

## Simple Mixtures

CHEM 323 Physical Chemistry I

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## Review and Observations

- Solutions and Mixtures
  - Solvent, solute
  - Miscible, immiscible
  - Soluble, insoluble
  - Saturated, supersaturated
- What can be measured?
  - Mole fraction, molality
  - Partial vapor pressures
  - Partial molar volumes
- Relationship of Observables to Molecules

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## Model

- Matter is Particulate
- Particles can interact with each Other
  - Manifested on macroscopic scale
- Particle Interaction characterized by some Energy
  - Ideal case: interaction energy = 0
  - Real case: interaction energy  $\neq$  0
- Procedure work from Ideal to Real Case
  - Reality vs. pedagogy

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## Partial Molar Volumes

- For pure Substance adding more Substance increases Volume
- When two, or more, pure Substances are mixed Volume can go up or down
  - Environment
- Define Partial Molar Volume,  $V_J$ 
  - Can be either positive or negative
  - Found experimentally (depends on  $p$  and  $T$ )

$$V_J = \left( \frac{\partial V}{\partial n_J} \right)_{p,T,n'}$$

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## Partial Molar Volume

- Extend Treatment to a two-component Mixture

$$dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B$$

- In terms of the partial molar volumes

$$dV = V_A dn_A + V_B dn_B$$

- Total volume is

$$V = n_A V_A + n_B V_B$$

- Assumptions

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## Chemical Potential

- Need Thermodynamic description of Mixtures
- Define Chemical Potential for a component of a Mixture,  $\mu_J$

$$\mu_J = \left( \frac{\partial G}{\partial n_J} \right)_{p,T,n'} \quad G = n_A \mu_A + n_B \mu_B$$

- Fundamental Equation of Chemical Thermodynamics

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B$$

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## Chemical Potential

- With no Change in  $p$  or  $T$ , Fundamental Equation of Chemical Thermodynamics is

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$dw_{\text{add,max}} = \mu_A dn_A + \mu_B dn_B$$

- Work can be done by changing chemical composition of solution

- Can be extended to  $U$ ,  $H$  and  $A$

$$\mu_J = \left( \frac{\partial U}{\partial n_J} \right)_{S,V,n'} \quad \mu_J = \left( \frac{\partial H}{\partial n_J} \right)_{S,p,n'} \quad \mu_J = \left( \frac{\partial A}{\partial n_J} \right)_{V,T,n'}$$

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## Chemical Potential

- Gibbs-Duhem Equation
  - Chemical potentials in mixture are not independent

$$\sum_J n_J d\mu_J = 0$$

- Thermodynamics of Mixing for Ideal Gas

$$\Delta_{\text{mix}} G = nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$

$$\Delta_{\text{mix}} S = - \left( \frac{\partial \Delta G}{\partial T} \right)_{p,n_A,n_B} = -nR(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$

$$\Delta_{\text{mix}} H = 0$$

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## Chemical Potential and Solutions

- Measurable Quantities
  - Total pressure over solution
  - Mole fraction (molality)

- Raoult's Law

- From solvent's point of view

$$p_{\text{solvent}} = \chi_{\text{solvent}} p_{\text{solvent}}^*$$

- Henry's Law

- From solute's point of view

$$p_{\text{solute}} = \chi_{\text{solute}} K_{\text{solute in solvent}}$$

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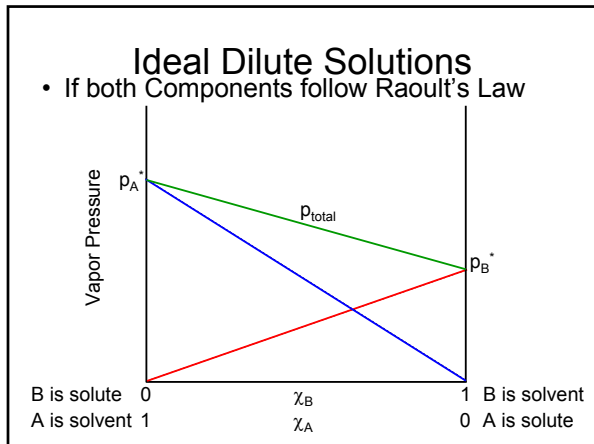
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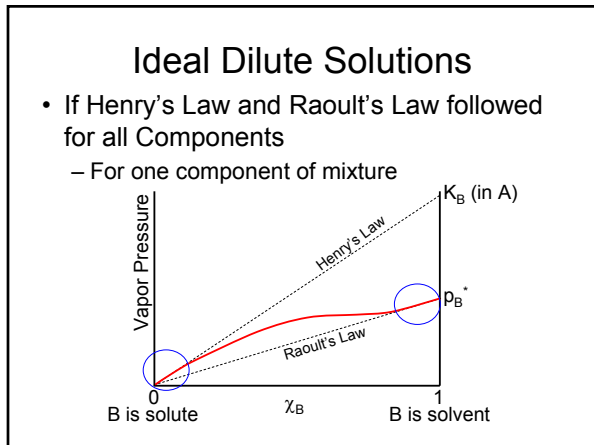
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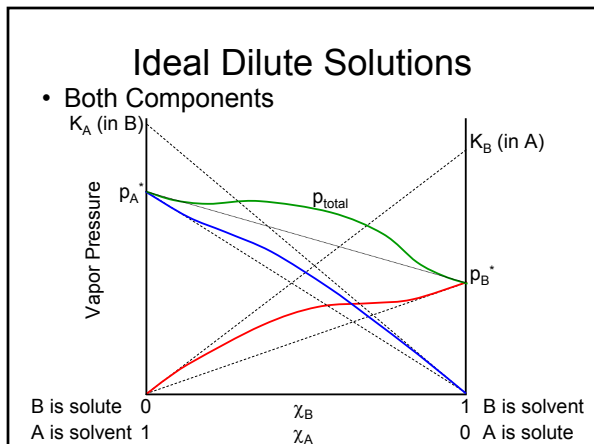
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## Ideal Dilute Solutions

