CH365 Chemical Engineering Thermodynamics

Lesson 36
Fugacity & Fugacity Coefficients: Species in Solution

Block 6 – Solution Thermodynamics

Today:
Properties of ideal gas mixtures
Excess properties (of ideal gas mixtures)
Fugacity

Lesson 35 Recap – Fugacity Defined

$$G_i^{ig} = \Gamma_i(T) + RT \ln P \qquad \text{(Eq. 10.28)}$$

$$-$$

$$G_i = \Gamma_i(T) + RT \ln f_i \qquad \text{(Eq. 10.31)}$$

$$G_i - G_i^{ig} = RT \ln \frac{f_i}{P}$$

$$G_i^R = RT \ln \phi_i \qquad \text{(Eq. 10.33)}$$

$$\phi_i \equiv \frac{f_i}{P} \qquad \text{(Eq. 10.34)}$$

- units of pressure; "escaping tendency"
- *residual Gibbs energy*:

  $$G_i^R = G_i - G_i^{ig} \qquad \text{(Eq. 6.41)}$$

- for ideal gases:

  $$f_i^{ig} = P \qquad \text{(Eq. 10.32)}$$

- The residual Gibbs energy of component *i* in a mixture is a function of fugacity

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$$\frac{G^R}{RT} = \int_0^P (Z-1)\,dP \qquad \text{(Eq. 6.49)}$$

$$\Rightarrow \quad \frac{G_i^R}{RT} = \ln \phi_i \qquad \text{(Eq. 10.33)}$$

$$\Rightarrow \quad \ln \phi_i = \int_0^P (Z_i - 1)\,dP \qquad \text{(Eq. 10.35)}$$

Cubic Equations of State:

Derived in Chapter 6

$$\ln \phi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \qquad \text{(Eq. 13.85)}$$

$$\beta_i = \Omega \frac{P_{r_i}}{T_r} \qquad \text{(Eq. 3.50)}$$

$$q_i = \frac{\Psi \alpha}{\Omega T_{r_i}} \qquad \text{(Eq. 3.51)}$$

$$I_i = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{Z_i + \sigma\beta}{Z_i + \varepsilon\beta}\right) \qquad \text{(Eq. 13.72)}$$

Vapor-Liquid Phase Equilibrium & Fugacity

(Eq. 10.31) $\rightarrow$ $$G_i^{vapor} = \Gamma_i(T) + RT \ln f_i^{vapor} \quad \text{(Eq. 10.37)}$$

$$-\quad G_i^{liquid} = \Gamma_i(T) + RT \ln f_i^{liquid} \quad \text{(Eq. 10.38)}$$

$$G_i^{vapor} - G_i^{liquid} = RT \ln \frac{f_i^{vapor}}{f_i^{liquid}}$$

(Equilibrium, Eq. 6.83)

$$G_\alpha = G_\beta \quad \rightarrow \quad G_i^{vapor} = G_i^{liquid} \quad \text{when } \ln(1) = 0$$

$$f_i^{vapor} = f_i^{liquid} = f_i^{sat} \quad \text{(Eq. 10.39)}$$

When the escaping tendency is the same for the two phases, they are in equilibrium. When the escaping tendency of a species is higher in one phase than another, that species will tend to transfer to the phase where is fugacity is lower.

$$\phi_i \equiv \frac{f_i}{P} \quad \text{(Eq. 10.34)}$$

$$\phi_i^{sat} \equiv \frac{f_i^{sat}}{P_i^{sat}} \quad \text{(Eq. 10.40)}$$

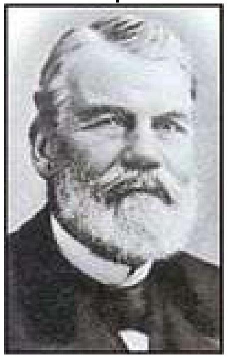
$$\phi_i^{vapor} = \phi_i^{liquid} = \phi_i^{sat} \quad \text{(Eq. 10.41)}$$

For pure species, coexisting liquid and vapor phases are in equilibrium when they have the same temperature, pressure, fugacity, and <u>fugacity coefficient</u>

Raoult's Law

"General Law of the Vapor Pressure of Solvents," in the French Journal, *Comptes Rendus* (May 23, 1887)

Wikipedia



Francois-Marie Raoult, 1830-1901

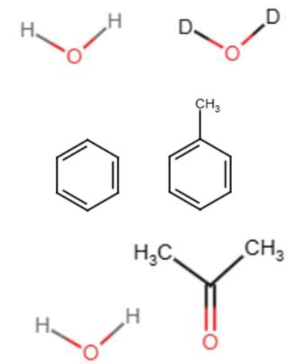
The partial pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the liquid mixture.

