OVERALL SUMMARY OF THE TWO PROPOSED MODIFICATIONS TO THE VAN DER WAALS EQUATION OF STATE

Background

A series of four papers have been proposed which present two separate modifications to the original van der Waals equation of state. In reality, these papers are no doubt only of academic interest because more than 100 modifications, e.g. the Redlich-Kwong and Soave equations, have been proposed and tested in the past. However, the modifications presented here retain the integrity of the original van der Waals equation. This author pursued this study more out of a sense of curiosity rather than anything else.

1. Part 1: Prediction of Saturated Liquid Volumes from a Modified Van Der Waals Equation

2. Part 2: Prediction of Saturated Liquid Volumes from a Modified Van Der Waals Equation

3. Part 3: Prediction of Vapor Pressures and Mixture VLE from a Second Modification of the Van Der Waals Equation

4. Part 4: Prediction of Petroleum Fraction Enthalpies from the Second (Alpha) Modification of theVan Der Waals Equation

Summary of the Two Modifications

The first modification is developed and discussed in the first two papers. Here we are proposing a 3-parameter modification of the original VDW equation which produces a significant improvement for the prediction of saturated liquid specific volumes for pure component hydrocarbons and several nonhydrocarbons, including water. The main feature of this modification is to make the b parameter temperature-dependent by introducing a parameter β such that,

$$b = \beta(T) \bullet b_c$$

where b_c is the original VDW b parameter which accounts for the volume occupied by the molecules themselves. A successful correlation of the β parameter as a function of the reduced temperature T_r and the Pitzer acentric factor ω was achieved. The β function developed here insures that the term $v^L - b > 0$ in all cases. In other words no singularities or negative values for this term are possible any more.

In the third paper we propose a second 3-parameter modification which provides an improvement for the prediction of pure component vapor pressures and vapor-liquid equilibria for mixtures.

For this modification we followed a similar approach as did Soave (Chem. Engr. Sci. 27, No. 6-A, 1972, Page 233) in his modification of the Redlich-Kwong equation. We proceeded to make the VDW a parameter a general function of temperature by introducing a temperature-dependent function α such that,

$$a = \alpha(T) \bullet a_c$$

where a_c is the original VDW a parameter which accounts for the effect of intermolecular forces.

Just as for the β parameter, we achieved a successful correlation for the α parameter as a function of T_r and ω.

In the fourth and final paper, we applied the alpha-modification of the VDW eqn. (Paper 3) to the prediction of petroleum fraction enthalpies. The objective here was to propose an alternative procedure to that published by Lee and Kesler (Hydrocarbon Proc. Vol. 55, No. 3 (1976) Page 153) for generating H vs. T diagrams for specific petroleum cuts.

A concise summary of the two modifications to the basic VDW equation of state is given below:

I. General Format of the van der Waals Equation:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad where\ \ v = molar\ \ volume$$

$$a = \alpha(T) \bullet a_c \quad ; \quad b = \beta(T) \bullet b_c \quad \text{"mod}ifications\text{"}$$

$$a_c = \frac{27}{64}\frac{R^2 T_c^2}{P_c} \quad ; \quad b_c = \frac{R T_c}{8 P_c}$$

$$A = \frac{a P}{(RT)^2} \quad ; \quad B = \frac{b P}{RT} \quad ; \quad v = \frac{Z RT}{P} \quad ; \quad Z_c = 0.375$$

$$Z^3 - (B+1) Z^2 + AZ - AB = 0$$

II. For the Prediction of Saturated Specific Liquid Volume of Pure Components:

$$\alpha(T)=1 \quad ; \quad \beta(T)=\frac{b}{b_c}=1+\frac{A_1(T_r-1)}{1-A_2\left(T_r-1\right)}$$

$$A_1=3.110396+9.734409\,\omega$$

$$A_2=10.5792+17.02544\,\omega$$

where $\omega=-1-Log_{10}\left(P_r^S\right)_{T_r=0.7}$, *the Pitzer acentric factor*

The expressions above for A_1 and A_2 are applicable to hydrocarbons and carbon dioxide. For ammonia, hydrogen sulfide and water it is best to use the individual values for these constants as listed in Table 3 of the first paper.

