CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)
05 – FUGACITY IN A MIXTURE

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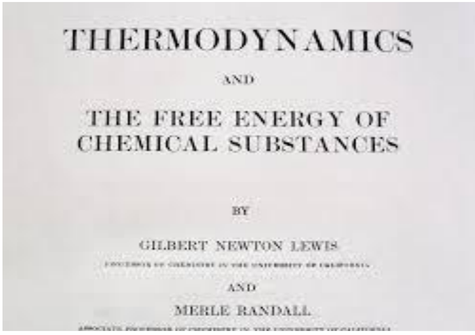
Outline

- Lewis-Randall Rule
- Fluid Models Web
- Activity and Activity Coefficient
- Fugacity in a Mixture
- Fugacity Coefficient from Virial EOS
- Fugacity Coefficient from PR-EOS


THERMODYNAMICS

AND

THE FREE ENERGY OF
CHEMICAL SUBSTANCES

BY

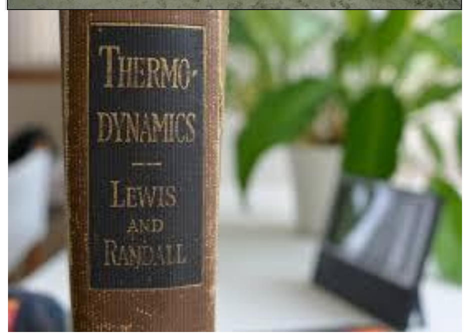
GILBERT NEWTON LEWIS

AND

MERLE RANDALL

Fugacity = urge to flee

- Fugacity is how happy the chemical is in its environment
- Fugacity is like temperature.
- At equilibrium, everything has the same fugacity (temperature) even though they may contain different concentrations (amounts) of the chemical (heat).



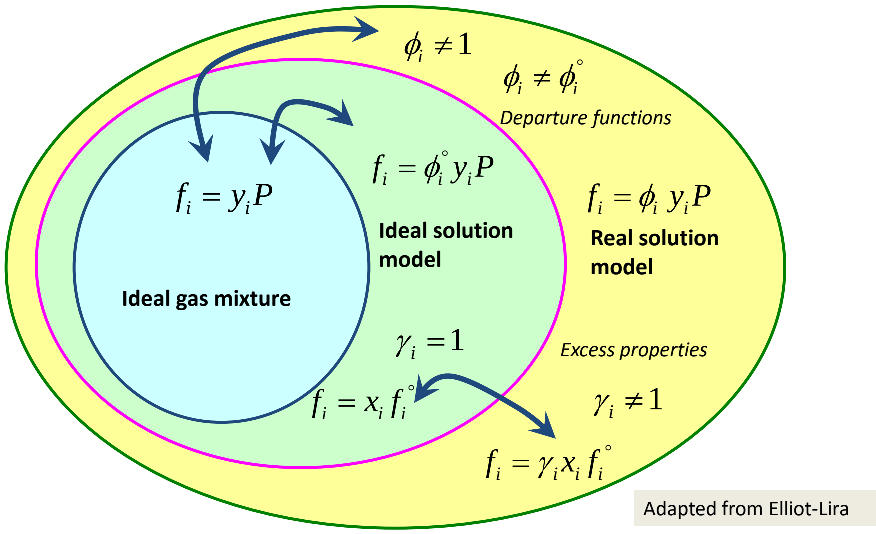
Lewis-Randall Rule

- Assumes ideal solution which includes the effect of T and P but neglects effect of other components present.
  - Composition dependence is through the mole fractions!

$$f_i = \phi_i^\circ y_i P = y_i f_i^\circ$$

  - Obtain pure component fugacity from virial EOS, CST or any other EOS such as PR-EOS or SRK-EOS.

