CH365 Chemical Engineering Thermodynamics

Lesson 36
Fugacity & Fugacity Coefficients: Species in Solution

Block 6 – Solution Thermodynamics

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Lesson 35 Recap - Fugacity

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

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

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

$$G_i^R = RT \ln \phi_i \qquad\qquad \phi_i \equiv \frac{f_i}{P}$$

(Eq. 10.33) (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

$$\frac{G^R}{RT} = \int_0^P (Z-1)\,dP \qquad \Rightarrow \qquad \frac{G_i^R}{RT} = \ln \phi_i \qquad \Rightarrow \qquad \ln \phi_i = \int_0^P (Z_i - 1)\,dP$$

(Eq. 6.49) (Eq. 10.33) (Eq. 10.35)

Cubic Equations of State:
Derived in Chapter 6

$$\beta_i = \Omega \frac{P_{r_i}}{T_r} \qquad q_i = \frac{\Psi \alpha}{\Omega T_{r_i}} \qquad I_i = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{Z_i + \sigma\beta}{Z_i + \varepsilon\beta}\right)$$

$$\ln \phi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i$$

(Eq. 3.50) (Eq. 3.51) (Eq. 13.72)

(Eq. 13.85)

Vapor/Liquid Equilibrium

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

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

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

(Equilibrium, Eq. 6.83)

$$G_\alpha = G_\beta \quad \longrightarrow \quad G_i^{vapor} = G_i^{liquid} \qquad \ln(1) = 0$$

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

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.

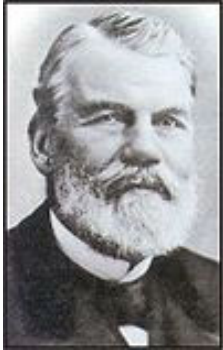$$\phi_i \equiv \frac{f_i}{P} \qquad \text{(Eq. 10.34)}$$

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

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

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

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.

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

Partial pressure of each component

Vapor pressure multiplied by liquid solution mole fraction

Raoult, 1887

Phenomenological; assumes ideal behavior; ideal behavior in a solution is when IMFs between unlike molecules are equal to IMFs between similar molecules.
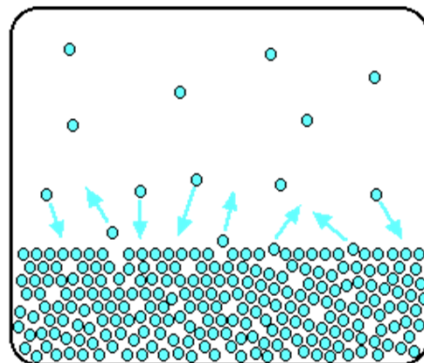
The more similar the components are, the more their behavior approaches ideal solution (Raoult's Law) behavior. For example, H_2O and D_2O follow RL exactly. Benzene and toluene follow it very closely. Acetone and water do not follow RL.

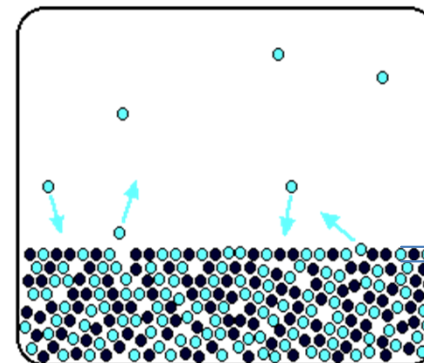Vapor pressure depression – one of the "colligative properties"

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 "●."

Equilibrium between volatile molecules in liquid and gas phases

Equilibrium between volatile molecules in liquid and gas phases with solute present

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 can be described by Raoult's Law, and the vapor pressure of each molecule is reduced by the mole fraction of the other in the liquid.
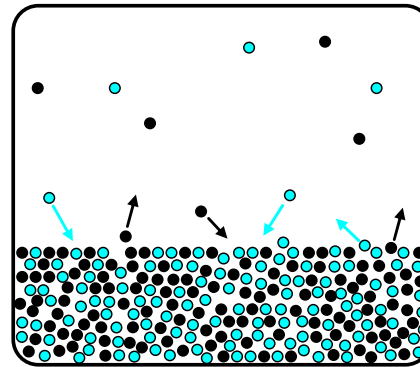
● volatile

○ volatile

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

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

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

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

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

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

Equilibrium Condition

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

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

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

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

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

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

Replace pressures in Raoult's Law with fugacities

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

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

Raoult's Law K-values

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

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

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 is the same.

fugacity of species i in solution in phase α

$$\hat{f}_i^\alpha$$

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

$$\bar{G}_i^R = RT \ln \hat{\phi}_i \qquad\qquad \hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$$

$$\text{(Eq. 10.51)} \qquad\qquad\qquad \text{(Eq. 10.52, page 383)}$$

Fugacity of Liquids

by Equation 10.34

$$f_i^{sat}$$

Poynting equation:

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

Derived on pp. 378-379

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

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

P_i^{sat} saturation vapor pressure

V_i^l liquid molar volume, assumed constant

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

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

(vapor-phase fugacity coefficient)

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

(Eq. 10.35)

(Eq. 10.35 and 10.42)

Homework

Problem 10.21

From the data in the steam tables, determine a good estimate for f / f^{sat} for liquid water at 150 deg C and 150 bar, where f^{sat} is the fugacity of saturated liquid at 150 deg C.