- All Real Solutions show Deviations from Ideal Behavior when not Dilute
  - Can be positive deviation (as shown on previous slide)
  - Or negative deviation
- Caused by Intermolecular Interactions
- Need to have Thermodynamic Description of Solution Formation

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## Thermodynamics of Real Solutions

- In Low-Concentration Limit Real Solution behaves like Mixture of Ideal Gases
  - Intermolecular interactions between solute and solvent are negligible
  - Know  $\Delta_{\text{mix}}G$ ,  $\Delta_{\text{mix}}S$  and  $\Delta_{\text{mix}}H$  for these
- For Real Solution  $\Delta_{\text{mix}}G$  does not have to be Negative (Miscible versus Immiscible)
  - Because  $\Delta_{\text{mix}}H \neq 0$
  - And  $\Delta_{\text{mix}}S$  does not have to be positive
  - Remember  $\Delta G = \Delta H - T\Delta S$

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## Thermodynamics of Real Solutions

- Define Excess Functions
  - Difference between observed thermodynamic function of mixing and its ideal counterpart
  - Example:  $S^E = \Delta_{\text{mix}}S(\text{measured}) - \Delta_{\text{mix}}S(\text{ideal})$
- Define Regular Solution as having  $S^E = 0$ , but  $H^E \neq 0$ 
  - For regular solution  $H^E = \eta\beta RT\chi_A\chi_B$
  - Where  $\beta$  is an empirical function of  $T$  and measures intermolecular interactions

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## Thermodynamics of Real Solutions

- Sign of  $\beta$  determines  $\Delta_{\text{mix}}H$
- For  $\beta < 0$ 
  - Mixing is exothermic
  - Solute-solvent interactions more favorable than solute-solute or solvent-solvent
- For  $\beta > 0$ 
  - Mixing is endothermic
  - Solute-solvent interactions less favorable than solute-solute or solvent-solvent

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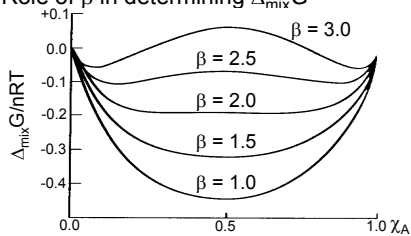
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## Thermodynamics of Real Solutions

- For Real Solutions  $\Delta_{\text{mix}}G$  is  

$$\Delta_{\text{mix}}G = nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B + \beta \chi_A \chi_B)$$
- Role of  $\beta$  in determining  $\Delta_{\text{mix}}G$




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## Activities

- Activity defined as Effective Mole Fraction
- Always referenced to a Standard State
  - For solvent this is the pure solvent
  - For solute this a hypothetical state of pure solute
- Chemical Potentials are

$$\mu_{\text{solvent}} = \mu_{\text{solvent}}^* + RT \ln a_{\text{solvent}} \quad a_{\text{solvent}} = \frac{p_{\text{solvent}}}{p_{\text{solvent}}^0}$$

$$\mu_{\text{solute}} = \mu_{\text{solute}}^* + RT \ln a_{\text{solute}}$$

$$a_{\text{solute}} = \frac{p_{\text{solute}}}{K_{\text{solute}}} \quad \text{or} \quad a_{\text{solute}} = \frac{b_{\text{solute}}}{b_{\text{solute}}^0}$$

