# Chapter 11

#### Properties of solutions

#### Solutions are Matter



### Key Definitions

• Solvent

• Solute

### Key Definitions

• Solvent

• Solute

• Examples

#### Solution Strength

• Molarity

• Normality

• Molality

#### Solution Strength

• Mass percent (Wt. %)

Mass of solute x 100% Mass of solution

#### Solution Strength

• Mole Fraction

 $n_A -$ 

#### Mole fraction of A:



#### Heat of solution

- Amount of heat absorbed or release when a solute dissolves in a particular solvent.
  - Exothermic:

Endothermic:

### 3 steps to solution

- $\Delta H_1$ : energy required to separate the solute or expand it.
- $\Delta H_2$ : energy required to separate the solvent.
- $\Delta H_3$ : the interaction between solvent and solute.

### 3 steps to solution



## Example

- What is the  $\Delta H_{sol}$  of NaI given:
- <u>Lattice energy</u> is -686 kcal/mol
- Enthalpy of Hydration -694 kcal/mol
- Is this substance soluble, if so is it endothermic or exothermic.

## Example

- We are unmaking a lattice so flip sign on <u>Lattice energy</u> is +686 kcal/mol
- Enthalpy of Hydration -694 kcal/mol
- Sum the energy changes:
- 686 kcal/mol + -694 kcal/mol = -8 kcal/mol.
- $\Delta H$  sol is small so... Soluble
- $\Delta H$  sol is negative so... exothermic

#### **Predicting Solution Formation**

Solvent/					
Solute	ΔH <sub>1</sub>	∆H₂	∆H₃	∆H <sub>sol'n</sub>	Outcome
Polar/ Polar	+ large	+ large	- large	+/- small	Solution forms
Polar/ Nonpolar	+ small	+ large	+/- small	+ large	No solution forms
Nonpolar/ Nonpolar	+ small	+ small	+/- small	+/- small	Solution forms
Nonpolar/ polar	+ large	+ small	+/- small	+ large	No solution forms

#### "Like Dissolves Like"

Nonpolar solutesdissolve best in nonpolar solventsFatsBenzeneSteroidsHexaneWaxesToluene

Polar and ionic solutesdissolve best in polar solventsInorganic SaltsWaterSugarsSmall alcohols

Acetic acid

#### Watch out for this...

- Solubility is a constant for a given solute and solvent at a specified temperature
- But
- The rate of dissolving can be increased by

- Solubility of MOST solids increases with increasing temperature.
- Solubility of gases DECREASES with increasing temperature
- Solubility of gases is directly proportional to the pressure of the gas above the solvent (Henry's Law)





- So in summary
- Solids
  - heating
  - grinding
  - stirring
- Gases
  - cold
  - high pressure

#### Saturation

• Saturation

• Under saturation

• Super saturation (metastable)

### Henry's Law

• Concentration of a gas in a solvent is directly proportional the the pressure of the gas above the solution. Or ...

## C = kP where

- C = concentration
- P = pressure
- k = Henry's constant

#### Henry's Law

If we double the pressure....



### Henry's Law

- Works most accurately for low gas concentrations (dilute solutions)
- Gases that do not react with solvent (dissociate into ions)
- $CO_2$ ,  $N_2 O_2$  Yes
- HCl, HI

NO!

### Henry's Law Example

- What is the amount of O<sub>2</sub> that will dissolve in H<sub>2</sub>O at 1 atm pressure and a 25°C? Given Henry's constant is 756.7 L·atm/mol and the mole fraction O<sub>2</sub> in the atmosphere is .
  2095 so at 1 atm the partial pressure of O2 is 0.2095 atm.
- $0.2095 \text{ atm} | 1 \text{ mol} = 2.769 \text{ x } 10^{-4} \text{ mol/L}$ 756.7 atm·L



Raoult's Law **Raoult's Law** The presence of a nonvolatile solute lowers the vapor pressure of the solvent.  $P_{solution} = \chi_{solvent} P_{solvent}^{0}$ **P**<sub>solution</sub> = Observed Vapor pressure of the solution X<sub>solvent</sub> = Mole fraction of the solvent  $P_{solvent}^{0}$  = Vapor pressure of the pure solvent

#### Raoult's Law



Fewer volatile molecules pushing on surface, less pressure

#### Raoult's Law Example

The vapor pressure of a solution containing 53.6 g glycerin in 133.7 g ethanol is 113 torr at 40C. What is the the vapor pressure of pure ethanol at 40C (Treat gylcerin as nonvolatile and molecular)

$$P_{soln} = \chi P^{o} so P^{o} = P_{soln} / \chi_{ethanol}$$

#### Raoult's Law Example

- •Find  $\chi$
- $\bullet \chi = n_a / n_a + n_b$
- moles of glycerin  $(C_3H_8O_3)$

•moles of ethanol ( $C_2H_5OH$ )

#### Raoult's Law Example

 $\bullet P^{o} = P_{soln} / \chi_{ethanol}$ 

#### • $\chi_{\text{ethanol}} =$

•  $P^{o} = 114 \text{ torr} / (2.90 \text{ mol}/3.48 \text{ mol})$ 

### What happens if

• Both solvent and solute are volatile

- Solvent pushes to the best of its ability
- Solute pushes to the best of its ability
- So we modify Raoult's Law a bit

