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Thermodynamic properties of unsaturated vapour and liquid states from a cubic equation of state: saturated and subcritical regions

J. Lielmezs [1] and P.C.N. Mak

Chemical Engineering Department, The University of British Columbia, Vancouver, BC (Canada)

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Abstract

The Lielmezs–Merriman (LM)-modification of the Peng–Robinson (PR) equation of state has been applied to the entire $P-V-T$ surface except the critical iostherm. The applicability of this modification has been presently tested for the saturated and subcritical regions by comparing its predictions of thermodynamic properties (vapour pressure, liquid and vapour volumes, departure functions—ΔH, $\Delta \mathscr{A}$, ΔG, ΔS and ΔU, and fugacity) of pure compounds with the experimental data and calculations made by the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state.

INTRODUCTION

Earlier, Lielmezs and Merriman [1] proposed a modification of the Peng–Robinson equation of state [2] for predicting the saturated states of liquid–vapour equilibrium. Cheok et al. [3] applied this modification to calculate the $P–V–T$ properties of saturated liquid–vapour binary mixtures. We extend this modification for pure substances to include the entire (apart from the critical isotherm) $P–V–T$ surface. We have divided the $P–V–T$ surface into four regions (Fig. 1): saturation, subcritical, supercritical and compressed. In this paper we test the saturated and subcritical regions. The properties tested for the saturation region are: vapour pressure, vapour and liquid volumes, and enthalpy and entropy of vaporization (Fig. 2, Tables 1 and 2). In the subcritical region the properties studied are volume, pressure, temperature, the departure functions ΔH, $\Delta \mathscr{A}$, ΔG, ΔS and ΔU, and the fugacity coefficient (Figs. 3–5, Tables 3, 4a and 4b). This correlation is tested against the available experimental data (Tables 1, 2, 4a and 4b) with the RMS% error and the AAD values of this work against the RMS% error and AAD values obtained by means of the Soave modifica-

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[1] Author to whom correspondence should be addressed.

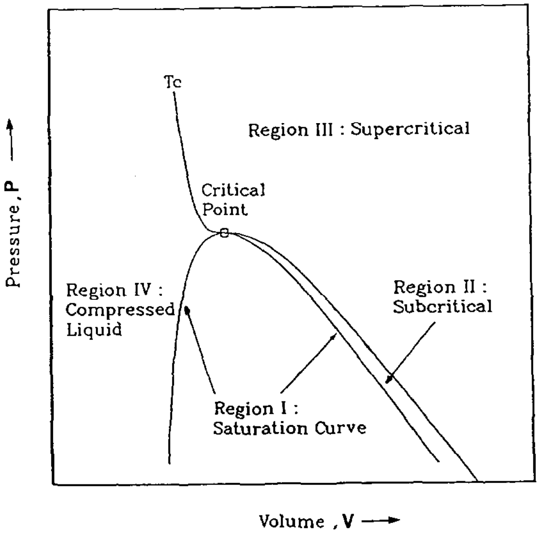

Fig. 1. Division of pressure—volume surface.

tion of the Redlich–Kwong (SRK) equation [4–6] and the Peng–Robinson (PR) equation of state [2].

The RMS% error is defined as

$$\text{RMS\% error} = \left[\frac{\sum (\%\text{error})^2}{N}\right]^{1/2}$$

where

$$\%\ \text{error} = \frac{\text{experimental} - \text{calculated}}{\text{experimental}} \times 100$$

AAD is defined as

$$\text{AAD} = \frac{|\text{deviation}|}{N}$$

where deviation = experimental – calculated and N is the number of data points.

EXTENSION OF LM EQUATION TO UNSATURATED VAPOUR AND LIQUID STATES

The LM modification [1] of the Peng–Robinson equation of state [2] may be written as

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

TABLE 1

Summary of data[a] and curve-fitted constants p, q (eqn. (5)) used

Compound	MW	P_c (atm)	T_c (K)	T_b (K)	ω	p	q
Methane	16.042	45.80	190.65	111.70	0.008	0.19584	0.78426
Ethane	30.068	48.20	305.42	184.47	0.098	0.25183	0.83742
Propane	44.094	42.01	369.96	231.10	0.152	0.27413	0.85176
n-Butane	58.123	37.47	425.16	272.67	0.193	0.28984	0.87067
i-Butane	58.123	36.00	408.13	261.32	0.176	0.27968	0.87124
n-Pentane	72.1498	33.25	469.65	309.19	0.251	0.30395	0.86468
i-Pentane	72.1498	33.37	460.39	301.025	0.227	0.29387	0.85979
Neopentane	72.1498	31.54	433.75	282.628	0.197	0.27709	0.87028
n-Hexane	86.170	29.91	507.87	341.87	0.296	0.30876	0.81677
n-Heptane	100.205	27.00	540.20	371.60	0.351	0.32020	0.82035
n-Octane	114.232	24.50	568.80	398.80	0.394	0.32632	0.81321
Benzene	78.108	48.70	562.65	353.25	0.212	0.30668	0.82281
Carbon monoxide	28.010	34.52	132.92	81.70	0.049	0.20444	0.80737
Carbon dioxide	44.011	72.80	304.19	194.70	0.225	0.31364	0.89550
Carbon disulphide	76.131	75.19	546.15	319.37	0.115	0.28184	0.72832
Hydrogen sulphide	34.0758	88.20	373.07	212.875	0.100	0.28655	0.84269
Sulphur dioxide	64.066	77.79	430.65	263.00	0.251	0.36256	0.83570
Methanol	32.042	78.59	513.15	337.696	0.559	0.47075	0.80070
Ethanol	46.069	60.56	513.92	351.443	0.6436	0.47769	0.84658
1-Propanol	60.090	50.21	537.04	370.93	0.624	0.45585	0.91571
t-Butanol	74.1224	41.77	508.87	356.48	0.618	0.45101	0.90728
Acetylene	26.036	61.64	308.69	189.20	0.184	0.30632	0.80464
Ethylene	28.054	50.50	283.05	169.40	0.085	0.24542	0.81586
Propylene	42.078	45.60	364.91	225.45	0.148	0.27311	0.83694
1-Butene	56.104	39.67	419.59	266.90	0.187	0.29085	0.85773
Water	18.0152	218.3	647.30	373.15	0.344	0.44221	0.73237
n-Deuterium	4.032	16.43	38.35	23.66	−0.130	0.06394	0.61602
n-Hydrogen	2.016	12.98	33.18	20.38	−0.220	0.01877	0.36720
p-Hydrogen	2.016	12.75	32.976	20.268	−0.220	0.01582	0.30806
Nitrogen	28.016	33.49	125.95	77.40	0.040	0.20477	0.81713
Ammonia	17.032	111.3	405.59	239.70	0.250	0.38595	0.85842
Oxygen	32.000	50.08	154.76	90.2056	0.021	0.20734	0.81007
Neon	20.179	26.19	44.40	27.09	0.000	0.14466	0.76353
Argon	39.944	48.33	150.86	87.29	−0.004	0.18893	0.78649
Krypton	83.80	54.25	209.39	119.80	−0.002	0.19626	0.80560
Xenon	131.30	57.60	289.74	165.02	0.002	0.20060	0.79778

