

CHAPTER 9 IDEAL AND REAL SOLUTIONS

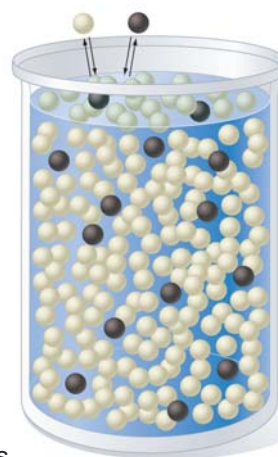
- Raoult's law: ideal solution
- Henry's law: real solution
- Activity: correlation with chemical potential and chemical equilibrium

Ideal Solution

- Raoult's law: The partial pressure (P_i) of each component in a solution is directly proportional to the vapor pressure of the corresponding pure substance (P_i^*) and that the proportionality constant is the mole fraction (x_i) of the component in the liquid

$$P_i = x_i P_i^* \quad i = 1, 2$$

- Ideal solution
 - any liquid that obeys Raoult's law
 - In a binary liquid, A-A, A-B, and B-B interactions are equally strong



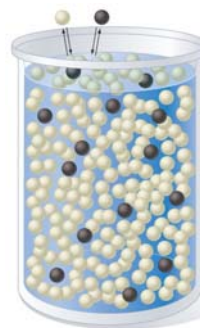
Chemical Potential of a Component in the Gas and Solution Phases

- If the liquid and vapor phases of a solution are in equilibrium

$$\left. \begin{aligned} \mu_i^{\text{solution}} &= \mu_i^{\text{vapor}} \\ \mu_i^{\text{vapor}} &= \mu_i^\circ + RT \ln \frac{P_i}{P^\circ} \end{aligned} \right\} \mu_i^{\text{solution}} = \mu_i^\circ + RT \ln \frac{P_i}{P^\circ}$$

- For a pure liquid,

$$\begin{aligned} \mu_i^* &= \mu_i^\circ + RT \ln \frac{P_i^*}{P^\circ} \\ \mu_i^{\text{solution}} &= \mu_i^* + RT \ln \frac{P_i}{P_i^*} \\ \mu_i^{\text{solution}} &= \mu_i^* + RT \ln x_i \end{aligned}$$



Ideal Solution

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i$$

- $\Delta G_{\text{mixing}} = nRT \sum_i x_i \ln x_i$
- $\Delta S_{\text{mixing}} = -nR \sum_i x_i \ln x_i$

Similar to ideal gas mixing

$$\Delta V_{\text{mixing}} = \left(\frac{\partial \Delta G_{\text{mixing}}}{\partial P} \right)_{T, n_1, n_2} = 0 \quad \text{and}$$

$$\Delta H_{\text{mixing}} = \Delta G_{\text{mixing}} + T \Delta S_{\text{mixing}}$$

$$= nRT \sum_i x_i \ln x_i - T \left(nR \sum_i x_i \ln x_i \right) = 0$$

Example 9.2

- An ideal solution is made from 5 mole of benzene and 3.25 mole of toluene. (a) Calculate ΔG_{mixing} and ΔS_{mixing} at 298 K and 1 bar. (b) Is mixing a spontaneous process?

$$\Delta G_{\text{mixing}} = nRT \sum_i x_i \ln x_i$$

$$\Delta S_{\text{mixing}} = -nR \sum_i x_i \ln x_i$$

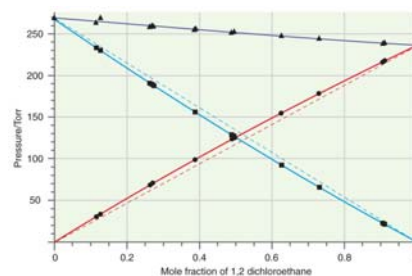
Ideal Solution Model for Binary Solutions

- Both components obey Raoult's law

$$P_{\text{total}} = P_1 + P_2 = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* + (P_1^* - P_2^*) x_1$$