### What happens if

How much there is

$$P_{TOTAL} = P_A + P_B = \chi_A P_A^0 + \chi_B P_B^0$$
  
How hard it pushes  
P<sup>0</sup> is the vapor pressure of the pure solvent  
P\_A and P\_B are the partial pressures

#### Two Volatiles

- What is the vapor pressure above a mixture made from  $0.0300 \text{ mol } \text{CH}_2\text{Cl}_2$ and 0.0500 mol $\text{CH}_2\text{Br}_2$  at 25C
- $P_{CH2C12}^{o} = 133 \text{ torr}$
- $P_{CH2Br2}^{o} = 11.4 \text{ torr}$

- Modified Raoults Law
- Steps
  - Find mole fraction of each substance
  - multiply by Po
  - Add the portions up

#### Two Volatiles

- $P_{total} = PCH_2Cl_2 + PCH_2Br_2$
- $P_{total} = \chi P^{o}CH_{2}Cl_{2} + \chi P^{o}CH_{2}Br_{2}$
- $P_{total} = 0.375(133 \text{ torr}) + 0.625(11.4)$

- $P_{total} = 57.0$  torr.
- Kinda like weighted averages for grades ; )

#### Negative Deviations from Raoult's Law Strong solute-solvent interaction results in a vapor pressure lower than predicted Exothermic mixing = Negative deviation



#### Positive Deviations from Raoult's Law Weak solute-solvent interaction results in a vapor pressure higher than predicted Endothermic mixing = Positive deviation



#### Electrolytes/Nonelectrolytes

- Aqueous solutions conduct e-
  - Ionically bonded
  - Ionized
- Aqueous solutions do not conduct e-
  - Covalently bonded
  - Molecules stay together

### Examples

- Pentane
- Solid NaCl
- NaCl solution
- Distilled water
- Tap water
- Ethanol

### **Colligative Properties**

- Depend on the amount of solute
- Does not depend on the identity of solute

• Vapor Pressure

(Boiling point)

- Freezing Point
- Osmotic Pressure



- Water wants to equalize the concentrations
- Flows in until the pressure rises enough to prevent more flow. This is osmotic pressure.

### Freezing Point Depression

• No matter what the solute\* water's freezing point is lowered by

• 
$$\Delta \mathbf{T} = i \cdot K_f \cdot m_{solute}$$

- I is the van't Hoff factor
  - the effective number of mole of ions supplied
- $K_f \text{ is } 1.86 \text{ }^{\circ}\text{C} \cdot \text{kg/mol}$
- *m* is the molality of the solute

### **Boiling Point Elevation**

• No matter what the solute\* water's boiling point is raised by

• 
$$\Delta T = i \cdot K_b \cdot m_{solute}$$

- I is the van't Hoff factor
  - the effective number of moles of ions supplied
- $K_b$  is 0.51 °C ·kg/mol
- *m* is the molality of the solute

### Example

• Mr K wants to make sure that his truck is protected this winter. He wants his antifreeze to be good to - 20 C. How much antifreeze should he use? There are 20 L of coolant in the truck. Antifreeze is 1,2ethanediol.

• 
$$\Delta T = i \cdot K_f \cdot m_{solute}$$

### Example

- $\Delta T = i \cdot K_f \cdot m_{solute}$
- $-20 \ ^{\circ}C = i \cdot 1.86 \ ^{\circ}C \cdot kg/mol \cdot m_{solute}$
- $-20 \circ C = 1.0 \cdot 1.86 \circ C \cdot kg/mol \cdot m_{solute}$
- 10.75 m solute needed or 10.75 mol/kg
- <u>10.75 mol</u> <u>20 kg</u> <u>62.1 g</u> <u>1 ml</u> <u>1L</u> kg water 1trk 1mol 1.1 g 1000ml

#### Different van't Hoff factors

Dissociation Equations and the Determination of *i* 

i = 2NaCl(s) → Na⁺(aq) + Cl⁻(aq)  $AgNO_3(s) \rightarrow Ag^+(aq) + NO_3^-(aq)$ i = 3 $MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2 Cl^{-}(aq)$  $Na_2SO_4(s) \rightarrow 2 Na^+(aq) + SO_4^{2-}(aq)$  $A|C|_{3}(s) \rightarrow A|^{3+}(aq) + 3 C|^{-}(aq)$ 

#### Real world

• Ideal van't Hoff factors only achieved with extremely dilute solutions.

	Molality, m							
Solute	1.0	0.10	0.010	0.0010		Inf dil <sup>*</sup>		
NaCl	1.81	1.87	1.94	1.97		2		
$MgSO_4$	1.09	1.21	1.53	1.82		2		
$Pb(NO_3)_2$	1.31	2.13	2.63	2.89		3		

#### Osmosis

• Diffusion of water across a membrane **Contractor** 

- Water will flood across a membrane to dilute high concentrations of solute.
- It is trying to reach equilibrium

• Pressure needed to stop osmosis



# Osmotic Pressure Calculations

# $\Pi = iMRT$

I = Osmotic pressure
 M = Molarity of the solution
 R = Gas Constant = 0.08206 L·atm/mol·K
 I = Osmotic pressure

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