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## Activity Coefficient

- Define Activity Coefficient,  $\gamma$ ,  $a_i = \gamma_i \chi_i$
- Chemical Potential
  - All non-ideality is in  $\gamma$

$$\mu_i = \mu_i^* + RT(\ln \chi_i + \ln \gamma_i)$$

- Margules Equations
  - Relationship to vapor pressure
  - Measurement of  $\beta$

$$\ln \gamma_A = \beta \chi_B^2 \quad \ln \gamma_B = \beta \chi_A^2$$

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## Solutions of Ionic Compounds

- Treatment of Solutions to this Point
  - Intermolecular interactions accounted for
  - Activities (activity coefficients) account for non-ideal behavior
  - Theories work best for non-electrolytes
- Observations
  - Some compounds dissociate into ions upon dissolving
  - More particles in solution than added, but . . .
  - Effects of ions are not separable

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## Thermodynamics of Ions

- Can measure Changes in Thermodynamic Quantities for Ionic Compounds
  - Examples
- Formation Enthalpy and Gibbs Energy and Third-Law Entropies are not Measurable
- Define a Standard based on  $H^+$  (aq)
  - $\Delta_f H^\circ(H^+, aq) = 0$
  - $\Delta_f G^\circ(H^+, aq) = 0$
  - $S^\circ(H^+, aq) = 0$

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## Measuring Thermodynamic Quantities for Ions in Solution

- Can measure  $\Delta_f H^\circ$  by Calorimetry
- For  $\Delta_f G^\circ$ , use Thermodynamic Cycles
  - $\frac{1}{2} \text{H}_2 (\text{g}) + \frac{1}{2} \text{Cl}_2 (\text{g}) \rightarrow \text{H}^+ (\text{aq}) + \text{Cl}^- (\text{aq})$
  - Need to measure  $\Delta_{\text{solv}} G^\circ$  for each ion
- Born Equation predicts  $\Delta_{\text{solv}} G^\circ$

$$\Delta_{\text{solv}} G^\circ = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right)$$

- What does this predict?

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## Measuring Thermodynamic Quantities for Ions in Solution

- Entropies are usually calculated from Enthalpy and Gibbs Energy Data
- Always measured relative to the Ordering caused by  $\text{H}^+$  in aqueous Solution
  - Small, highly charged ions cause more ordering than large ions with low charge
  - Ion-dipole interactions in polar solvents
  - Expectations in non-polar solvents?

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## Ion Activities

- Define Activity for an Ideal Dilute Solution
  - As before  $a = \gamma b/b^\circ$
  - where  $b^\circ$  is a hypothetical solution with  $b^\circ = 1$  and ions behaving ideally
- For any Species in Solution
 
$$\mu = \mu^\circ + RT \ln b + RT \ln \gamma = \mu^{\text{ideal}} + RT \ln \gamma$$
- For real Solution of Salt  $\text{C}_p\text{A}_q$ 
  - Introduce mean activity coefficients,  $\gamma_\pm$

$$\mu_j = \mu_j^{\text{ideal}} + RT \ln \gamma_\pm \quad \gamma_\pm = (\gamma_+^p \gamma_-^q)^{1/p+q}$$

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## Debye-Hückel Laws

- Used to calculate  $\gamma_{\pm}$ 
  - Define ionic strength,  $I$ ,  $I = \frac{1}{2} \sum_i z_i^2 \left( \frac{b_i}{b^0} \right)$
- Debye-Hückel Limiting Law ( $m \leq \sim 0.01$ )
  - $A$  is a constant (0.509 for H<sub>2</sub>O)

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

- Extended Debye-Hückel Law ( $m \leq \sim 0.1$ )

$$\log \gamma_{\pm} = -\frac{A|z_+ z_-| I^{1/2}}{1 + B I^{1/2}}$$

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## Colligative Properties

- Properties of Solutions that depend only on Number of Solute Particles present
  - Boiling point elevation
  - Freezing point depression
  - Osmotic pressure
  - Solubility\*
- Result from reduction of  $\mu_{\text{solvent}}$  because of Solute's Presence

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## Colligative Properties

- Boiling Point Elevation
  - $K_b$  is ebulliscopic constant
$$\Delta T_{\text{boiling}} = K_b \chi_B \quad K_b = \frac{RT_{\text{vap}}^2}{\Delta_{\text{vap}} H}$$
- Freezing Point Depression
  - $K_f$  is cryoscopic constant
$$\Delta T_{\text{melting}} = K_f \chi_B \quad K_f = \frac{RT_{\text{fus}}^2}{\Delta_{\text{fus}} H}$$
- Osmotic Pressure  $\Pi = [B]R$
- Solubility  $\ln \chi_B = \frac{\Delta_{\text{fus}} H}{R} \left( \frac{1}{T_{\text{fusion}}} - \frac{1}{T} \right)$

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