- Mole fractions in the vapor phase (y_i)

$$y_1 = \frac{P_1}{P_{\text{total}}} = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*) x_1}$$



Benzene + DCE

Ideal Solution

$$y_1 = \frac{P_1}{P_{total}} = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*)x_1}$$

$$x_1 = \frac{y_1 P_2^*}{P_1^* + (P_2^* - P_1^*)y_1}$$

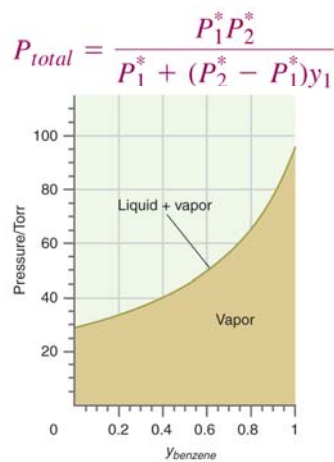
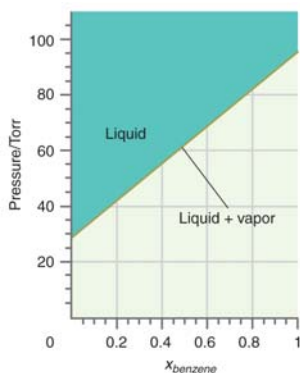
$$P_{total} = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*)y_1}$$

$$y_1 = \frac{P_1^* P_{total} - P_1^* P_2^*}{P_{total}(P_1^* - P_2^*)}$$

Mole fraction in the vapor phase

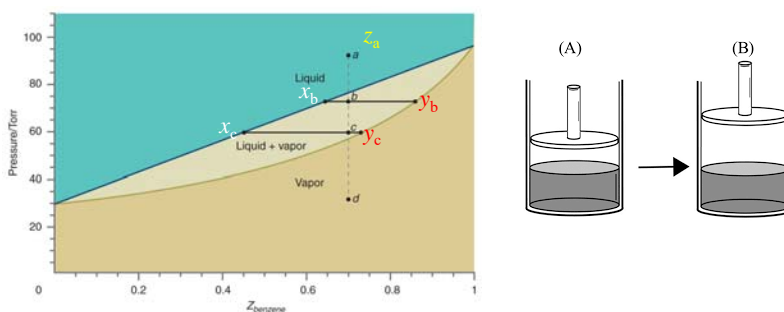
Variation of Total Pressure with x and y

$$P_{total} = P_1 + P_2 = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* + (P_1^* - P_2^*)x_1$$



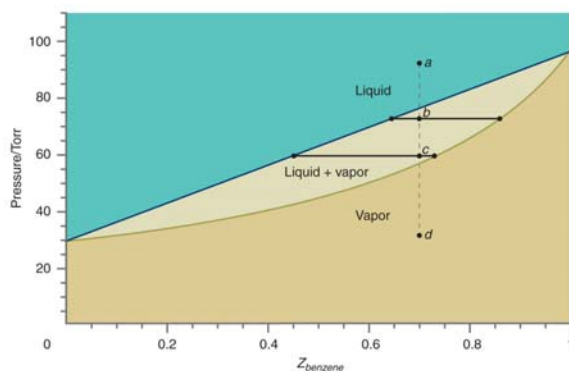
Average Composition (z)

- $Z_{benzene} = \frac{n_{benzene,liquid} + n_{benzene,vapor}}{n_{benzene,liquid} + n_{benzene,vapor} + n_{toluene,vapor} + n_{toluene,liquid}} = \frac{n_{benzene}}{n_{total}}$
- In the liquid phase, $Z_{benzene} = x_{benzene}$
- In the vapor phase, $Z_{benzene} = y_{benzene}$



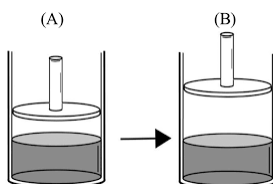
Phase Rule

- In a binary solution, $F = C - p + 2 = 4 - p$, as $C = 2$



Example 9.3

- An ideal solution of 5 mole of benzene and 3.25 mole of toluene is placed in a piston and cylinder assembly. At 298 K, the vapor pressure of the pure substances are 96.4 torr for benzene and 28.9 torr for toluene.
 - a. The pressure above this solution is reduced from 760 torr. At what pressure does the vapor phase first appear?
 - b. What is the composition of the vapor at this point?