Fluid Models Web



Activity and Activity Coefficient

- Deviations from ideal solution behavior, usually for liquids, are quantified by:
  - Activity

$$a_i = \frac{f_i}{f_i^\circ}$$

  - Activity coefficient

$$\gamma_i = \frac{f_i}{x_i f_i^\circ} = \frac{a_i}{x_i}$$

$$a_i = x_i \gamma_i$$

Qualitative Behavior of Activity and Activity Coefficient

- Activity
  - The activity of a component in an ideal solution is the mole fraction of that component $a_i^{IM} = x_i$.
- Activity coefficient
  - In an ideal solution $\gamma_i^{IM} = 1$.
  - If activity coefficient is greater than one then we have positive deviations from Raoult's law.
  - If activity coefficient is less than one then we have negative deviations from Raoult's law.
  - If an azeotrope exists
    - Positive deviations from Raoult's law yield minimum boiling azeotrope.
    - Negative deviations from Raoult's law yield maximum boiling azeotrope.

Fugacity in a Mixture

- Fugacity coefficient in a mixture in a form suitable for application using volumetric EOS

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{i\neq j}} - \frac{RT}{V} \right] dV - RT \ln z$$

Fugacity Coefficient from Virial EOS

- Determine using

$$\ln\phi_i = \ln\frac{f_i}{y_i P} = \frac{2}{v}\sum_{j=1}^{C} y_j B_{ij} - \ln(z)$$

- Required are
  - Compressibility factor (z) and specific molar volume (v) determined from the virial EOS

$$Z = \frac{PV}{RT} = 1 + \frac{B_{mix}P}{RT}$$

$$v = \frac{zRT}{P}$$

  - Second virial coefficients (pure and cross) determined from Pitzer's correlation.

Estimation of Virial Coefficients in Mixtures

- Obtain pure component properties

$$z_{c,ij} = \left(\frac{z_{c,ii} + z_{c,jj}}{2}\right) \rightarrow \omega_{ij} = \left(\frac{\omega_{ii} + \omega_{jj}}{2}\right) \rightarrow T_{c,ij} = \left(T_{c,ii}T_{c,jj}\right)^{1/2}(1 - k_{ij})$$

$$\downarrow$$

$$P_{c,ij} = z_{c,ij}\frac{RT_{c,ij}}{v_{c,ij}} \leftarrow v_{c,ij} = \frac{1}{8}\left[\left(v_{c,ii}\right)^{1/3} + \left(v_{c,jj}\right)^{1/3}\right]^3$$

- Estimate second virial coefficients from

$$B_{r,ij} = \frac{B_{ij}P_{c,ij}}{RT_{c,ij}} = \left(0.083 - 0.422/T_{r,ij}^{1.6}\right) + \omega_{ij}\left(0.139 - 0.172/T_{r,ij}^{4.2}\right)$$

- Mixture second virial coefficient

$$B_{mix} = \sum_{i=1}^{C}\sum_{j=1}^{C} y_i y_j B_{ij}$$

Fugacity Coefficient from PR-EOS

- PR-EOS

$$\ln \phi_i = \frac{B_i}{B}(z-1) - \ln(z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2}{A}\sum_{j=1}^{C} y_j A_{ij} - \frac{B_i}{B}\right)\ln\left[\frac{z+\left(1+\sqrt{2}\right)B}{z+\left(1-\sqrt{2}\right)B}\right]$$

$$A = \frac{a(T)P}{(RT)^2}; \quad B = \frac{bP}{RT}$$

- Required are
  - Compressibility factor (z) obtained by solving the cubic equation.
  - Pure and cross covolumes (b) and energy parameters (a) obtained from mixing rules.

Peng-Robinson EOS for a Mixture

- Peng-Robinson EOS is given by

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

- Mixing rule gives a and b

$$a = \sum_{i=1}^{C}\sum_{j=1}^{C} y_i y_j a_{ij}, \quad b = \sum_{i=1}^{C} y_i b_{ii}$$

- Combining rule

$$a_{ij} = \sqrt{a_{ii}a_{jj}}\left(1-k_{ij}\right)$$

$$b_{ij} = \frac{b_{ii}+b_{jj}}{2}$$

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