[a] Physical properties that are not given in the original data source are taken from ref. 33.

where the coefficient b is given as

$$b = 0.0777960\frac{RT_c}{P_c} \qquad (2)$$

and the temperature dependent $a(T)$ function is written as

$$a(T) = a(T_c, P_c)\alpha(T^*) \tag{3}$$

Following the work of Lielmezs and Merriman [1] we write the first term of eqn. (3) as

$$a(T_c, P_c) = 0.4572355 \frac{R^2 T_c^2}{P_c} \tag{4}$$

The temperature dependent $\alpha(T^*)$ term of eqn. (3) is modified as follows [1,3,7–10]

$$(T^*) = 1 \pm p(T^*)^q \tag{5}$$

where p and q are the two characteristic constants of the pure compound determined at the saturated liquid–vapour equilibrium states and have the same values for all P–V–T surface regions (Fig. 1). The (+) and (−) sign conditions of eqn. (3) denote the two introduced separate regions of the temperature field of the P–V–T surface, defined as $T < T_c$ and $T > T_c$, respectively.

For the first temperature field $T < T_c$, we introduce the dimensionless temperature T^* [1,3,7–10] as

$$T^* = \frac{(T_c/T) - 1}{(T_c/T_b) - 1} \tag{6}$$

For the second P–V–T surface region, for which the temperature field is set to be $T > T_c$, the dimensionless temperature T^* is defined as

$$T^* = \frac{(T/T_c) - 1}{(T_c/T_b) - 1} \tag{7}$$

We rewrite a and b (eqns. (2) and (3)) as new parameters A and B, respectively

$$A = 0.4572355\alpha(T^*)P_r/T_r^2 \tag{8}$$

$$B = 0.0777960P_r/T_r \tag{9}$$

Substituting A and B of eqns. (8) and (9) into eqn. (1) we obtain a cubic equation for the compressibility factor Z

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{10}$$

The proposed modification of the PR equation must satisfy the thermodynamic requirement that

$$\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right) \mathrm{d}P \tag{11}$$

Applying eqn. (10) to eqn. (11) we have

$$\ln\left(\frac{f}{P}\right) = (Z-1) - \ln(Z-B) + \frac{A}{2\sqrt{2}B}\ln\left(\frac{Z-0.414B}{Z+2.414B}\right) \tag{12}$$

The solution of eqn. (12) and, hence, the determination of the values of the characteristic constants p and q (eqn. (5)) must satisfy the thermodynamic requirements of phase equilibrium for the pure substances

$$T_s^L = T_s^V;\ P_s^L = P_s^V;\ f_s^L = f_s^V \tag{13}$$

where T is temperature, P is pressure and f is fugacity in the saturated (s), liquid (L) and vapour (V) states, respectively. The numerical values of constants p and q (eqn. (5)) are determined by curve-fitting the experimental saturated vapour pressure data to the α-function [7]. When experimental data are not available, use of an independent vapour pressure equation such as Frost–Kalkwarf–Thodos [11] or Gomez-Nieto–Thodos [12–14] is recommended. The list of compounds studied, along with the least-squares curve-fitted p and q values, are given in Table 1. The proposed α-function (eqn. (5)) is applicable to the entire P–V–T surface for volumetric prediction. For thermodynamic property calculations, where the derivative of the α-function with respect to temperature is needed, the proposed function is applicable in all regions (Fig. 1) except along the critical isotherm, where its temperature derivative is not defined. However, this instability of the α–T relation at T_c does not pose any practical problem, because most industrial processes do not operate near the critical state.

APPLICATION OF THE PROPOSED METHOD

In this section we compare thermodynamic property predictions made in the saturated and subcritical states (Fig. 1) by means of three cubic equations of state: SRK, PR, and LM (this work). All the relationships needed to calculate these properties have been derived from the generalized equation of state [15] and are listed in the Appendix. For carbon dioxide and acetylene their triple point pressures are above 1 atm; therefore, the saturated state temperature at 1 atm has been taken for each of these compounds as their "normal" boiling point temperature (Tables 1, 2, 4a and 4b). The physical constants used as input data for calculations have been listed in Table 1.

Region I—saturation

Properties tested in the saturation region (Fig. 1) include saturated vapour pressure, liquid and vapour volumes, and enthalpy and entropy of vaporization. The experimental data sources for 36 non-polar, inert and quantum mechanical compounds are given in Table 2. To ensure internal

TABLE 2

Comparison of prediction errors: Region I—saturation

Compound	RMS% error									Average absolute deviation (AAD)						T_r range	N	Ref [a]
	P_V			V^L			V^V			ΔH_v, cal/mol^{-1}			ΔS_v, cal/mol^{-1} K^{-1}					
	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM			
Methane	1.605	1.592	0.423	9.722	8.523	8.372	2.765	4.554	2.710	48.9	30.8	30.6	0.333	0.183	0.210	0.586–0.990	29	32
Ethane	0.920	0.420	0.812	18.03	9.290	8.157	3.140	2.385	0.842	97.1	82.1	56.8	0.356	0.283	0.228	0.604–0.999	23	34
Propane	1.027	0.421	0.714	15.35	6.775	6.109	0.771	2.863	1.741	87.3	66.0	71.9	0.283	0.205	0.252	0.625–0.991	30	32
n-Butane	1.115	0.769	0.702	22.61	11.91	10.73	4.932	2.280	2.323	129.7	131.7	94.0	0.321	0.330	0.260	0.641–0.998	32	19
i-Butane	1.036	0.700	0.742	20.71	10.53	9.456	6.244	1.544	3.156	69.0	63.7	40.1	0.181	0.167	0.130	0.640–0.998	30	20
n-Pentane	0.991	0.336	0.803	24.27	13.41	12.05	4.843	0.981	2.371	167.3	139.8	95.1	0.406	0.327	0.257	0.658–0.999	27	21
i-Pentane	0.987	0.493	0.502	22.91	12.56	11.19	5.884	1.122	2.917	141.6	124.3	52.6	0.337	0.289	0.142	0.654–0.999	27	22
Neopentane	0.687	0.358	0.555	20.57	10.85	9.842	3.718	2.195	1.015	164.0	142.4	112.9	0.415	0.348	0.302	0.652–0.999	25	23
n-Hexane	1.725	1.822	1.325	17.71	7.179	5.912	1.936	1.763	2.838	116.6	102.2	84.4	0.287	0.262	0.250	0.538–0.995	43	32
n-Heptane	1.865	1.034	1.412	18.20	6.891	5.790	2.660	1.871	2.318	127.0	93.0	100.3	0.309	0.224	0.277	0.545–0.987	30	35
n-Octane	1.620	4.395	2.711	20.08	7.086	6.779	1.325	3.799	3.413	113.2	141.5	159.5	0.236	0.369	0.457	0.488–0.976	27	35
Benzene	1.297	1.011	1.077	14.60	6.009	5.144	2.366	3.679	2.308	130.4	121.2	74.3	0.296	0.285	0.200	0.553–0.997	47	32
Carbon monoxide	0.897	2.455	0.972	5.819	9.227	9.286	4.797	3.618	4.071	22.4	26.9	16.0	0.226	0.312	0.193	0.513–0.981	24	32
Carbon dioxide	0.540	0.704	0.385	15.78	6.191	5.804	2.293	1.772	1.867	57.9	41.3	59.8	0.231	0.162	0.236	0.712–0.995	32	32
Carbon disulphide	4.490	4.850	2.317	9.156	6.861	6.888	5.528	5.023	8.480	224.4	146.7	241.3	0.587	0.362	0.606	0.500–0.976	26	36