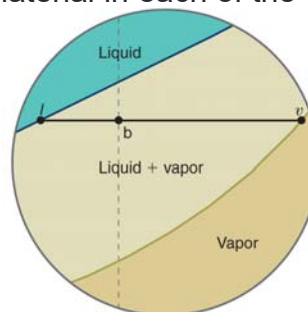


Lever Rule

- To calculate the relative amount of material in each of the two phases in a coexistence region

$$lb = Z_B - x_B = \frac{n_B^{tot}}{n^{tot}} - \frac{n_B^{liq}}{n^{liq}}$$

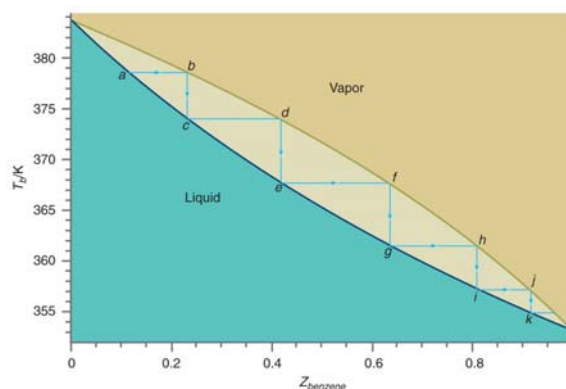
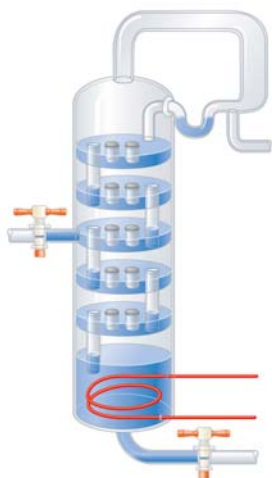
$$bv = y_B - Z_B = \frac{n_B^{vapor}}{n^{tot}} - \frac{n_B^{tot}}{n^{tot}}$$



$$lb n_{liq}^{tot} - bv n_{vapor}^{tot} = \frac{n_B^{tot}}{n^{tot}} (n_{liq}^{tot} + n_{vapor}^{tot}) - (n_B^{liq} + n_B^{vapor}) = n_B^{tot} - n_B^{tot} = 0$$

We conclude that $\frac{n_{liq}^{tot}}{n_{vap}^{tot}} = \frac{bv}{lb}$ $n_{liq}^{tot}(Z_B - x_B) = n_{vapor}^{tot}(y_B - Z_B)$

Fractional Distillation (T – z diagram)



Gibbs-Duhem Equation

- The chemical potentials of the two components in a binary solution is not independent

$$dG = -S dT + V dP + \sum_i \mu_i dn_i$$

const T and P

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \quad \longrightarrow \quad \int_0^G dG' = \mu_1 \int_0^{n_1} dn'_1 + \mu_2 \int_0^{n_2} dn'_2 \quad \text{or}$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

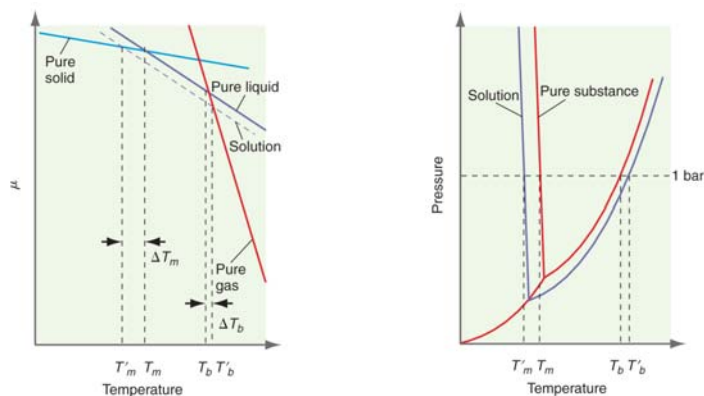
$$d\mu_2 = -\frac{n_1 d\mu_1}{n_2}$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{or} \quad x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Colligative Properties

