Solutions

Chem 36

Spring 2002

What is a Solution?

➢ Definition:

"A <u>homogeneous</u> mixture of a *solute* distributed through a *solvent*."

<u>Examples:</u>

- **Air** (gas/gas)
- **Soft Drink** (gas/liquid)
- **Vodka** (liquid/liquid)
- **Ocean Water** (solid/liquid)
- **Metal Alloy** (solid/solid)
- **Hg Amalgam** (liquid/solid)

2

Liquid Solvent Solution Concentrations

Focus on # *moles solute (n):*

1) Mole Fraction (χ)

$$\chi = \frac{\text{mol solute}}{\text{total mol}}$$

→ Need to know complete solution composition

NOTE: $n_{total} = n_1 + n_2 + \ldots n_i$

and $1 = \chi_1 + \chi_2 + \ldots \chi_i$

3

More Concentrations

2) Molarity (*M*)

$$M = \frac{\text{mol solute}}{\text{liters sol'n}}$$

→ *Total volume* of solution

- Most commonly used concentration unit

4

Yet *another* concentration definition . . .

3) Molality (*m*)

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

Mass of **solvent** (not solution!)

➢ Why/when use molality instead of molarity?

✓*Volume* is temperature dependent

✓*Mass* is temperature *in*dependent

5

Molality versus Molarity

➢ For a *dilute, aqueous solution:*

1 liter sol'n ≈ 1 kg solvent

(so, molarity ≈ molality)

■ What happens at higher solute levels?

$$\frac{\text{mol solute}}{\text{L sol'n}} \quad \textit{versus} \quad \frac{\text{mol solute}}{\text{kg solvent}}$$

kg solvent → unchanged

Molarity	<	Molality

6

Characterizing Solubility

- How much *solute* can be dissolved in a liquid **solvent**?

Three Cases:

1) *Un*saturated Solution (all solute dissolved)
2) Saturated Solution (some undissolved solute)
   (*equilibrium* between solid and dissolved solid)
3) **Super**saturated Solution
   (all solute dissolved . . . *unstable!*)

7

Dissolution Energetics

- Three Steps:

1) Overcome *SOLUTE* intermolecular forces (ΔH_1)
2) Overcome *SOLVENT* intermolecular forces (ΔH_2)
3) Allow *solute* and *solvent* to interact (ΔH_3)

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Hypothesis: If $\Delta H_{soln} > 0$, then solute is *not* soluble

If $\Delta H_{soln} < 0$, then solute is soluble

8

Is Oil *Miscible* in Water?

Oil: *Nonpolar* (London Forces)

Water: *Polar* (Hydrogen Bonding)

Oil/Water: *Nonpolar/Polar* (Dipole-Induced Dipole)

So: $\Delta H_1 + \Delta H_2$ = *large (+)*

ΔH_3 = *very small (-)*

$\Delta H_{sol'n}$ = ***Large (+)*** (> 0)

✓Thus: oil and water are NOT miscible

9

Is Methyl Alcohol *Miscible* in Water?

Methyl Alcohol: *Polar* (Hydrogen Bonding)

Water: *Polar* (Hydrogen Bonding)

Alcohol/Water: *Polar/Polar* (Hydrogen Bonding)

So: $\Delta H_1 + \Delta H_2$ = *large (+)*

ΔH_3 = *large(-)*

$\Delta H_{sol'n}$ = ***small (+/-)***

? Why *is* methyl alcohol miscible in water?

10

Will NaCl Dissolve In Water?

NaCl(s): *Strong Ionic Bond*

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H_1 = 786$ kJ/mol

H_2O and NaCl/H_2O: *Ion-Dipole/H-Bonding*

$H_2O(l) + Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq)$

$\Delta H_{hyd} = \Delta H_2 + \Delta H_3 = -783$ kJ/mol

So: $\Delta H_{sol'n} = 786 + (-783) =$ ***+3 kJ/mol***

? So *why* does NaCl dissolve in water?

11

Enter: *Entropy*

- "Nature favors disorder"
- *Processes which increase disorder tend to be favored* (spontaneous)

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ *increased disorder*

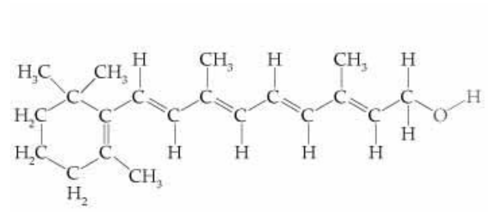
•Since ΔH_{soln} is very small, process is said to be:

Entropically-Driven

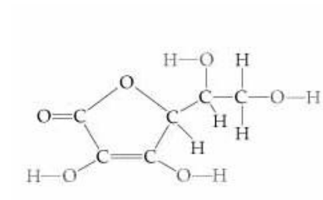
12

Structure and Solubility

- If solute and solvent *IM Forces* are very different: **not soluble**
- If solute and solvent *IM Forces* are similar: **soluble**
- "Like dissolves like"