Hydrogen sulphide	1.138	1.808	1.630	12.19	7.738	7.378	4.283	6.410	5.522	107.5	136.5	145.8	0.301	0.435	0.468	0.565–0.997	30	35
Sulphur dioxide	2.244	2.022	1.263	18.41	7.475	6.133	2.456	1.510	2.325	99.2	77.7	118.8	0.187	0.141	0.359	0.593–0.992	35	32
Methanol	8.043	4.442	4.504	41.69	26.02	24.40	13.77	8.519	11.20	563.3	433.8	402.1	1.643	1.250	1.166	0.532–0.996	44	37
Ethanol	3.877	2.315	4.480	26.45	12.92	11.86	5.041	1.641	5.286	236.2	87.2	281.6	0.703	0.250	0.856	0.543–0.979	29	38
1-Propanol	4.743	10.01	3.413	23.18	11.05	10.77	8.311	10.03	5.927	275.1	365.9	309.7	0.620	0.942	0.844	0.555–0.993	13	39
t-Butanol	1.769	2.121	1.365	9.883	4.605	4.700	5.584	3.926	5.051	246.8	195.0	298.7	0.574	0.437	0.705	0.701–0.993	12	40
Acetylene	2.583	1.929	0.415	14.68	6.344	5.314	1.285	1.239	2.459	110.2	97.5	49.9	0.441	0.397	0.213	0.623–0.989	20	32
Ethylene	1.533	1.226	0.772	9.648	7.246	7.054	2.517	2.068	2.483	52.9	27.4	36.9	0.239	0.145	0.201	0.599–0.981	19	32
Propylene	1.254	0.666	0.699	11.85	6.004	5.539	2.887	1.582	1.835	82.7	48.8	47.0	0.268	0.174	0.158	0.618–0.989	26	32
1-Butene	1.536	0.923	0.874	13.36	5.147	4.727	1.615	2.627	1.732	84.6	67.5	98.7	0.241	0.184	0.301	0.651–0.979	26	32
Water	13.34	7.905	5.823	41.19	25.82	23.44	19.28	10.16	10.97	426.8	284.5	349.5	1.144	0.729	0.894	0.422–0.995	43	32
n-Deuterium	9.206	5.065	1.359	7.544	15.98	15.92	14.10	7.694	6.286	27.0	18.9	13.4	1.057	0.719	0.467	0.488–0.991	21	41
n-Hydrogen	2.096	3.671	0.690	6.990	15.46	16.20	2.982	3.090	2.316	9.10	5.20	5.20	0.386	0.203	0.220	0.615–0.964	13	42
p-Hydrogen	2.157	2.910	0.705	6.932	14.10	14.66	2.689	5.333	1.989	9.20	6.70	4.40	0.380	0.252	0.180	0.615–0.970	13	41
Nitrogen	1.503	1.560	0.633	9.506	8.853	8.750	3.477	5.198	3.626	28.3	28.8	26.4	0.250	0.254	0.247	0.614–0.991	18	32
Ammonia	0.910	0.746	1.465	30.75	15.90	15.48	7.656	6.036	7.286	209.8	174.5	220.5	0.434	0.326	0.489	0.602–0.986	29	32
Oxygen	1.140	0.795	0.643	6.661	8.828	8.873	3.860	4.888	3.695	39.4	23.8	25.1	0.330	0.181	0.221	0.583–0.986	24	32
Neon	9.074	7.716	0.771	5.449	13.23	12.62	11.77	9.438	0.779	26.5	20.4	3.50	0.851	0.648	0.118	0.563–0.968	19	43
Argon	1.371	1.450	0.677	7.579	9.876	9.864	2.248	2.887	1.315	32.4	17.1	24.9	0.291	0.122	0.239	0.555–0.994	15	43
Krypton	1.104	1.043	0.599	7.946	8.528	8.488	1.849	3.044	1.818	42.0	30.4	38.3	0.260	0.171	0.241	0.573–0.984	20	43
Xenon	1.174	1.313	0.694	6.481	7.900	7.995	1.335	2.109	0.915	39.9	25.6	38.0	0.192	0.118	0.186	0.569–0.932	12	44
Average	2.57	2.31	1.36	15.94	10.34	9.77	4.78	3.86	3.53	123.5	100.7	103.6	0.433	0.339	0.355	Total number of data points, 933		

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[a] Vapour pressure, liquid and vapour volumes, enthalpy and entropy of vaporization data are taken from the same source.