- Freezing point depression (with nonvolatile solute)
- Boiling point elevation



Freezing Point Depression

$$\begin{aligned}
 \mu_{\text{solution}} &= \mu_{\text{solid}}^* \Rightarrow \ln x_{\text{solvent}} = \frac{\mu_{\text{solid}}^* - \mu_{\text{solvent}}^*}{RT} \Rightarrow \ln x_{\text{solvent}} = \frac{-\Delta G_{\text{fusion}}}{RT} \\
 \mu_{\text{solvent}}^* + RT \ln x_{\text{solvent}} &= \mu_{\text{solid}}^* \\
 \left(\frac{\partial \ln x_{\text{solvent}}}{\partial x_{\text{solvent}}} \right)_P &= \frac{1}{x_{\text{solvent}}} = -\frac{1}{R} \left(\frac{\partial \frac{\Delta G_{\text{fusion}}}{T}}{\partial T} \right)_P \left(\frac{\partial T}{\partial x_{\text{solvent}}} \right)_P \\
 \frac{1}{x_{\text{solvent}}} &= \frac{\Delta H_{\text{fusion}}}{RT^2} \left(\frac{\partial T}{\partial x_{\text{solvent}}} \right)_P \quad \text{or} \\
 \frac{dx_{\text{solvent}}}{x_{\text{solvent}}} &= d \ln x_{\text{solvent}} = \frac{\Delta H_{\text{fusion}}}{R} \frac{dT}{T^2} \quad (\text{constant } P) \Rightarrow \int_1^{x_{\text{solvent}}} \frac{dx}{x} = \int_{T_{\text{fusion}}}^T \frac{\Delta H_{\text{fusion}}}{R} \frac{dT'}{T'^2} \\
 \frac{1}{T} &= \frac{1}{T_{\text{fusion}}} - \frac{R \ln x_{\text{solvent}}}{\Delta H_{\text{fusion}}} \\
 \Delta T_f &= -\frac{RM_{\text{solvent}} T_{\text{fusion}}^2}{\Delta H_{\text{fusion}}} m_{\text{solute}} = -K_f m_{\text{solute}}
 \end{aligned}$$

Boiling Point Elevation

$$\left(\frac{\partial T}{\partial m_{\text{solute}}} \right)_{P, m \rightarrow 0} = \frac{RM_{\text{solvent}} T_{\text{vaporization}}^2}{\Delta H_{\text{vaporization}}}$$

$$\Delta T_b = \frac{RM_{\text{solvent}} T_{\text{vaporization}}^2}{\Delta H_{\text{vaporization}}} m_{\text{solute}} = K_b m_{\text{solute}}$$

TABLE 9.2 Freezing Point Depression and Boiling Point Elevation Constants

Substance	Standard Freezing Point (K)	K_f (K kg mol ⁻¹)	Standard Boiling Point (K)	K_b (K kg mol ⁻¹)
Acetic acid	289.6	3.59	391.2	3.08
Benzene	278.6	5.12	353.3	2.53
Camphor	449	40.	482.3	5.95
Carbon disulfide	161	3.8	319.2	2.40
Carbon tetrachloride	250.3	30.	349.8	4.95
Cyclohexane	279.6	20.0	353.9	2.79
Ethanol	158.8	2.0	351.5	1.07
Phenol	314	7.27	455.0	3.04
Water	273.15	1.86	373.15	0.51

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton, FL: CRC Press, 2002.