$$y_i \cdot P = x_i \cdot P_i^{sat}$$

Partial pressure of each component

Vapor pressure multiplied by liquid solution mole fraction

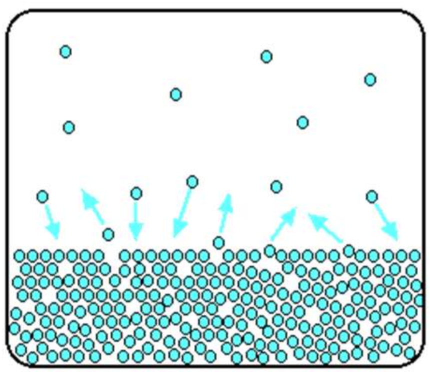
Phenomenological Raoult, 1887



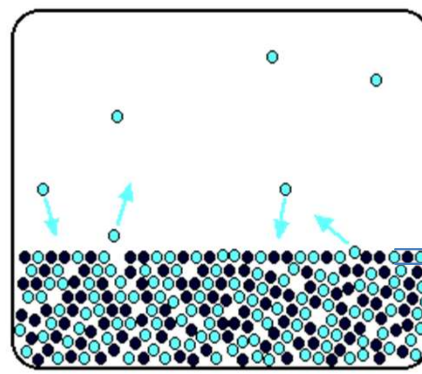
Assumes ideal solution behavior: Intermolecular forces (IMFs) between different molecules are similar to the IMFs between the same molecules.

The more similar the components are, the more they follow ideal solution Raoult's Law (RL) behavior. For example, H_2O and D_2O follow RL exactly. Benzene and toluene follow RL closely. Acetone and water do not follow RL.

Vapor pressure depression – one of the "colligative properties"



Equilibrium between volatile molecules in liquid and gas phases



Equilibrium between volatile molecules with nonvolatile liquid-phase component

IMFs:

If ●--● = ●--●, then $x_i P_i^{sat}$ accurately describes reduction

If ●--● ≠ ●--●, then we introduce the "activity coefficient" γ_i.

The fraction of sites in the surface layer occupied by "●" is equal to the mole fraction of "●" in the bulk solution. The "●" reduce the "●" in the surface layer.

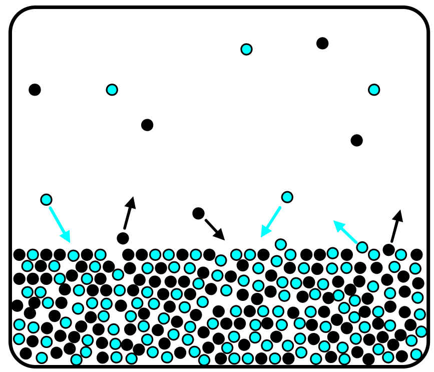
A(liq) ⇌ A(vap)

Raoult's Law K-values: $\dfrac{y_i}{x_i} = \dfrac{P_i^{sat}}{P} = K_i$

with unequal IMFs: $x_i P_i^{sat}$ is replaced with $\gamma_i x_i P_i^{sat}$ ⇒ $\dfrac{y_i}{x_i} = \dfrac{\gamma_i P_i^{sat}}{P} = K_i$

Raoult's Law

When both molecules can escape to the vapor, the behavior of each substance can be described by Raoult's Law, and the vapor pressure of each substance is reduced by the mole fraction of the substance in the liquid.



$\bullet$ volatile $\quad$ ${\color{cyan}\circ}$ volatile

$$y_{\bullet} \cdot P = x_{\bullet} P_{\bullet}^{sat}$$

$$y_{\color{cyan}\bullet} \cdot P = x_{\color{cyan}\bullet} P_{\color{cyan}\bullet}^{sat}$$

$$y_{\color{cyan}\bullet} \cdot P + y_{\bullet} \cdot P = P_{TOT} = x_{\color{cyan}\bullet} P_{\color{cyan}\bullet}^{sat} + x_{\bullet} P_{\bullet}^{sat}$$

$$y_{\color{cyan}\bullet} \cdot P + y_{\bullet} \cdot P = P_{TOT} = \gamma_{\color{cyan}\bullet} x_{\color{cyan}\bullet} P_{\color{cyan}\bullet}^{sat} + \gamma_{\bullet} x_{\bullet} P_{\bullet}^{sat}$$

IMFs:

If $\bullet$--${\color{cyan}\bullet}$ = ${\color{cyan}\bullet}$--${\color{cyan}\bullet}$ = $\bullet$--$\bullet$, then $x_i P_i^{sat}$ accurately describes partial pressure.