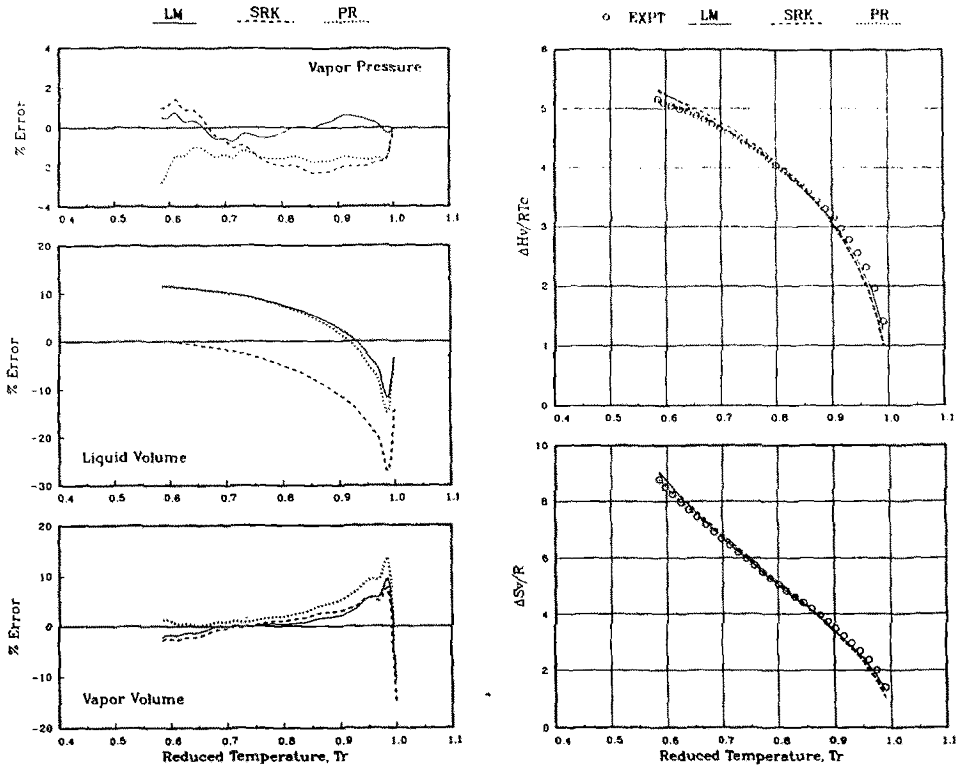

Fig. 2. Region I. Error distribution curves and enthalpy and entropy of vaporization of methane.

consistency, the P–V–T data for each individual compound tested were taken from the same source. The RMS% error plot (Fig. 2) for saturated vapour pressure, liquid and vapour volumes against the reduced temperature T_r, using methane as an example, suggest that for this work vapour pressure has the least error within the temperature range considered, whereas the SRK and PR equations present higher RMS% error values. For saturated liquid and vapour volumes studied over the same temperature range (Fig. 2), this work shows a slight edge over the PR equation, while the SRK equation gives almost double the RMS% error values presented by this work or the PR equation. Figure 2 also shows that, for enthalpy and entropy of vaporization, both this work and the PR equation yield similar results. However, the PR equation gives better results in the low temperature range, whereas this work yields better results at higher temperatures. The separation is in the vicinity of $T_r = 0.7$. The SRK equation is the least accurate. Table 2 shows that, for all the five properties compared from compound to compound in this region, this work is the most accurate in estimating the vapour pressure and the saturated liquid and vapour volumes. The PR equation of state gives the lowest deviations for the two derivative properties—the enthalpy and entropy of vaporization.

Region II—subcritical

The subcritical region is the area between the saturated vapour curve and the critical isotherm (Fig. 1). In this region, predictions of P–V–T properties, the five departure functions (enthalpy, $H - H^\circ$; entropy, $S - S^\circ$; Helmholtz free energy, $\mathscr{A} - \mathscr{A}^\circ$; Gibbs free energy, $G - G^\circ$; internal energy, $U - U^\circ$) and the fugacity coefficient f/P, obtained by means of SRK, PR and LM (this work) equations, have been tested for 22 compounds against the available experimental data (Tables 4a and 4b). Some enthalpy and entropy departure function input data were taken from TRC Thermodynamic Tables of Hydrocarbons [16], other input data sets were calculated from P–V–T data using a modified Benedict–Webb–Rubin equation [17–23] or the BACK [24–31] equation of state. The other departure functions were calculated

$$G - G^\circ = (H - H^\circ) - T(S - S^\circ) \tag{14}$$

$$\mathscr{A} - \mathscr{A}^\circ = (G - G^\circ) - RT(Z - 1) \tag{15}$$

$$U - U^\circ = (H - H^\circ) - RT(Z - 1) \tag{16}$$

$$\ln\frac{f}{P} = \frac{H - H^\circ}{RT} - \frac{S - S^\circ}{R} + \ln\frac{P^\circ}{P} \tag{17}$$

where $P^\circ = 1$ atm is the reference state pressure. The H° and S° values were obtained from the data tabulations of Canjar and Manning [32]. The tabulated H° and S° values were fitted by the least squares method to a polynomial of the form (Tables 3a and 3b)

$$H^\circ = A + BT + CT^2 + DT^3 \tag{18}$$

$$S^\circ = E + FT + GT^2 + HT^3 \tag{19}$$

TABLE 3a

Coefficients of ideal gas enthalpy polynomial (eqn. 18)

Compound	A	B (10^3)	C (10^6)	D (10^9)	Temp. range	Variance
n-Hexane	−30.8531	7.19076	52.6134	−11.044	298–1500	0.0030616
Carbon dioxide	−93.9989	6.16733	5.33631	−1.25588	200–1500	0.00020066
Sulphur dioxide	−70.3422	7.15136	4.83196	−1.23718	200–1500	0.00016076
Acetylene	53.8343	8.07757	5.58979	−1.08690	298–1500	0.00013930
Propylene	8.74913	3.61053	22.3577	−4.58043	298–1500	0.00048150
Water	−56.9968	7.14874	1.36210	−0.0135023	200–1500	0.00003452
Ammonia	−9.23274	6.82980	2.33560	0.704254	200– 800	0.00001325

TABLE 3b

Coefficients of ideal gas entropy polynomial (eqn. 19)

Compound	E	$F\,(10^2)$	$G\,(10^5)$	$H\,(10^9)$	Temp. range	Variance
n-Hexane	55.8375	13.3747	−3.36104	4.19050	298–1500	0.00020731
Carbon dioxide	40.7596	4.04572	−2.25648	5.70186	200–1500	0.01134
Sulphur dioxide	48.0444	4.44643	−2.61622	6.73076	200–1500	0.01998
Acetylene	36.4355	4.53894	−2.32769	5.58302	298–1500	0.003852
Propylene	47.4536	5.94086	−1.58523	2.24722	298–1500	0.00016728
Water	35.5415	3.84262	−2.54623	7.13967	200–1500	0.03261
Ammonia	33.7072	5.54379	−5.65984	26.9856	200– 800	0.003709

