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APPLICATION OF THE MODIFIED VAN DER WAALS EQUATION FOR UNSATURATED VAPOUR AND LIQUID STATES

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ABSTRACT

The Law–Lielmezs (L–L) modification of the Van der Waals equation of state:

$P = RT/(V - b) - a(T)/V^2$

where:

$a(T) = a(T_c) \cdot a(T^*)$

and:

$a(T^*) = 1 + pT^{*^q}$

has been extended to include unsaturated states in terms of a correcting function C_f such that the $\alpha(T^*)$ term becomes:

$a(T^*) = 1 + pC_fT^{*^q}$

The proposed extension has been compared with the results obtained by the use of the original Van der Waals equation of state.

INTRODUCTION

Recently Law and Lielmezs [1] proposed a modification of the Van der Waals equation of state [2] for the saturated liquid–vapour equilibrium of pure substances. Besher et al. [3] applied this modification to calculate P–V–T properties of saturated binary mixtures. The present work extends this modification to include the unsaturated vapour and liquid region at and below the critical isotherm and isobar. This is done by introducing a correction term C_f as a function of temperature and pressure relating the saturated vapour–liquid equilibrium curve to the given unsaturated state of the fluid.

The extension is tested by comparing the RMS% error values in volume against the RMS% error values obtained by the use of the original Van der

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Waals equation of state. 13 compounds were tested with 1197 data points in their unsaturated vapour state and 12 compounds with 877 data points in the unsaturated liquid state.

EXTENSION TO UNSATURATED FLUID STATES

The L–L modification of the Van der Waals equation [1] is:

$$P = \frac{RT}{V-b} - \frac{a(T_c, P_c)\alpha(T^*)}{V^2} \tag{1}$$

where:

$$a(T_c, P_c) = (27R^2T_c^2)/(64P_c) \tag{2}$$

$$\alpha(T^*) = 1 + pT^{*q} \tag{3}$$

$$b(T_c, P_c) = (RT_c)/(8P_c) \tag{4}$$

$$T^* = \left(\frac{T_c}{T_{\text{exp}}} - 1\right) \bigg/ \left(\frac{T_c}{T_{\text{NB}}} - 1\right) \tag{5}$$

The parameters p and q are characteristic constants of the substance at its saturated vapour–liquid equilibrium state.

We rewrite a and b as new parameters, A and B, respectively:

$$A = 0.421875\alpha(T^*)(P_r/T_r^2) \tag{6}$$

$$B = 0.125(P_r/T_r) \tag{7}$$

Putting eqns. (6) and (7) into eqn. (1) and introducing the compressibility factor Z, we have:

$$Z^3 - (B+1)Z^2 + AZ - AB = 0 \tag{8}$$

The L–L modification of Van der Waals equation of state must satisfy the general thermodynamic requirement that:

$$\ln(f/P) = \int_0^P [(V/RT) - (1/P)]\,dP \tag{9}$$

Combining eqns. (8) and (9), we have:

$$\ln(f/P) = Z - 1 - (A/Z) - \ln(Z - B) \tag{10}$$

The solution of eqn. (10), and hence the determination of substance characteristic parameters, p and q are subject to the general condition that fugacities of the saturated liquid and vapour phases are equal:

$$f_s^l = f_s^v \tag{11}$$

The numerical evaluation of the parameters p and q (eqn. 3) subject to the restraint of eqn. (11) at the saturated vapour–liquid equilibrium state and

TABLE 1

Data used [a] and comparison of results

Compound	Data used range		Number of data points	Ref.	m	n	RMS% error in volume	
	ΔT_r	ΔP_r					This work	Van der Waals
Vapours								
Methane	0.525-0.997	0.0043-0.862	130	5	8.230	−1.460	1.00	2.24
Ethane	0.665-0.982	0.023-0.814	100	5	6.210	−1.212	1.57	3.50
N-Butane	0.659-0.997	0.0267-0.961	53	6	5.007	−8.250	4.66	7.02
N-Pentane	0.660-0.979	0.0301-0.842	32	7	0.598	−3.042	2.98	6.70
N-Hexane	0.678-0.995	0.0023-0.910	148	8	−9.372	−10.200	3.32	6.31
Methanol	0.660-0.985	0.00086-0.867	56	9	−19.957	−3.618	2.29	6.92
t-Butanol	0.720-0.993	0.0239-0.570	76	10	154.320	22.84	5.15	5.62
Water	0.453-0.978	0.000045-0.678	409	11	8.230	−1.460	0.78	1.90
H_2S	0.743-0.922	0.0112-0.459	37	12, 13	−1.055	−2.031	0.92	2.07
N-Hydrogen	0.662-0.963	0.076-0.760	19	5	−6.816	−5.824	0.86	3.00
P-Hydrogen	0.667-0.970	0.0773-0.773	18	5	−14.360	−10.409	1.54	3.38
Neon	0.563-0.901	0.0038-0.377	18	5	−4.580	−4.23	1.13	3.00
Argon	0.002-0.900	0.597-0.994	101	5	12.550	−0.190	2.00	3.41
Average RMS% error							2.17	4.24
Liquids								
Methane	0.499-0.945	0.0043-0.862	156	5	72.28	0.25	34.00	45.42
Propane	0.622-0.919	0.0235-0.938	119	5	51.27	0.34	45.45	57.63
N-Butane	0.690-0.925	0.527-0.790	16	5	−224.40	−7.03	20.00	63.62
N-Pentane	0.624-0.837	0.296-0.889	24	5	116.18	1.00	27.42	64.61
N-Hexane	0.676-0.951	0.330-0.990	23	5	30.39	0.81	59.62	68.47
Methanol	0.581-0.953	0.0647-0.836	46	7, 14	21.27	0.02	86.22	115.06
Water	0.422-0.978	0.000045-0.904	256	11	11.90	0.0003	94.47	105.37
H_2S	0.743-0.922	0.153-0.957	17	12, 13	−301.52	−18.61	16.92	52.63
N-Hydrogen	0.434-0.993	0.0762-0.912	45	5	88.15	8.96	18.77	22.59
P-Hydrogen	0.424-0.970	0.0773-0.928	46	5	751.63	44.32	33.80	23.26
Neon	0.563-0.901	0.0377-0.942	26	5	121.29	0.303	19.70	36.14
Argon	0.563-0.994	0.02-1.00	103	5	38.10	−0.045	43.47	40.26
Average RMS% error							41.65	57.92

