0.0428419
C	2596.79	2233.75	2544.81	30377.5	119086.0	128990.0	577.119
C_0	27111.8	22186.6	26339.4	213291.0	616456.0	677646.0	7972.74
D	0.629449	0.43672	1.38748	5.50164	17.2373	51.9117	0.259388
D_0	641379.0	489854.0	608679.0	9425970.0	34418900.0	40375700.0	164675.0
E_0	3196140.0	760626.0	751224.0	227585000.0	1.10494×10^9	1.4901×10^9	828294.0
α	0.000110234	0.00011405	0.00012435	0.0002526	0.000529357	0.0006071	0.000119127
γ	0.0054529	0.005792	0.006	0.0118525	0.0214382	0.022	0.004644
RMS percent error (eqn. 1)	1.22	1.25	1.12	1.25	0.95	1.64	1.67

[a] The constants were taken from the following reference articles: I, ref. 22; II, ref. 11; III, ref. 42.

[b] These are our values; numerical mistake has been found in the original article (given reference).

TABLE 7

Lee–Kesler constants [21] (eqns. 18–23)

	Simple fluid $Z^{(0)}$ calculation	Reference fluid $Z^{(r)}$ calculation
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1 \times 10^4$	0.155488	0.48736
$d_2 \times 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

TABLE 8

Conversion for equation of state constants

	To convert from British to metric units divide by
A	6.04118×10^4
A_0	3.77122×10^3
B	2.56615×10^2
B_0	1.60192×10
C	1.957342×10^5
C_0	1.221875×10^4
D	1.087410×10^5
D_0	2.19937×10^4
E_0	3.95887×10^4
α	4.11076×10^3
γ	2.56615×10^2

British: $R = 10.7335$ p.s.i.a. ft.^{3} (lb. mole °R)$^{-1}$.
Metric: $R = 0.08206$ l atm (g mole K)$^{-1}$.

TABLE 9

Comparison of RMS-percent error [eqn. (1)] for pure compounds [a,b]

Compound	Starling generalized equations	Lee–Kesler generalized equations	Benedict–Webb–Rubin equation multiproperty regression analysis constant sets
CO_2	7.89	1.68	0.77
N_2	1.51	1.06	2.15
Ar	1.34	0.79	3.40
H_2	3.88	2.65	2.21
He	1.61	2.14	1.35
CH_4	1.17	1.24	0.63
C_2H_6	0.95	1.15	1.26
C_3H_8	1.15	1.17	0.66
Average	2.44	1.49	1.55

[a] Input compressibility data taken from Table 1.

[b] The calculated errors obtained with the equations fall within the corresponding experimental range.

Benedict–Webb–Rubin (BWR) equation

BWR-equation of state is [1–6,28]

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2} \right)\rho^2 + (bRT - a)\rho^3$$
$$+ a\alpha\rho^6 + \frac{c\rho^2}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \tag{5}$$

Originating 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 [23]. Indeed for the systems where the constants and interaction coefficients needed are available, the BWR equation may be highly reliable [7a,8,10,23]. As a result of this work, it is felt that these constants should be preferably generated by means of the presently popular multiproperty regression method [7a,8]. Indeed, when compared (Tables 2 and 3), the predictive ability of the simpler to use BWR-generalized method was found for the same compounds to be less reliable, notably in the critical region. Table 2 presents the best set of constants from among the other sets available for some compounds (Table 3). However, it is also felt that the fit of the BWR-generalized method may be improved if more reliable constant sets are generated.

Starling equation

Already at the beginning of the use of the BWR-equation difficulties were encountered for some systems and in applications in the cryogenic region [38]. Starling [39–42], therefore, modified the empirical BWR equation by introducing temperature corrections to constants C_0 and a (eqn. 5), so that the new equation contained an additional three constants (D_0, E_0 and d) yielding

$$P = \rho RT + \left(B_0RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right)\rho^2 + \left(bRT - a - \frac{d}{T} \right)\rho^3$$
$$+ \alpha\left(a + \frac{d}{T} \right)\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \tag{6}$$