The input data, H and S, were converted to departure functions

$$(H - H^\circ) = H(\text{literature}) - H^\circ(\text{eqn. 18}) \tag{20}$$

$$(S - S^\circ) = S(\text{literature}) - S^\circ(\text{eqn. 19}) \tag{21}$$

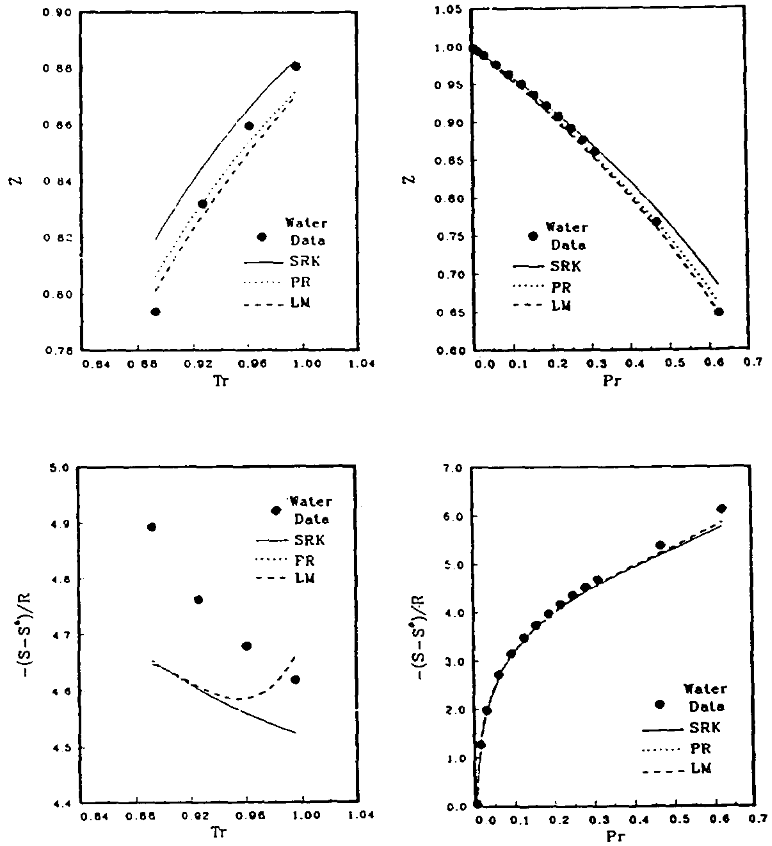

Fig. 3. Region II. Compressibility factors and reduced entropy departure functions of water versus reduced temperature and pressure.

The enthalpy function and fugacity coefficient equations derived from the generalized cubic equation of state are to be found in the Appendix.

Tables 4a and 4b list the RMS% errors obtained in P–V–T value predictions by means of the three considered equations of state: SRK, PR and LM (this work). As may be seen from Tables 4a and 4b these equations are similar in accuracy, the PR equation having a slight edge over the LM equation (this work). Figure 3, chosen as a typical example, presents the compressibility factors of water plotted against the reduced temperature and pressure. These plots show that the PR and LM (this work) equations predict with nearly the same accuracy; the SRK equation is more accurate near the critical isotherm, while the PR and LM equations are better in the region below $T_r = 0.95$. Table 4a shows that, for the subcritical region, the PR equation is most accurate in volume prediction and the SRK equation is the least accurate. The deviations from experimental data (AAD values) have been obtained for the departure functions of enthalpy, entropy, internal energy, Helmholtz and Gibbs free energies and for the fugacity

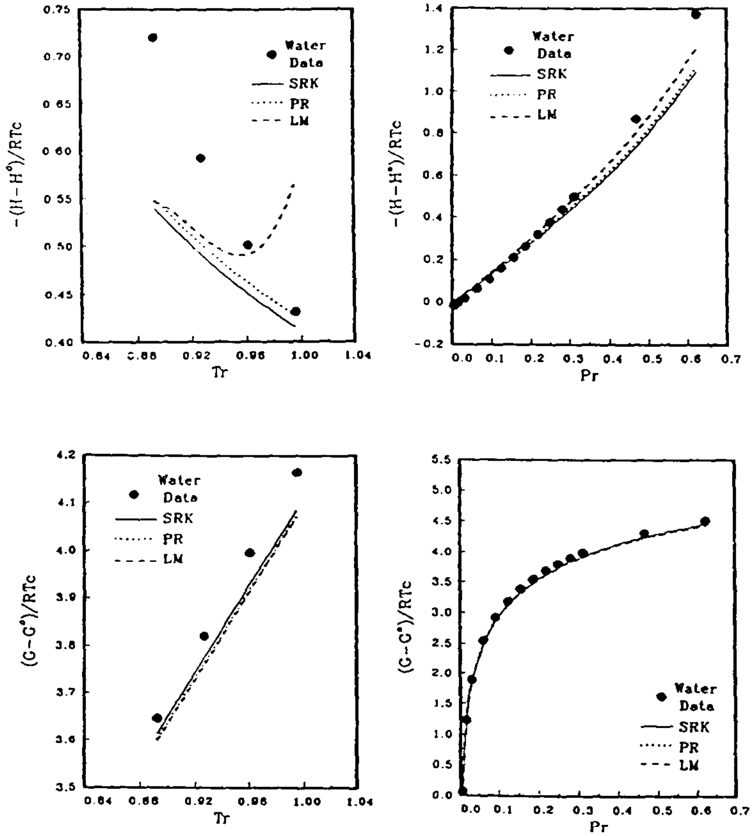

Fig. 4. Region II. Reduced enthalpy and reduced Gibbs free energy departure functions of water versus reduced temperature ($P_r = 0.31$) and reduced pressure ($T_r = 0.96$).