Osmotic Pressure (π)

$$\mu_{\text{solvent}}^{\text{solution}}(T, P + \pi, x_{\text{solvent}}) = \mu_{\text{solvent}}^*(T, P)$$

$$\mu_{\text{solvent}}^{\text{solution}}(T, P + \pi, x_{\text{solvent}}) = \mu_{\text{solvent}}^*(T, P + \pi) + RT \ln x_{\text{solvent}}$$

$$\mu_{\text{solvent}}^*(T, P + \pi, x_{\text{solvent}}) - \mu_{\text{solvent}}^*(T, P) = \int_P^{P+\pi} V_m^* dP'$$

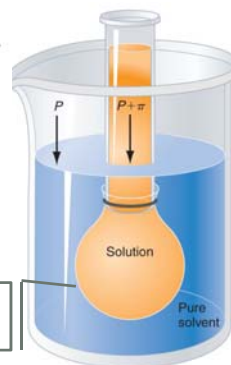
$$\pi V_m^* + RT \ln x_{\text{solvent}} = 0$$

$$\ln x_{\text{solvent}} = \ln(1 - x_{\text{solute}}) \approx -x_{\text{solute}} = -\frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} \approx -\frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

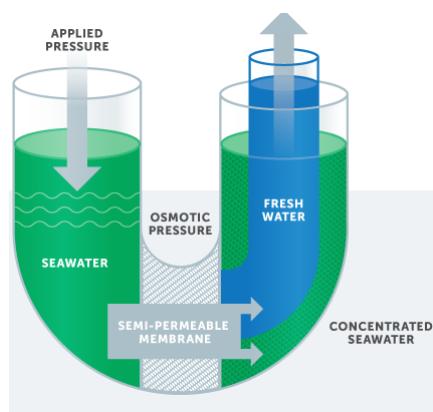
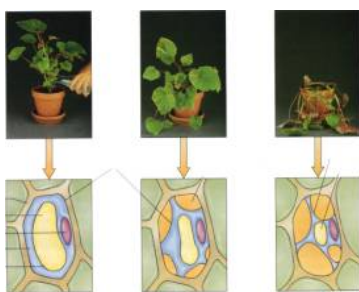
$$\pi = \frac{n_{\text{solute}} RT}{V}$$

van't Hoff equation

Semipermeable membrane



Implication of Osmotic Pressure



Sea water contains 1.1 M NaCl, which means that it will require a pressure of at least 27 bar to reverse osmosis and obtain pure water.

Real Solution

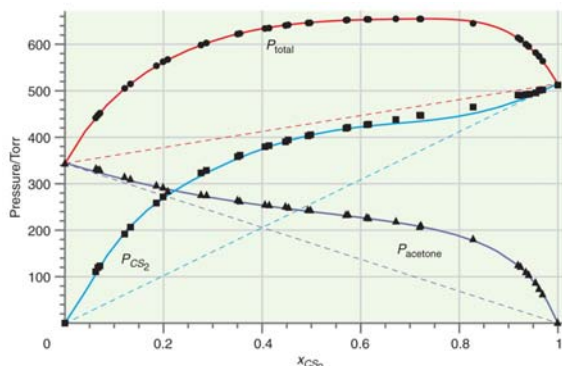
- Deviation from Raoult's law
- Real solution: A-A, B-B and A-B interactions are distinctly different

$$\Delta G_{\text{mixing}} < 0$$

$$\Delta S_{\text{mixing}} > 0$$

$$\Delta V_{\text{mixing}} \neq 0$$

$$\Delta H_{\text{mixing}} \neq 0$$



Real Solution

- ΔV_{mixing} and ΔH_{mixing} can be positive or negative

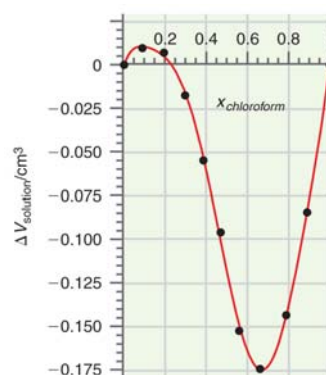
$$V_m^{\text{ideal}} = x_A V_{m,A}^* + (1 - x_A) V_{m,B}^*$$