Starling and Ham [40,41] generalized eqn. (6) by the following relations [compare with eqn. (5)]

$$\rho_{c_i} B_{0_i} = A_1 + B_1\omega_i \tag{7}$$

$$\rho_{c_i} A_{0i}/RT_{c_i} = A_2 + B_2\omega_i \tag{8}$$

$$\rho_{c_i} C_{0_i}/RT_{c_i}^3 = A_3 + B_3\omega_i \tag{9}$$

$$\rho_{c_i}^2 \gamma_i = A_4 + B_4\omega_i \tag{10}$$

$$\rho_{c_i}^2 b_i = A_5 + B_5 \omega_i \tag{11}$$

$$\rho_{c_i}^2 a_i / RT_{c_i} = A_6 + B_6 \omega_i \tag{12}$$

$$\rho_{c_i}^3 \alpha_i = A_7 + B_7 \omega_i \tag{13}$$

$$\rho_{c_i}^2 c_i / RT_{c_i}^3 = A_8 + B_8 \omega_i \tag{14}$$

$$\rho_{c_i} D_{0_i} / RT_{c_i}^4 = A_9 + B_9 \omega_i \tag{15}$$

$$\rho_{c_i}^2 d_i / RT_{c_i}^2 = A_{10} + B_{10} \omega_i \tag{16}$$

$$\rho_{c_i} E_{0_i} / RT_{c_i}^5 = A_{11} + B_{11} \exp(-3.8\,\omega_i) \tag{17}$$

Starling and Ham [40,41] determined the values of A_j and B_j ($j = 1,2,\ldots,11$, Table 5) by simultaneous multiproperty regression analysis of PVT, enthalpy and vapour pressure data. Multiproperty analysis calculated constant sets are available for the lighter hydrocarbons and nitrogen. As in the case of the BWR-equation, the Starling equation was also tested with both the generalized relations and the multiproperty analysis method (Tables 5, 6 and 9). The results obtained indicate (the same as for the BWR-equation) that more accurate P–V–T properties are obtained using the multiproperty regression method rather than the generalized correlation. It is regretable that constant sets have been published for relatively few compounds.

Lee–Kesler equation

The Lee–Kesler equation unlike the empirical Benedict–Webb–Rubin and Starling equations, is a classical corresponding states correlation [21,29–32,43]. In order to predict the compressibility factors, Lee and Kesler [21] took the macroscopic corresponding states correlation of Pitzer [29–32,43]

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{18}$$

then used a modified BWR-equation given in reduced coordinates as

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp(-\gamma/V_r^2) \tag{19}$$

to predict the values of $Z^{(0)}$ and $Z^{(1)}$ (eqn. 18). Constants B, C, D (eqn. 19) are defined as *

$$B = b_1 - (b_2/T_r) - (b_3/T_r) - (b_4/T_r^3) \tag{20}$$

$$C = c_1 - (c_2/T_r) + (c_3/T_r^3) \tag{21}$$

$$D = d_1 + (d_2/T_r) \tag{22}$$

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* Constants used [eqns. (20)–(22)] are found in Table 7. Note that ω in the Pitzer relation (eqn. 18) is replaced by $\omega/0.3978$ for the Lee–Kesler equation. A value of 0.3978 represents the ω-value for the reference fluid used—octane.

The pseudo-reduced volume V_r is given as

$$V_r = P_c V / R T_c \tag{23}$$

The theoretical basis of the predictive ability of the Lee–Kesler method is determined through the inherent characteristics of the Pitzer's macroscopic theorem of corresponding states [29–32] and the range of applicability of the modified BWR-correlation [11] [eqn. (19)]. It is well known that Pitzer's macroscopic theorem of corresponding states (using critical state properties and acentric factors) cannot be used for substances consisting of large (such as polymers), non-spherical molecules because this theorem is a first order perturbation about simple fluid (reference fluid, acentric factor $\omega = 0$) corresponding states; it is based on the use of Taylor's series expansion in ω, retaining only the first term of the expansion. Since the higher order terms of this expansion are neglected, the theorem effectively can be applied only to moderately large non-spherical molecules *. Indeed, the work of Lee and Kesler is based on experimental data for hydrocarbons ranging from methane to n-octane as the heavy reference fluid with a subsequent adjustment to other substances. Whether the Lee–Kesler method may be extended through the inclusion of higher order Taylor expansion terms [eqn. (18)] is an open question, especially as at present these terms are not available **.

Our results (Table 9) however indicate that the Lee–Kesler method predicts reliably and appears to be applicable to a series of compounds some of which have not even been included in the original work of Lee and Kesler. In view of our results, the range of the predictive applicability of the Lee–Kesler method should be further investigated, especially for the vapour pressure calculations.