TABLE 4a

Comparison of prediction errors [a]: Region II—subcritical

Compound	RMS% error									T_r range	P_r range	N	ref.
	P			T			V						
	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM				
Methane	0.309	1.458	1.644	0.207	0.878	0.947	0.565	2.759	3.258	0.629–0.986	0.022–0.895	51	16
Ethane	0.581	0.797	0.929	0.371	0.487	0.531	1.227	1.535	2.095	0.655–0.982	0.021–0.892	26	45
Propane	0.650	0.711	0.784	0.456	0.476	0.520	1.298	1.118	1.369	0.649–0.995	0.024–0.952	40	16
n-Butane	0.603	0.737	0.800	0.428	0.494	0.523	0.802	1.034	1.138	0.659–0.988	0.027–0.747	35	19
i-Butane	1.096	0.635	0.684	0.546	0.412	0.506	2.779	0.998	1.115	0.662–0.999	0.028–0.972	59	20
n-Pentane	1.033	0.462	0.520	0.647	0.346	0.372	1.740	0.589	0.708	0.660–0.980	0.030–0.842	31	21
i-Pentane	1.324	0.388	0.336	0.663	0.223	0.230	3.279	1.058	0.659	0.673–0.988	0.030–0.899	37	22
Neopentane	0.693	0.714	0.783	0.480	0.462	0.482	1.197	1.211	1.455	0.669–0.991	0.032–0.919	28	23
n-Hexane	2.030	0.828	0.670	1.223	0.582	0.502	3.224	1.154	0.840	0.722–0.995	0.033–0.910	40	32
n-Heptane	0.349	1.010	1.135	0.267	0.738	0.803	0.432	1.425	1.729	0.703–0.963	0.037–0.731	35	16
n-Octane	0.563	1.263	1.401	0.416	0.911	0.980	0.739	1.778	2.065	0.703–0.985	0.041–0.806	37	16
Benzene	0.170	0.621	0.686	0.114	0.478	0.511	0.335	0.816	0.990	0.658–0.978	0.021–0.811	51	16
Carbon dioxide	2.687	1.732	1.729	1.662	1.125	1.127	3.904	2.381	2.388	0.730–0.986	0.014–0.888	33	32
Sulphur dioxide	0.851	0.631	0.769	0.536	0.395	0.441	1.453	1.140	1.500	0.645–0.993	0.013–0.918	56	32
Methanol	1.216	1.836	2.022	0.765	1.188	1.297	1.644	2.501	2.795	0.702–0.974	0.013–0.628	51	16
Ethanol	0.579	1.193	1.328	0.368	0.761	0.826	0.784	1.650	1.871	0.701–0.973	0.017–0.652	43	16
1-Propanol	0.474	1.015	1.010	0.327	0.699	0.693	0.602	1.318	1.321	0.708–0.968	0.020–0.590	40	16
Acetylene	2.523	1.141	0.908	1.205	0.511	0.390	6.196	2.961	2.326	0.971–0.998	0.016–0.971	43	32
Propylene	1.074	0.816	0.864	0.658	0.530	0.558	2.101	1.256	1.266	0.822–0.989	0.022–0.895	37	32
1-Butene	0.209	0.543	0.581	0.154	0.422	0.445	0.283	0.678	0.737	0.667–0.953	0.025–0.498	33	16
Water	1.206	0.756	0.702	0.801	0.560	0.554	2.157	1.199	0.840	0.652–0.995	0.005–0.935	93	16
Ammonia	1.859	0.850	0.795	1.099	0.563	0.546	3.081	1.354	1.196	0.630–0.986	0.009–0.856	48	16
Average	1.00	0.92	0.96	0.61	0.60	0.63	1.81	1.45	1.53		Total number of data points, 947		

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[a] P–V–T, departure function and fugacity coefficient data have been taken from the same reference.

TABLE 4b

Comparison of prediction errors [a]: Region II—subcritical

Compound	Average absolute deviation (AAD)																		T_r range	P_r range	N	Ref.
	ΔH (cal mol^{-1})			ΔS (cal mol^{-1} K^{-1})			$\Delta\mathscr{A}$ (cal mol^{-1})			ΔG (cal mol^{-1})			ΔU (cal mol^{-1})			f/P						
	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM				
Methane	8.1	5.0	10.6	0.053	0.058	0.051	0.5	0.7	0.6	1.3	5.7	6.1	8.6	9.4	8.6	0.0029	0.0123	0.0132	0.629–0.986	0.022–0.895	51	16
Ethane	35.9	29.2	19.9	0.120	0.123	0.093	1.1	1.6	1.0	2.0	5.9	6.3	32.8	33.1	24.8	0.0030	0.0078	0.0083	0.655–0.982	0.021–0.892	26	45
Propane	35.5	29.1	24.2	0.101	0.102	0.076	1.8	2.2	1.9	2.0	6.1	6.4	31.9	31.9	24.3	0.0029	0.0071	0.0074	0.649–0.995	0.024–0.952	40	16
n-Butane	40.5	33.2	29.2	0.098	0.099	0.090	0.7	1.0	0.8	2.9	5.7	6.0	36.9	37.1	33.5	0.0035	0.0060	0.0063	0.659–0.988	0.027–0.747	35	19
i-Butane	86.8	73.3	61.2	0.205	0.206	0.162	3.5	4.6	4.1	5.9	8.7	9.1	77.5	76.7	62.3	0.0059	0.0084	0.0087	0.662–0.999	0.028–0.972	59	20
n-Pentane	59.8	51.5	47.3	0.126	0.127	0.119	1.4	1.7	1.4	6.3	4.2	4.7	52.1	52.2	48.8	0.0064	0.0041	0.0045	0.660–0.980	0.030–0.842	31	21
i-Pentane	54.6	44.0	28.9	0.107	0.108	0.076	3.0	3.6	3.0	8.2	3.3	3.9	43.4	43.0	29.1	0.0077	0.0031	0.0036	0.673–0.988	0.030–0.899	37	22
Neopentane	49.4	40.7	31.2	0.116	0.117	0.094	1.1	1.6	1.3	3.7	6.5	6.9	44.6	44.5	34.5	0.0042	0.0064	0.0067	0.699–0.991	0.032–0.919	28	23
n-Hexane	183.0	171.2	146.5	0.173	0.172	0.110	94.5	94.4	94.5	109.0	101.0	100.2	164.3	163.7	140.8	0.0216	0.0119	0.0109	0.722–0.995	0.033–0.910	40	32
n-Heptane	13.2	16.8	20.0	0.024	0.025	0.034	1.6	1.7	1.4	4.5	10.1	10.7	12.0	12.4	16.3	0.0041	0.0093	0.0098	0.703–0.963	0.037–0.731	35	16
n-Octane	22.2	27.2	37.1	0.034	0.035	0.054	1.0	1.1	1.0	6.1	12.5	13.4	18.4	18.7	28.9	0.0053	0.0108	0.0115	0.703–0.985	0.041–0.806	37	16
Benzene	7.8	9.2	12.5	0.017	0.018	0.025	1.5	1.6	1.5	2.1	6.5	6.8	7.4	7.9	11.8	0.0020	0.0058	0.0060	0.658–0.978	0.021–0.811	51	16
Carbon dioxide	32.3	35.1	38.2	0.147	0.148	0.149	65.8	66.1	65.9	53.3	59.6	59.7	38.2	38.4	41.3	0.0117	0.0204	0.0205	0.730–0.986	0.014–0.888	33	32
Sulphur dioxide	48.1	40.7	33.5	0.118	0.118	0.092	28.0	27.8	28.1	31.7	26.6	26.2	43.5	43.1	33.6	0.0039	0.0078	0.0084	0.645–0.993	0.013–0.918	56	32
Methanol	24.1	27.0	33.8	0.038	0.038	0.053	0.9	0.9	0.8	8.3	12.5	13.3	18.2	18.0	24.8	0.0079	0.0118	0.0126	0.702–0.974	0.013–0.628	51	16
Ethanol	16.8	19.1	24.2	0.030	0.030	0.042	1.4	1.5	1.3	5.1	9.3	9.9	14.4	14.3	19.4	0.0049	0.0088	0.0093	0.701–0.973	0.017–0.652	43	16
1-Propanol	15.0	16.9	15.5	0.028	0.029	0.029	1.0	1.0	1.0	4.2	8.1	8.0	13.3	13.5	13.1	0.0040	0.0076	0.0074	0.708–0.968	0.020–0.590	40	16
Acetylene	65.9	56.0	33.8	0.154	0.154	0.099	17.6	17.7	17.5	24.3	19.9	19.5	49.8	49.1	34.5	0.0158	0.0044	0.0037	0.971–0.998	0.016–0.971	43	32
Propylene	61.1	54.8	48.2	0.137	0.138	0.123	30.3	30.0	30.2	34.8	27.9	27.6	56.3	56.5	50.5	0.0044	0.0109	0.0113	0.822–0.989	0.022–0.895	37	32
1-Butene	9.5	8.5	9.0	0.029	0.031	0.032	1.3	1.3	1.3	1.2	4.4	4.5	8.9	9.4	9.9	0.0015	0.0053	0.0055	0.667–0.953	0.025–0.498	33	16
Water	72.7	68.1	80.8	0.181	0.182	0.160	58.4	58.6	58.0	52.2	58.8	60.3	64.2	64.5	77.5	0.0057	0.0056	0.0058	0.652–0.995	0.005–0.935	93	16
Ammonia	147.1	139.0	131.6	0.398	0.398	0.381	67.9	67.9	68.0	64.6	66.3	66.4	136.5	136.2	129.4	0.0114	0.0030	0.0028	0.630–0.986	0.009–0.856	48	16
Average	49.5	45.3	41.7	0.111	0.112	0.097	17.5	17.7	17.5	19.7	21.3	21.6	44.2	44.3	40.8	0.0064	0.0081	0.0084		Total number of data points, 947		