$$\Delta V_m = V_{m,\text{real}} - V_{m,\text{ideal}}$$

- Partial molar quantity (any extensive variable, U, H, S, A, G, etc)
 - partial molar volume

$$\bar{V}_1(P, T, n_1, n_2) = \left(\frac{\partial V}{\partial n_1} \right)_{P, T, n_2}$$

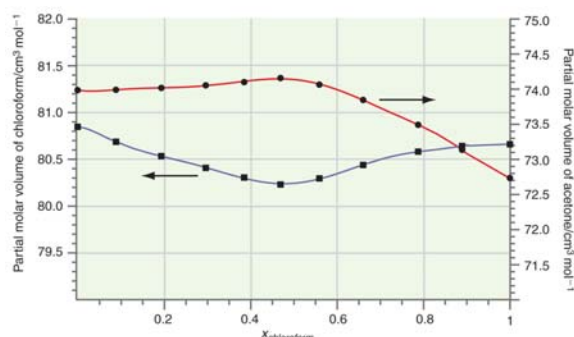
$$V = n_1 \bar{V}_1(P, T, n_1, n_2) + n_2 \bar{V}_2(P, T, n_1, n_2)$$



Gibbs-Duhem Equation

- Applicable to both real and ideal solutions

$$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0 \quad \text{or} \quad d\bar{V}_1 = -\frac{x_2}{x_1} d\bar{V}_2$$



Ideal Dilute Solution

- In a real solution, $\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}$ just like in an ideal solution, but $P_i \neq x_i P_i^*$

- Activity $a_{\text{solvent}} = \frac{P_{\text{solvent}}}{P_{\text{solvent}}^*}$ $\mu_i^{\text{solution}} = \mu_i^* + RT \ln a_i$

- Activity coefficient: quantify the degree to which the solution is nonideal (similar to fugacity plays in real gas)

$$\gamma_{\text{solvent}} = \frac{a_{\text{solvent}}}{x_{\text{solvent}}}$$

Henry's Law

Ideal dilute solution

- solvent follows Raoult's law
- solute is described by Henry's law

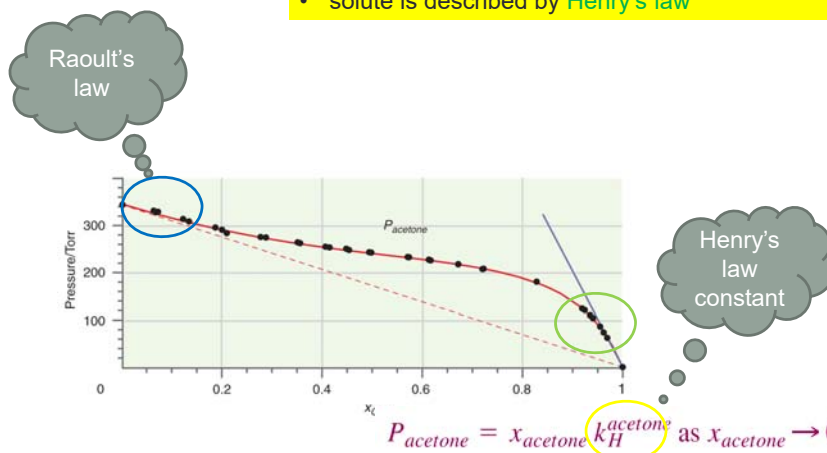


TABLE 9.4 Henry's Law Constants for Aqueous Solutions Near 298 K

Substance	k_H (Torr)	k_H (bar)
Ar	2.80×10^7	3.72×10^4
C ₂ H ₆	2.30×10^7	3.06×10^4
CH ₄	3.07×10^7	4.08×10^4
CO	4.40×10^6	5.84×10^3
CO ₂	1.24×10^6	1.65×10^3
H ₂ S	4.27×10^5	5.68×10^2
He	1.12×10^8	1.49×10^6
N ₂	6.80×10^7	9.04×10^4
O ₂	3.27×10^7	4.95×10^4

Source: Alberty, R. A., and Silbey, R. S. *Physical Chemistry*. New York: John Wiley & Sons, 1992.