EXPERIMENTAL DATA USED AND COMPUTER PROGRAMMING

The summary of experimental data used, along with their temperature and pressure ranges, is given in Table 1. The experimental gas and liquid (near critical point) state compressibility values for CH_4, C_2H_6, C_3H_8, Ar, CO_2, N_2, He and H_2 were taken from the data collection of Vargaftik [45]. Then these data were cross-checked for accuracy against the values given by Din [15] and Reamer et al. [35]. At this point we considered the presented data (Table 1) to be sufficiently reliable and did not make any further study to re-evaluate their accuracy. Hence the data set used for the present study is only a representative one.

The computer programs to calculate pure compound and their mixture densities, heat capacities and enthalpies by means of BWR-equation had been set up already

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* This observation is strengthened by the work of Hsiao and Lu [20] regarding an extension of the Pitzer's correlation for compressibility factor calculations.

** It is of interest to note that Hsiao and Lu [20] indicate through Z vs. ω plots that it is not feasible nor plausible to correlate the higher terms of eqn. (18). It is felt however that further studies should be conducted along these lines.

in 1968 and 1969 by Johnson and Colver [7b]. Following the prototype of Johnson and Colver [7b], our program reads-in the experimentally determined compressibility factor Z at the T and P of interest, and compares these data with the compressibility factor calculated by means of the given state equation at the same thermodynamic conditions. The RMS–percent error [eqn. (1)] is used as a basis for comparison introducing a measure of accuracy of fit for the given set of constants for each of the equations of state tested to the experimental data (Tables 1 and 9). The interaction loop of this program has been made more efficient by starting with the ideal gas density (ideal gas state $PV = nRT$ is considered to be the reference state) rather than with the zero-density state as proposed by Johnson and Colver [7b].

Similar programs have been set-up for mixture calculations [26]. Results from these calculations will be presented in a separate work.

RESULTS AND DISCUSSION

Table 1 contains the experimental data used for testing the Benedict–Webb–Rubin, Starling and Lee–Kesler equations of state. Table 2 contains the constant sets for the Benedict–Webb–Rubin equation judged (this work) to be most accurate for PVT-calculations for the given substances. Other constant sets from the literature are found in Table 3. Included in each of these tables are the calculated RMS percent error [eqns. (1) and (2)] values giving a measure of the accuracy of each constant set considered. The listed "best" results (Table 2) obtained for CH_4, C_2H_6, C_3H_8 and CO_2 show the great accuracy obtainable even in the critical and liquid regions. It should be noted that these suggested "best" constant sets (Table 2) have been obtained by means of multiproperty regression analysis. Of interest is to note that the poorer results found for N_2 and Ar (Table 2) imply the overall inadequacy of the presently available constant sets used for PVT-calculations for these compounds.

In order to obtain more accurate results for the quantum fluids (in this case H_2 and He) it is noted that reasonable results are obtained if at least one constant of the constant set needed is made a function of temperature. The B correction for H_2 has already been suggested by Eubanks [19] some time ago; while we (this work) suggest the B_0-correction for He [eqn. (4)] effectively reducing errors at temperatures above 70 K.

While Table 2 indicated the accuracy possible with the Benedict–Webb–Rubin equation, Table 3 shows how significant errors may be introduced if inappropriate constant sets are chosen. However it appears (Table 3) that these errors are hardly significant at low pressures and high temperatures (i.e. fluid approaches the ideal gas state) but increase at the critical and liquid states. Our analysis, nevertheless, did indicate (Tables 2, 3 and 9) that errors in general tend to be greater when constant sets determined from vapour pressure data alone are used to perform PVT-calculations despite a few noted exceptions (Tables 2 and 3). In addition, the C_0–temperature correction originally suggested by Benedict–Webb–Rubin [1–6] to fit the vapour pressure curve, does not appear to be needed for PVT-calculations *.

Table 3 also includes corrected constant sets where at least one of the constants used appears to have had an incorrect form in the original article; for instance, errors in converting the constants to appropriate units. Table 8 lists conversion factors used in this work.

The generalized Benedict–Webb–Rubin constants used (Table 3) are those of Cooper and Goldfranck [12] and those of Edmister et al. [17] (see Yorizane and Masuoka [47] for additional discussion). A weakness in both the Benedict–Webb–Rubin generalized methods tested is that they do not start out with sufficiently accurate constant sets near the critical state. Consequently, the results near the critical state are very poor for both of the methods tested.