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[a] P–V–T, departure function and fugacity coefficient data have been taken from the same reference.

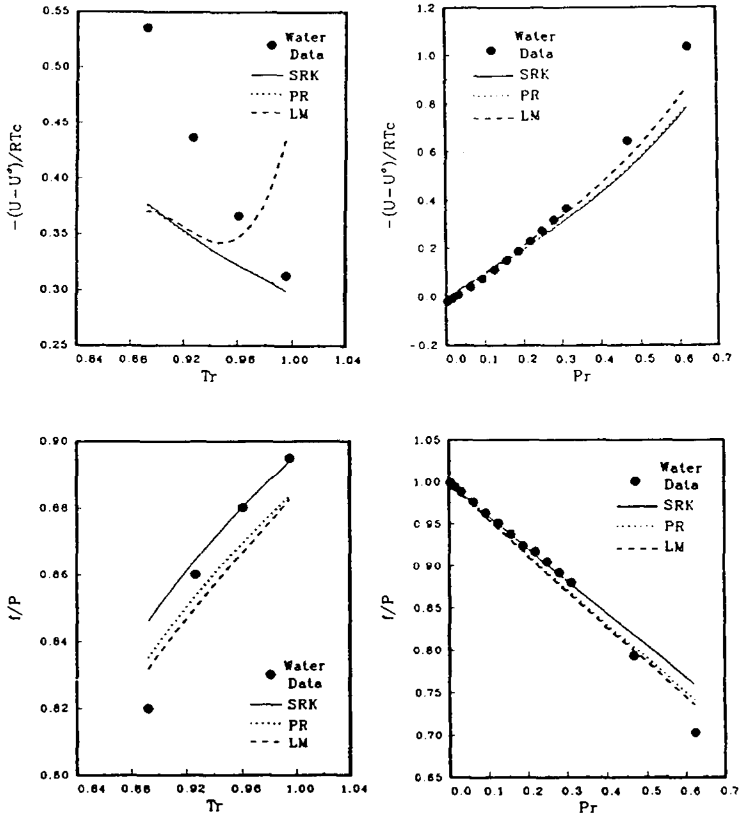

Fig 5. Region II. Reduced internal energy departure functions and fugacity coefficients of water versus reduced temperature ($P_r = 0.31$) and reduced pressure ($T_r = 0.96$).

coefficient by means of the three equations of state: SRK, PR and LM (this work), and are tabulated in Table 4b. This table shows that the predictive accuracy differs very little between the three equations of state compared. Figures 3–5 present the plots of the five departure functions and the fugacity coefficient of water versus the reduced temperature and pressure. For the enthalpy, entropy and internal energy departure functions, the LM equation shows rapid change in the region above $T_r = 0.95$; below this temperature the predictions of the LM equation are similar to those of the SRK and PR equations. This radical behaviour of the LM equation, as already noted, is due to the fact that the derivative of the α-function with respect to the temperature becomes infinite as it approaches the critical temperature. The LM equation, however, does not show this behaviour in the calculations of the Helmholtz and Gibbs free energy departure functions and the fugacity coefficient because these three functions involve both the enthalpy and the entropy and the subtraction of these two functions cancels out the effect near the critical point. Thus, those three functions are well behaved even near the critical temperature. Despite the rapid change of the enthalpy, entropy and internal energy departure functions, the overall average deviations from the LM equation for the prediction of the enthalpy, entropy and internal energy departure functions are the lowest among the three equations compared (Table 4b, Figs. 3–5). For the Helmholtz and Gibbs free energy departure functions and the fugacity coefficients, the accuracy of prediction for all the considered equations is nearly the same (Table 4b, Figs. 3–5).

SUMMARY

Along the saturated vapour–liquid equilibrium curve (Region I—saturation; Tables 1 and 2; Figs. 1 and 2) for the given set of compounds, the LM equation (this work) was found to be the most accurate equation for predicting the saturated vapour pressure and the saturated liquid and vapour volumes. For predicting the two derivative properties enthalpy and entropy of vaporization the PR equation proved to be the most accurate. In the subcritical region (Region II; Tables 3a, 3b, and 4b; Figs. 3–5) the predictions from the SRK, PR and LM equations for the temperature range below $T_r = 0.95$ are very similar. The LM equation should, however, be used with caution when derivative properties such as the enthalpy, entropy and internal energy departure functions are calculated above $T_r = 0.95$.

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LIST OF SYMBOLS

a	parameter in the attraction pressure term of the cubic equation of state
$\mathscr{A}$	molar Helmholtz free energy
A	dimensionless constant defined by eqn. (8)
AAD	average absolute deviation
b	parameter of the cubic equation of state
B	dimensionless constant defined by eqn. (9)
f	fugacity
G	molar Gibbs free energy
H	molar enthalpy
ΔH_v	enthalpy of vaporization
m	constant
MW	molecular weight

N	number of data points
NC	number of compounds
p	substance-dependent parameter in the LM equation
P	pressure
q	substance-dependent parameter in the LM equation
R	universal gas constant
RMS	root mean square
S	molar entropy
ΔS_v	entropy of vaporization
T	absolute temperature
T^*	dimensionless temperature coordinate, eqn. (6)
u	generalized cubic equation of state parameter
U	molar internal energy
V	molar volume
w	generalized cubic equation of state parameter
Z	compressibility factor