If $\bullet$--${\color{cyan}\bullet}$ $\neq$ ${\color{cyan}\bullet}$--${\color{cyan}\bullet}$ or $\bullet$--$\bullet$, then we introduce the "activity coefficient" γ_i to model the partial pressures.

Vapor pressure given by P^{sat} from the Antoine Equation

$$P_{\bullet}^{sat} = e^{A_{\bullet} - \frac{B_{\bullet}}{T + C_{\bullet}}} \qquad P_{\color{cyan}\bullet}^{sat} = e^{A_{\color{cyan}\bullet} - \frac{B_{\color{cyan}\bullet}}{T + C_{\color{cyan}\bullet}}}$$

Vapor-Liquid Equilibrium and Fugacity

$$\mu_i^\alpha = \mu_i^\beta = \ldots = \mu_i^\pi \quad \text{(Eq. 10.6, page 361)}$$

$$f_i^{vapor} = f_i^{liquid} = f_i^{sat} \quad \text{(Eq. 10.39, page 377)}$$

$$\phi_i^{vapor} = \phi_i^{liquid} = \phi_i^{sat} \quad \text{(Eq. 10.41, page 378)}$$

For pure species, coexisting liquid and vapor phases are in equilibrium when they have the same temperature, pressure, Gibbs energy, chemical potential, fugacity and fugacity coefficient.

Replace pressures in Raoult's Law with fugacities

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} \Rightarrow K_i = \frac{y_i}{x_i} = \frac{f_i^{sat}}{f_i}$$

Raoult's Law K-values

$$y_i P = x_i P_i^{sat}$$

$$y_i f_i = x_i f_i^{sat}$$

$$\frac{P_i}{P} f_i = x_i f_i^{sat}$$

$$\frac{f_i}{P} P_i = x_i f_i^{sat}$$

$$\phi_i P_i = x_i f_i^{sat}$$

$$\phi_i y_i P = x_i f_i^{sat}$$

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \Rightarrow K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^{sat}}{f_i}$$

Modified Raoult's Law K-values

For solutions, multiple phases at the same T and P are in equilibrium when the fugacity of each species in solution is the same.

fugacity of species i in solution in phase α

$\hat{f}_i^\alpha$

$$\text{in solution, } \hat{f}_i^\alpha = \hat{f}_i^\beta = \ldots = \hat{f}_i^\pi \quad \text{(Eq. 10.47, page 382)}$$

$$G_i^R = RT \ln \phi_i \quad \text{(pure i, Eq. 10.33)} \longleftrightarrow \bar{G}_i^R = RT \ln \hat{\phi}_i \quad \text{(Eq. 10.51)}$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P} \quad \text{(Eq. 10.52, page 383)} \longleftrightarrow \phi_i \equiv \frac{f_i}{P} \quad \text{(pure i, Eq. 10.34)}$$

Fugacity Ratio

Poynting equation:

Derived on pp. 378-379

$$f_i = \underbrace{\phi_i^{sat} P_i^{sat}}_{f_i^{sat}\text{ by Equation 10.34}} \exp\left[\frac{V_i^l\left(P - P_i^{sat}\right)}{RT}\right]$$ (Eq. 10.44, page 379)

$$K_i = \frac{y_i}{x_i} = \frac{f_i^{sat}}{f_i}$$

$$\therefore \frac{f_i}{f_i^{sat}} = \exp\left[\frac{V_i^l\left(P - P_i^{sat}\right)}{RT}\right] = \text{Poynting factor}$$

P_i^{sat} saturation vapor pressure

V_i^l liquid molar volume, assumed constant

$$\phi_i^{sat} = \frac{f_i^v\left(P_i^{sat}\right)}{P_i^{sat}}$$ (Eq. (A), page 378)

read as "fugacity evaluated at saturation pressure," not "multiplied by"

(vapor-phase fugacity coefficient)

$$\ln \phi_i = \int_0^P \left(Z_i - 1\right) dP \quad \Rightarrow \quad \ln \phi_i^{sat} = \int_0^{P_i^{sat}} \left(Z_i^v - 1\right) dP$$

(Eq. 10.35) (Eq. 10.35 and 10.42)

Questions?