

## Equations-of-state (EOS)

Equations-of-state provide a relation among temperature, pressure, volume and an amount of substance  $f(T, p, V, n) = 0$ . For ideal gas (infinitely small molecules, no intermolecular interactions) the **ideal gas equation-of-state** is

$$pV = nRT \quad pV_m = RT \quad (V_m = V/n)$$

For real systems this EOS is valid only at temperatures far above **critical point** ( $T_k, p_k, V_{mk}$  above which distinct liquid and gas phases do not exist).

Estimation Methods: critical properties are often estimated from empirical correlations with other, experimentally more easily available properties such as molar mass, normal boiling point etc. Such estimation approaches are rather common. The most important estimation methods namely for organic compounds are Quantitative Structure-Activity Relationship such as group contribution method, based on the assumption of structural additivity of a given property (the property of interest is given as a sum of properties assigned to its constituent structural elements).

Data sources: Poling, B.E., Prausnitz, J.M., O'Connell, J.P.: The Properties of Gases and Liquids, McGraw-Hill, 2001.

NIST Webbook ([webbook.nist.gov/chemistry](http://webbook.nist.gov/chemistry))

**General EOS** is formally correcting the ideal gas EOS by addition of compressibility factor

$$z = pV/nRT$$

Compressibility factor has to be obtained experimentally at any given conditions or from another EOS, valid for real systems.

## EOS for Real Fluids

### Virial Expansion

$$z = 1 + B(T)/V_m + C(T)/V_m^2 + \dots = 1 + B(T)\rho_m + C(T)\rho_m^2 + \dots$$

Data sources on second virial coefficients: Dymond J.H., Smith B.E.: The Second Virial Coefficients of Pure Gases and Mixtures. Clarendon Press, Oxford, 1980.

### Redlich-Kwong EOS

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)} \quad a = 0,42748 \frac{R^2 T_k^{2,5}}{p_k} \quad b = 0,08664 \frac{RT_k}{p_k}$$

Relations for parameters were obtained from thermodynamic conditions at the critical point.

### Peng-Robinson EOS

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \quad a(T) = \alpha \cdot 0,45723552 \frac{R^2 T_k^2}{p_k} \quad b = 0,0777961 \frac{RT_k}{p_k}$$

$$\alpha = [1 + m(1 - \sqrt{T_r})]^2 \quad m = 0,379642 + 1,48503 \cdot \omega - 0,164423 \cdot \omega^2 + 0,016666 \cdot \omega^3$$

where  $T_r$  is the reduced temperature,  $T_r = T/T_k$  and  $\omega$  is acentric factor,  $\omega = -\log\left(\frac{p_{0,7}^\circ}{p_k}\right)$ ,  $p_{0,7}^\circ$  is saturated vapor pressure of a compound at temperature equal to  $0,7 \times T_r$ .

## EOS for Saturated Liquids

### Rackett EOS

$$V_m = V_k \left( \frac{p_k V_k}{RT_k} \right)^{(1-T/T_k)^{2,7}} \quad [\text{saturation}]$$

This equation can be used for estimating the change of molar volume of saturated liquid with temperature. Saturated liquid is in equilibrium with its vapor. (Saturated) vapor pressure is the lowest pressure at which the compound exists in liquid (equilibrium) state.

### EOS for solids

State behavior of solids is less significant, the coefficient of isobaric expansion  $\alpha$  and coefficient of isothermal compressibility  $\beta$  are usually applied

$$\alpha = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_p \quad \beta = -\frac{1}{V_m} \left( \frac{\partial V_m}{\partial p} \right)_T$$

### State Behavior of Mixtures – Mixing Rules

Mixing rules are designed for estimation of state behavior of mixtures using the knowledge of the EOS for pure components. Mixing rules are formulated for EOS parameters, for critical properties or for state functions.

#### Mixing Rules for EOS Parameters

Simple arithmetic or geometric average is often applied, corrected with empirical binary interaction parameters (omitted when no data are available for their evaluation).

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \frac{b_i + b_j}{2} (1 - l_{ij})$$

$k_{ij}$ ,  $l_{ij}$  are binary interaction parameters, available for Redlich-Kwong and Peng-Robinson EOS e.g. in Oellrich L., Plocker U., Prausnitz J.M., Knapp H.: Chem.-Ing.-Tech. 49, 955, 1977.

#### Pseudo-critical Properties – Kay

$$T'_k = \sum_{i=1}^N x_i T_{k,i} \quad p'_k = \sum_{i=1}^N x_i p_{k,i}$$

#### Pseudo-critical Properties – Joffe

$$K_1 = \frac{T'_k}{\sqrt{p'_k}} = \sum_{i=1}^N \frac{x_i T_{k,i}}{\sqrt{p_{k,i}}} \quad K_2 = \frac{T'_k}{p'_k} = 0,125 \cdot \sum_{i=1}^N \sum_{j=1}^N x_i x_j \left[ \left( \frac{T_{k,i}}{p_{k,i}} \right)^{1/3} + \left( \frac{T_{k,j}}{p_{k,j}} \right)^{1/3} \right]^3$$

$$T'_k = K_1^2 / K_2 \quad p'_k = \left( K_1 / K_2 \right)^2$$

#### Dalton's Law

$$p = \sum_{i=1}^N p_i^D \quad [T, c_1, c_2, c_3, \dots]$$

where  $p_i^D$  is the pressure of a pure component at the same temperature and concentration  $c_i$  ( $= n_i/V$ ) as in the mixture.

#### Amagat's Law

$$V = \sum_{i=1}^k V_i \quad V_m = \sum_{i=1}^k x_i V_{m,i} \quad z = \sum_{i=1}^k x_i z_i \quad [T, p]$$

where  $V_i$ ,  $z_i$  are molar volume and compressibility factor of a pure component in the same phase as the mixture and at the same temperature and pressure.

**Homework 2:** Estimate the density of (n-heptane and n-octane; 1-octanol and 1-propanol; 1-butanol and ethanol; water and methanol; diethylether and acetone; propionitrile and phenol; benzene and n-heptane; toluene and phenol) at 25°C and atmospheric pressure using the Redlich-Kwong and Rackett EOSs. Estimate also the density of a mixture of both liquids in 1:3 ratio using the Rackett EOS. Apply Joffe's pseudo-critical properties and Amagat's Law as mixing rules. Compare the results by different estimation methods.