Comparative testing of the Benedict–Webb–Rubin equation indicated (Tables 2 and 3) that for the same compounds, the results obtained via the multiproperty regression analysis were superior to those obtained by means of either one of the Benedict–Webb–Rubin generalized methods.

The Starling correlation (eqns. 6–17) was tested by both the generalized method and the specific constant sets (multiproperty regression analysis) published by Starling et al. [39–42]. Table 6 lists the results obtained by means of the specific constant sets (including the corrected errors found in the reference articles) while Table 9 gives the results calculated by means of the generalized method.

The generalized constant expressions for the quantal fluids H_2 and He (Table 9) were modified using calculated (this work, Tables 1 and 4) pseudocritical temperature dependent values **. Results obtained by means of the Starling generalized method (Table 9) in general seem to approach in accuracy those obtained by means of the multiproperty regression analysis (Table 6). Yet, results obtained for quadrupolar CO_2 and quantal H_2 do show large deviations. This erratic behaviour occurs near the critical point for CO_2, and at low temperatures (< 50 K) and/or high pressures (> 400 atm) for H_2. Whether similar observations could be made for other non-ideally behaving substances, is an open question worthy of further study.

Assuming that it is proper to generalize to that extent, the results in broad lines indicate (Tables 1, 6 and 9) that the Starling correlation should be reliable for hydrocarbons, less reliable for strongly interacting non-hydrocarbons especially within the range of the critical point.

The fully generalized, classical corresponding state method of Lee and Kesler was used with critical constants taken from Reid et al. [36], while the pseudocritical parameters needed for quantal fluids H_2 and He were calculated by means of the

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* This correction is in effect incorporated in the Starling correlation [eqns. (6)–(17)] as D_0 and E_0 terms; and in the Lee–Kesler method [eqns. (18)–(23)] as the b_4 term. It has also been used by Lin and Napthali [24] by changing the C_0/T^2 term into C_1/T^n term, where the exponent n varies (limits of variation not specified.)/

** These pseudocritical parameter–temperature relations were first introduced by Prausnitz and Chueh [33] for use in the Redlich–Kwong equation. We have used these functional relations in this work, for both, the Starling equation, and the Lee–Kesler method (Tables 1 and 4).

already introduced quantum correction (Table 1)*. The results obtained by the Lee–Kesler method are given in Table 9. These results show a high degree of reliability for all compounds in all regions studied. Comparing the three methods tested (Table 9) we note that the fully generalized Lee–Kesler method is easy to use and very accurate in predicting *PVT*-properties. Also accurate is the Starling equation in its generalized form although results appear to be less certain. The original Benedict–Webb–Rubin equation may give highly reliable results provided the input parameters are reliable. In general, the more recent constant sets** obtained via the time consuming multiproperty regression analysis appear to give good results. This study indicated that for the quantal fluids, H_2 and He, the Benedict–Webb -Rubin equation may be used if one constant is made temperature dependent. Additionally, both, the Starling and the Lee–Kesler generalized methods work well if temperature dependent quantum correction pseudocritical parameters are introduced (footnote **, p. 22) (Tables 1 and 4).

If the ease of use of the state equation is considered, then the Lee–Kesler method would appear to be the best all-around method for calculating the pure gas compressibilities (Table 9).

NOMENCLATURE

A_0, B_0, C_0, a, b, c, α, γ Benedict–Webb–Rubin equation constants
A_0, A_j, B_0, B_j, C_0, D_0, E_0, a, b, c, d, α, γ Starling and Starling–Han equation constants
B, C, D, b_1, b_2, b_4, c_1, c_2, c_3, c_4, d_1, d_2, β, γ Lee–Kesler equation constants

P	Pressure
R	universal gas constant
T	temperature
Z	compressibility factor
ρ	density
ω_i	acentric factor

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* For the Lee–Kesler equation quantum corrections work best with ω set at 0. Note, however, that the Lee–Kesler equation works well for H_2 at all temperatures and for the He at temperatures >50 K with experimental values of T_c, P_c, ω.

**Yet it should also be recalled that best constants for compressibility may not be best for vapour pressure data. For instance, Motard and Organick [27] reject Eubanks' set [19] of H_2 constants (Tables 2 and 3) for vapour pressure calculations. Yet if we compare, we find that Eubanks [19] set of constants is much better than the Motard and Organick [27] set for compressibility factors. This is also strengthened by observing that the Lin and Naphthali [24] constant sets determined from vapour pressure data, show poor performance for compressibility calculations.

Superscript

0 reference, ideal

Subscripts

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

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