Equations of States (EOS)

Simple, Ideal Gas [1834] – for gases at low P & high T

Empirical Cubic forms:

Stat mech approaches:

van der Waals (vdW) [1873] – simplest form using a & b as attractive and repulsive interaction terms based on composition

Corresponding States Principle (CSP) [1945] – fluid behavior represented with reduced properties

Redlich-Kwong (RK) [1949] – improvement upon vdW by imposing a temperature dependence term on the attractive term

Pitzer [1955] – introduction of an ascentric factor on a truncated power series of compressibility

Redlich-Kwong Soave (RKS) [1972] – includes an enhanced temperature dependent attractive term that reflects phase equilibrium information by Pitzer's ascentric factor dependence

Virial [1970s] – power series expansion of compressibility using statistical mechanics to develop coefficients/for low to moderate pressure or density

Peng-Robinson (PR) [1976] – a similar temperature dependent term on the attractive term with Pitzer's ascentric factor dependence

EOS Review

Simple Ideal Gas: PV = RT

Empirical Cubic forms:

van der Waals
$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Virial:
$$Z = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2}$$

Redlich-Kwong
$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}V(V+b)}$$

Redlich-Kwong Soave
$$P = \frac{RT}{V-b} - \frac{a(T)}{RT(V+b)}$$

Peng-Robinson
$$P = \frac{RT}{V-b} - \frac{a(T)}{RT[V(V+b)+b(V-b)]}$$

EOS Notes

- The four empirical cubic equations are mentioned because they show the major contributions to EOS development and more specifically focus on attractive term advancements.

- There have also been developments on the repulsive term by Carnahan and Starling (CS) [1972] and combining attractive and repulsive terms together (CS)(RK):

$$\frac{Pv}{RT} = \frac{1 + y + y^2 - y^3}{(1-y)^3} - \frac{a}{RT(v+b)}$$

- Additionally, considerable work has been conducted for chain molecules such as the perturbed hard chain theory (PHCT) [1957] and perturbed anisotropic chain theory (PACT) [1985-86]

  - PHCT is derived from a molecular vibrational and rotational partition function using free-volume concepts

$$Z = Z(hard\ chain) - \frac{a}{RTV}$$

  - PACT includes anisotropic multipolar forces in the PHCT equation and accounts for molecular size, shape, and intermolecular effects

$$Z = 1 + Z^{rep} + Z^{iso} + Z^{ani}$$

Statistical Associating Fluid Theory (SAFT) EOS Development

- The backbone of many systematic improvements to EOS involve a hard-sphere chain concept
  - A thermodynamic perturbation theory (TPT) was proposed by Wertheim [1987] which accommodates hard-chain molecules and Chapman et al. [1988] generalize it
  - Compressibility factor of hard-chain of m segments,

$$Z^{hc} = mZ^{hs} - (m-1)\left(1 + \eta \frac{\partial \ln g^{hs}(\sigma)}{\partial \eta}\right)$$

  Where $g^{hs}(\sigma)$ is the hard-sphere site-site correlation function at contact, σ is the hard-sphere diameter, and η is a packing function

- Associating Fluids EOS:
  - The associated perturbed anisotropic chain theory (APACT) [1986] is derived from the infinite equilibrium model and monomer-dimer model into the PACT and accounts for isotropic repulsive and attractive interactions, anisotropic molecular interactions, and is capable of predicting thermodynamic properties of pure associating components as well as mixtures

$$Z = 1 + Z^{rep} + Z^{att} + Z^{assoc}$$

  - The SAFT EOS [1989] describes hard-sphere repulsive forces, dispersion forces, chain formation (for nonspherical molecules) and association, and it's developed as residual helmhotlz energy

$$a^{res} = a^{seg} + a^{chain} + a^{assoc}$$

References

- Ya Song Wei and Richard J. Sadus. Equations of Sates for the Calculation of Fluid-Phase Equilibria. Thermodynamics Journal Review AIChE Journal. 46(1):169-196 (2000).

- Dr. Schaefer's Equations of State handout. ME3007 Fall 2007.

- Schaum Outline of Theory and Problems of Thermodynamics with Chemical Applications by Abbott and Van Ness. Second Edition, 1989.