Modifying the cubic ecuation of state by a Pèneloux volume shift

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1 Introduction

Based on the article by Péneloux et al.[2], the modification on the chemical potentials are investigated.

The volume shift introduced by Péneloux et al.,

$$c = \frac{1}{n}\sum_i c_i n_i, \tag{1}$$

where c_i is a component constant representing the component volume shift.

In order to preserve the consistency of the cubic EoS, the same correction is done on all phases. The effect of the shift for low pressure gas is small, because here the specific volume is large.

2 Cubic equations of state

The general cubic equation of state has the form

$$P = \frac{RT}{v_{\mathrm{cb}} - b_{\mathrm{cb}}} - \frac{\alpha a}{(v_{\mathrm{cb}} - m_1 b_{\mathrm{cb}})(v_{\mathrm{cb}} - m_2 b_{\mathrm{cb}})}, \tag{2}$$

where m_1 and m_2 are dimensionless constants defining the SRK, PR and Van der Waals equation of state, $v = V/n$ ($\mathrm{m}^3/\mathrm{mol}$) is the specific volume. The parameters a ($\mathrm{m}^3\mathrm{J}/\mathrm{mol}^2$) and b ($\mathrm{m}^3/\mathrm{mol}$) typically depend on the composition and the dimensionless quantity α is a function of temperature.

3 Cubic equations of state with volume shift

The actual volume v will be the cubic volume, v_{cb}, shifted by c,

$$v = v_{\mathrm{cb}} - c. \tag{3}$$

In the same manner the co-volume paramater is shifted,

$$b = b_{\text{cb}} - c. \tag{4}$$

That is, the actual eos to be solved is

$$P = \frac{RT}{v-b} - \frac{\alpha a}{(v+c-m_1(b+c))(v+c-m_2(b+c))} \tag{5}$$

$$= \frac{RT}{v-b} - \frac{\alpha a}{(m_1-m_2)(b+c)}\left(\frac{1}{v+c-m_1(b+c)} - \frac{1}{v+c-m_2(b+c)}\right) \tag{6}$$

There is no need to solve the shifted cubic eos, because

1. Given volume, the volume can be shifted before evaluating the cubic eos.
2. Given pressure, the resulting volume can be shifted.

But the corrections for all the thermodynamic potentials and properties must be known.

The fugacity coefficient is given by Pèneloux et al.,

$$\ln \varphi_i = \ln \varphi_{\text{cb},i} - \frac{c_i P}{RT}. \tag{7}$$

4 Required differentials

Need to know how the Gibbs free energy, entropy, enthalpy, and internal energy is affected.

The residual Gibbs free energy, from definition and Equation (7),

$$G^{\text{res}} = RT\sum_i n_i \ln \varphi_i \tag{8}$$

$$= G^{\text{res}}_{\text{cb}} - nPc. \tag{9}$$

The potentials only differ due to the shift in Z due to the volume shift. The residual entropy,

$$S^{\text{res}} = -\frac{\partial G^{\text{res}}}{\partial T}_{P,\boldsymbol{n}} = S^{\text{res}}_{\text{cb}}. \tag{10}$$

is unchanged.

The residual enthalpy,

$$H^{\text{res}} = G^{\text{res}} + TS^{\text{res}} = H^{\text{res}}_{\text{cb}} - nPc. \tag{11}$$

is affected in the same manner as the Gibbs free energy.

Internal energy,

$$U^{\text{res}} = H^{\text{res}} - PV^{\text{res}} = U^{\text{res}}_{\text{cb}}. \tag{12}$$

is not affected.

The compressibillity factor become,

$$Z = \frac{PV}{nRT} = Z_{\text{cb}} - \frac{nPc}{nRT}. \tag{13}$$

The nPc shift in enthalpy and Gibbs free energy must be differentiated.

$$\frac{\partial nPc}{\partial T}_{P,\boldsymbol{n}} = 0, \tag{14}$$

$$\frac{\partial nPc}{\partial P}_{T,\boldsymbol{n}} = nc, \tag{15}$$

$$\frac{\partial nPc}{\partial n_i}_{P,T,n_j} = Pc_i. \tag{16}$$

As it is seen these are straight forward.

Fugacity coefficient differentials:

$$\ln \varphi_{i,j} = \ln \varphi_{\text{cb},i,j}, \tag{17}$$

$$\ln \varphi_{iT} = \ln \varphi_{\text{cb},iT} + \frac{c_i P}{RT^2}, \tag{18}$$

$$\ln \varphi_{iP} = \ln \varphi_{\text{cb},iP} - \frac{c_i}{RT}. \tag{19}$$

Volume differentials:

$$v_i = v_{\text{cb},i} - c_i. \tag{20}$$

The compressibillity factor differentials:

$$Z_T = Z_{\text{cb},T} + \frac{Pc}{RT^2}, \tag{21}$$

$$Z_P = Z_{\text{cb},P} - \frac{c}{RT}, \tag{22}$$

$$Z_i = Z_{\text{cb},i} - \frac{Pc_i}{nRT} + \frac{Pc}{nRT}. \tag{23}$$

5 Calculating the c

The c for the SRK EOS is calculated from the following equation:

$$c_i = 0.40768 \frac{RT_{c_i}}{P_{c_i}} \left(0.29441 - Z_{\text{RA}}\right) \tag{24}$$

Z_{RA} are tabulated in TPlib. Reid et al. [3] also correlate Z_{RA} as follows:

$$Z_{\text{RA}} = 0.29056 - 0.08775\omega \tag{25}$$

Jhaveri and Youngren [1] have developed different paramaters for the PR EOS:

$$c_i^{\text{PR}} = 0.50033 \frac{RT_{c_i}}{P_{c_i}} \left(0.25969 - Z_{\text{RA}}\right) \tag{26}$$

References

[1] B. S. Jhaveri and G. K. Youngren. Three-parameter modification of the peng-robinson equation of state to improve volumetric predictions. *SPE Reservoir Engineering*, 8:1033 – 1040, 1988.

[2] André Péneloux, Evelyne Rauzy, and Richard Fréze. A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilibria*, 8(1):7 – 23, 1982.

[3] R. C. Reid, J. M. Prausnitz, and B. E. Poling. *The properties of gases & liquids*. McGraw-Hill, Inc., USA, 4 edition, 1987.