Activity and Activity Coefficient

- Raoult's law standard state $a_i = \frac{P_i}{P_i^*}$ and $\gamma_i = \frac{a_i}{x_i}$
- Henry's law standard state

$$\mu_{solute}^{solution} = \mu_{solute}^* + RT \ln \frac{k_H^{solute} x_{solute}}{P_{solute}^*} = \mu_{solute}^{*H} + RT \ln x_{solute} \text{ as } x_{solute} \rightarrow 0$$

$$\mu_{solute}^{*H} = \mu_{solute}^* + RT \ln \frac{k_H^{solute}}{P_{solute}^*}$$

$$a_i = \frac{P_i^H}{k_i^H} \text{ and } \gamma_i = \frac{a_i}{x_i}$$

Colligative Properties of Ideal Dilute Solution

- A useful way to determine the activity coefficient

$$\Delta T_f = -K_f \gamma m_{solute}$$

$$\Delta T_b = K_b \gamma m_{solute}$$

$$\pi = \gamma c_{solute} RT$$

- Example 9.11: in 500 g of water, 24 g of a nonvolatile solute of MW 241 g/mol is dissolved. The observed freezing point depression is 0.359 °C. Calculate the activity coefficient of the solute.

Chemical Equilibrium in Solution

$$\left(\sum_j \nu_j \mu_j(\text{solution}) \right)_{\text{equilibrium}} = 0$$

Henry's law
standard state
for each
component

$$\sum_j \nu_j \mu_j^{*H}(\text{solution}) + RT \sum_j \ln(a_i^{eq})^{\nu_j} = 0$$

$$\Delta G_{\text{reaction}}^{\circ} = -RT \sum_i \ln(a_i^{eq})^{\nu_j} = -RT \ln K$$

$$K = \prod_i (a_i^{eq})^{\nu_j} = \prod_i (\gamma_i^{eq})^{\nu_j} \left(\frac{c_i^{eq}}{c^{\circ}} \right)^{\nu_j}$$

Binding Equilibrium (Adsorption)



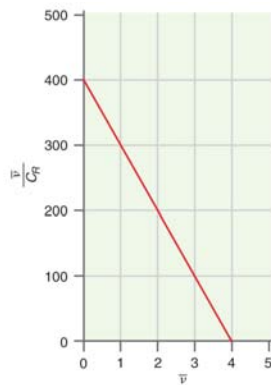
- Assuming a **single binding site** for the molecule, the average number of bound molecules per species

$$\bar{\nu} = \frac{c_{RM}}{c_M + c_{RM}}$$

$$\bar{\nu} = \frac{c_{RM}}{c_M + c_{RM}} \left(\frac{1/(c_R c_M)}{1/(c_R c_M)} \right) = \frac{K}{1/c_R + K} = \frac{K c_R}{1 + K c_R}$$

Multiple Binding Sites

- Independent site binding



Scatchard plot

$$\bar{\nu}_i = \frac{K_i c_R}{1 + K_i c_R}$$

N
binding
sites

$$\bar{\nu} = \sum_{i=1}^N \bar{\nu}_i = \sum_{i=1}^N \frac{K_i c_R}{1 + K_i c_R}$$

$$\bar{\nu} = \sum_{i=1}^N \frac{K_i c_R}{1 + K_i c_R} = \frac{N K c_R}{1 + K c_R}$$

$$\bar{\nu} = \frac{N K c_R}{1 + K c_R}$$

Scatchard equation

$$\frac{\bar{\nu}}{c_R} = -K \bar{\nu} + NK$$