[a] Critical point and normal boiling point temperature values taken from refs. 1, 3 and 4.

identified as p_s and q_s, follows the method developed by Lielmezs et al. [4]. To extend the L–L modification of the Van der Waals equation to the unsaturated vapour and liquid states, we introduce a new correcting function, C_f, so that the $\alpha(T^*)$ term becomes:

$$\alpha(T^*) = 1 + p_s C_f T^{*q_s} \tag{12}$$

where:

$$C_f = 1 + mT_h + nP_h \tag{13}$$

and:

$$T_h = \left.\frac{|T_{exp} - T_s|}{T_s}\right|_P \tag{14}$$

$$P_h = \left.\frac{|P_{exp} - P_s|}{P_s}\right|_T \tag{15}$$

Coefficients m and n of eqn. (13) are characteristic constants of the pure substance in question while subscripts exp and s (eqns. 14 and 15) represent the experimental (exp) and saturated (s) temperatures and pressures, respectively. Consequently, the term, T_s (eqn. 14) is defined as that temperature which is found for the given pressure, P_{exp}. On the other hand, the term, P_s (eqn. 15) is that saturated pressure which corresponds to the given temperature, T_{exp}. To establish the values of the characteristic constants m and n (Table 1), the value of the correcting function C_f (eqn. 13) was calculated for each thermodynamic state. To calculate, it was assumed that $C_f = 1$ at the saturation state. The values of terms T_h (eqn. 14) and P_h (eqn. 15) were calculated using saturated liquid–vapour equilibria data (Table 1) by means of the Aitken's interpolation method. In the event that many data are not available, the L–L modification of Van der Waals equation [1,2] may be used to obtain the necessary P_s and T_s values. The coefficients m and n were then obtained by means of multiple linear regression analysis methods.

DATA USED

The saturated and unsaturated P–V–T data (Table 1) were taken from various representative sources. The saturated state p and q values (eqn. 3) were taken as listed from the work of Lielmezs et al. [4]. All these data were thought to be sufficiently reliable and no further re-evaluation for accuracy was made. The RMS% error is used as a basis for comparison of accuracy of fit.

RESULTS

The results calculated provide a basis for extending the previously proposed L–L modification of the Van der Waals equation to unsaturated vapour and liquid states at and below the critical isotherm and isobar. Table 1 presents in terms of RMS% error a comparison between the unsaturated vapour and liquid state volume values obtained from this work and those calculated by the original Van der Waals [2] equation of state. As seen from Table 1, this work exhibits a better behaviour for both the liquid and vapour states than the Van der Waals equation of state. The proposed method satisfies the general requirement of the L–L modification of Van der Waals equation of state [1,2].

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LIST OF SYMBOLS

a, b	coefficients defined by eqns. (1), (2) and (4) as a function of critical temperature and pressure
A, B	dimensionless parameters introduced by eqns. (6) and (7)
C_f	correcting function defined by eqn. (13)
f	fugacity
m, n	coefficients, defined by eqn. (13)
p	coefficient, defined by eqn. (3)
P	pressure
q	coefficient, defined by eqn. (3)
R	universal gas constant
RMS	root mean square
T	absolute temperature
T^*	dimensionless temperature, defined by eqn. (5)
V	volume
Z	compressibility factor

Subscripts

c	critical state
exp	experimental
f	correcting function, eqn. (13)

h	identifies dimensionless T and P, defined by eqns. (14) and (15)
NB	normal boiling point
r	reduced state
rs	reduced, saturated state
s	saturated state

Superscripts

l	liquid state
v	vapour state

Greek letters

$\alpha(T^*)$	dimensionless temperature T^* dependent parameter, see eqns. (3), (5) and (12)

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