Subscripts

b	normal boiling point
c	critical property
r	reduced property
s	saturated

Superscripts

L	liquid phase
V	vapour phase
$^\circ$	reference state; ideal gas state

Greek symbols

α	temperature dependence of the parameter a in the cubic equation of state
κ	constant
Ω_a	coefficient of parameter a
Ω_b	coefficient of paremeter b

APPENDIX

The necessary constants and equations are derived from the generalized cubic equation of state [15]

$$P = \frac{RT}{V-b} - \frac{A(T)}{V^2 + ubV + wb^2} \tag{A1}$$

Critical compressibility factor

$$Z_c = \frac{X(X^2 - 2X - u - w)}{(X-1)^2(2X+u)} \tag{A2}$$

where

$X = V_c/b$

Constants for cubic equation of state, this work

Soave–Redlich–Kwong equation

$u = 1$
$w = 0$
$X = 3.8473221$
$\Omega_a = 0.4274802$
$\Omega_b = 0.0866403$
$Z_c = 0.3333333$

Peng–Robinson equation

$u = 2$
$w = -1$
$X = 3.9513730$
$\Omega_a = 0.4572355$
$\Omega_b = 0.0777960$
$Z_c = 0.3074013$

L–M equation, this work

$u = 2$
$w = -1$
$X = 3.9513730$
$\Omega_a = 0.4572355$
$\Omega_b = 0.0777960$
$Z_c = 0.3074013$

Constants A and B

$$A = \frac{aP}{R^2T^2} = \Omega_a \frac{P_r}{T^2} \tag{A3}$$

$$B = \frac{bP}{RT} = \Omega_b \frac{P_r}{T_r} \tag{A4}$$

where $a = a(T_c)\alpha$, $b = b(T_c)$.

Soave–Redlich–Kwong equation

$$\alpha = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2 \tag{A5}$$

where $m = 0.480 - 1.574\omega - 0.176\omega^2$, and ω is the Pitzer acentric factor for the given substance.

Peng–Robinson equation

$$\alpha = \left[1 + \kappa\left(1 - T_r^{0.5}\right)\right]^2 \tag{A6}$$

where $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$

L–M equation, this work
For $T_r < 1.0$

$$\alpha = 1 + p(T^*)^q \tag{A7}$$

$$T^* = \frac{(T_c/T - 1)}{(T_c/T_b - 1)} \tag{A8}$$

For $T_r > 1.0$

$$\alpha = 1 - p(T^*)^q \tag{A9}$$

$$T^* = \frac{(T/T_c - 1)}{(T_c/T_b - 1)} \tag{A10}$$

The constants p and q are empirical factors for the given substance.

Compressibility factor equation

Soave–Redlich Kwong equation

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{A11}$$

Peng–Robinson equation

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{A12}$$

L–M equation, this work

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{A13}$$

Fugacity coefficient

$$\ln\left(\frac{f}{P}\right) = (Z-1) - \ln(Z-B) + \frac{A}{2B\theta_1}\ln\frac{Z+\theta_2 B}{Z+\theta_3 B} \qquad \text{(A14)}$$

where $\theta_1^2 = [\mathrm{u}^2/4 - \omega]$; $\theta_2 = [\mathrm{u}/2 - \theta_1]$; $\theta_3 = [\mathrm{u}/2 + \theta_1]$

Soave–Redlich–Kwong equation

$\theta_1 = 0.5$; $\theta_2 = 0.0$; $\theta_3 = 1.0$

$$\ln\left(\frac{f}{P}\right) = (Z-1) - \ln(Z-B) + \frac{A}{B}\ln\left(\frac{Z}{Z+B}\right) \qquad \text{(A15)}$$

Peng–Robinson equation

$\theta_1 = \sqrt{2}$; $\theta_2 = 1 - \sqrt{2}$; $\theta_3 = 1 + \sqrt{2}$

$$\ln\left(\frac{f}{P}\right) = (Z-1) - \ln(Z-B) + \frac{A}{2\sqrt{2}B}\ln\left(\frac{Z-0.414B}{Z+2.414B}\right) \qquad \text{(A16)}$$

L–M equation, this work

$\theta = \sqrt{2}$; $\theta = 1 - \sqrt{2}$; $\theta = 1 + \sqrt{2}$

$$\ln\left(\frac{f}{P}\right) = (Z-1) - \ln(Z-B) + \frac{A}{2\sqrt{2}B}\ln\left(\frac{Z-0.414B}{Z+2.414B}\right) \qquad \text{(A17)}$$

Enthalpy departure function

$$H - H^\circ = RT(Z-1) + \left[\frac{a - T(\mathrm{d}a/\mathrm{d}T)}{2\theta_1 b}\right]\ln\left(\frac{Z+\theta_2 B}{Z+\theta_3 B}\right) \qquad \text{(A18)}$$

Soave–Redlich–Kwong equation

$a = a(T_\mathrm{c})\alpha = a(T_\mathrm{c})[1 + m(1 - T_\mathrm{r}^{0.5})]^2$

$$H - H^\circ = RT(Z-1) + R(1+m)\left(\frac{AT}{B\alpha^{0.5}}\right)\ln\left(\frac{Z}{Z+B}\right) \qquad \text{(A19)}$$

Peng–Robinson equation

$$a = a(T_\mathrm{c})\alpha = a(T_\mathrm{c})\left[1 + \kappa\left(1 - T_\mathrm{r}^{0.5}\right)\right]^2$$

$$H - H^\circ = RT(Z - 1) + \left[\frac{R(1+\kappa)}{2\sqrt{2}}\,\frac{A}{B}\,\frac{T}{\alpha^{0.5}}\right]\ln\left(\frac{Z - 0.414B}{Z + 2.414B}\right) \qquad \text{(A20)}$$

L–M equation, this work

For $T_\mathrm{r} < 1.0$

$$a = a(T_\mathrm{c})\alpha = a(T_\mathrm{c})\left[1 + p(T^*)^q\right]$$

$$T\,\mathrm{d}a/\mathrm{d}T = a\phi$$

$$\phi = \left[1 + \frac{aT_\mathrm{c}}{(T_\mathrm{c} - T)} - \frac{qT_\mathrm{c}}{\alpha(T_\mathrm{c} - T)}\right] \qquad \text{(A21)}$$

For $T > 1.0$

$$a = a(T_\mathrm{c})\alpha = a(T_\mathrm{c})\left[1 - p(T^*)^q\right]$$

$$\phi = \left[1 - \frac{qT}{(T - T_\mathrm{c})} + \frac{aT}{\alpha(T - T_\mathrm{c})}\right] \qquad \text{(A22)}$$

$$H - H^\circ + RT(Z - 1) + \left(\frac{RT\phi}{2\sqrt{2}}\,\frac{A}{B}\right)\ln\left(\frac{Z - 0.414B}{Z + 2.414B}\right) \qquad \text{(A23)}$$

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