III. For the Prediction of Pure Component Vapor Pressures, Mixture VLE and petroleum fraction enthalpies:

$$\beta(T)=1 \quad ; \quad \alpha(T)=\left[1+m\left(1-T_r^{0.5}\right)\right]^2$$

$$m=0.551088+1.452291\,\omega$$

IV. Mixing Rules for Single Phase Liquid or Vapor Mixtures - Primarily Intended for Mixture VLE Calculations:

$$a=\sum_{i=1}^{N}\sum_{j=1}^{N}z_i\,z_j\,a_{ij}=\sum_{i=1}^{N}\sum_{j=1}^{N}z_i\,z_j\,\alpha_{ij}\,a_{cij}$$

$$a_{cij}=\left(\frac{27}{64}\right)\left(\frac{R^2\,T_{cij}^2}{P_{cij}}\right)$$

$$\alpha_{ij}^{0.5}=1+m_{ij}\left(1-T_{rij}^{0.5}\right)$$

where $$T_{rij} = T / T_{cij} \quad ; \quad T_{cij} = \sqrt{T_{ci}\, T_{cj}}\left(1 - k_{ij}\right)$$

$$m_{ij} = 0.551088 + 1.452291\omega_{ij}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad ; \quad P_{cij} = \frac{P_{ci} + P_{cj}}{2}$$

$$b = \sum_{i=1}^{N} z_i\, b_i \quad ; \quad b_i = b_{ci} \quad \textit{for VLE calcs. only}$$

In principle, the above mixing rules could be used to calculate the specific volume for a single phase saturated vapor or liquid mixture with some degree of uncertainty. For these cases, the above mixing rules would employ the following values:

$$\alpha_{ij} = 1 \quad or \quad m_{ij} = 0$$

$$b_i = \beta_i\,(T) \bullet b_{ci}$$

V. Enthalpies for Petroleum Fraction Cuts:

For the calculation of petroleum fraction enthalpies, we are recommending the direct application of the alpha-modification of the VDW equation as described in Section III of this overall summary. The other relevant equations are:

Total stream enthalpy, H:

$$H = H^o + \left(H - H^o\right)$$

where H^o is the ideal gas enthalpy evaluated at the same temperature as the actual vapor or liquid phase. H - H^o is the enthalpy departure or isothermal effect of pressure on the ideal gas enthalpy. It is given by:

$$H - H^o = Pv - RT - \frac{a - T\dfrac{da}{dT}}{v}$$

where $$\frac{da}{dT} = a_c \frac{d\alpha}{dT} = -\frac{m\,\alpha^{0.5}\, a_c}{\sqrt{T\,T_c}}$$

Ideal gas enthalpies H^o are computed via Eqns. 33-36 of the fourth paper. The enthalpy datum is H^o = 1000 Btu/Lb for the ideal gas state at 0 deg. R.

Input parameters for the correlation (programs) are the normal boiling point and API liquid gravity (or specific gravity) for the petroleum cut of interest. These parameters are then used to calculate the molecular weight, critical constants and acentric factor via Eqns. 14-17 (correlations of Lee-Kesler, 1976 publication) cited in the fourth paper. And, finally, the enthalpy departure and subsequent total phase enthalpy can be computed.

VI. Fugacity Coefficient for Component i in a Single Phase Vapor or Liquid Mixture:

$$Ln\,\phi_i = Ln\left(\frac{v}{v-b}\right) + \frac{b_i}{v-b} - \frac{2\sum_{j=1}^{N} z_j\,\alpha_{ij}\,a_{cij}}{vRT} - Ln\,Z$$

This expression is used for mixture VLE calculations (See Section IV).

.