Vitamin A



Vitamin C

13

Gas Solubility: Henry's Law

It can be shown that:

$$P_A = K[A(aq)]$$

- P_A: partial pressure of gas A above solution
- K: Henry's Law Constant
- $[A(aq)]$: concentration of gas A dissolved in solution

Example: P_{CO2} (air) ≈ 3×10^{-4} atm - v. little dissolved CO_2

P_{CO2} (soda bottle) ≈ 5 atm - ~0.16 *M* CO_2

14

Henry's Law Example

"The Bends"

- Pressure 90 ft underwater: ***~3.7 atm***
- <u>*Henry's Law says:*</u>
  3.7x as much N_2 and O_2 dissolved in blood
- ***Problem:*** surfacing too quickly
- ***Solutions:***
  1. Surface *slowly*
  2. Breathe O_2/He mixture

15

Effects of *Temperature* on Solubility

<u>For gases:</u>

Solubililty ***decreases*** with **increasing** temperature

Example: <u>**Thermal Pollution**</u>

•Hot water dumped into lake kills fish

•***Why?***

•Decreased dissolved O_2 in hot water

•Layer of less dense hot water on top hinders O_2 dissolution

16

What about Boiler Scale?!

- CO_2 in water can form bicarbonate:

CO_3^{2-} (aq) + CO_2 (aq) + H_2O (l) ⇆ $2HCO_3^-$ (aq)

- If there's Ca^{2+} in the water:

  $Ca(HCO_3)_2$ or $CaCO_3$ will form
  (soluble) (insoluble)

- In *hot water*, CO_2 is *less soluble*:

$HCO_3^- \rightarrow CO_3^{2-}$

$+ Ca^{2+} \rightarrow CaCO_3$ (s)

17

Temperature Effects on Solubility of *Solids*

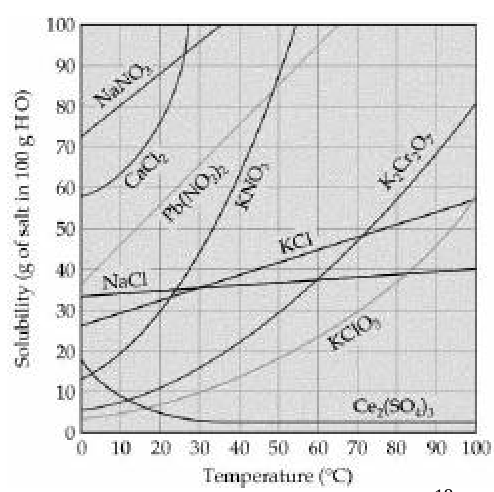
Usually:

Solubility **increases** with increasing temperature

Why?

DH$_{soln}$ > 0: adding heat facilitates *endothermic* process.

DH$_{soln}$ < 0: adding heat *hinders* exothermic process



18

Effects of Solute on Physical Properties of Solvent

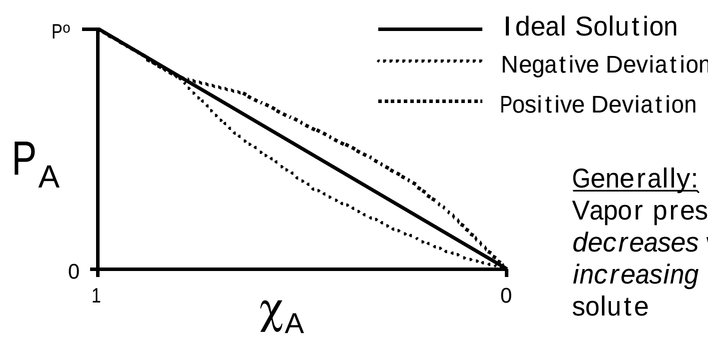
- Presence of dissolved solute can change the solvent's:
  1. Vapor Pressure
  2. Boiling Point
  3. Freezing Point
  4. Osmotic Pressure
- Collectively known as:

Colligative Properties

19

Effect on Vapor Pressure

- What happens to the vapor pressure of solvent A (P_A) as solute concentration increases?



Generally:
Vapor pressure *decreases* with *increasing* dissolved solute

20

Raoult's Law

For an Ideal Solution:

$$P_A = c_A P^o_A$$

Solvent Vapor Pressure above solution

Mole Fraction of Solvent

Vapor Pressure of Pure Solvent

In an *ideal solution*: all IM forces are of a similar magnitude

- Negative Deviations: *solute-solvent* IM forces **too strong**
- Positive Deviations: *solute-solvent* IM forces **too weak**

21

What if both *solute* and *solvent* are **volatile liquids?**

- **Raoult's Law** applies to *both:*

  $P_B = \chi_B P^o_B$ (for volatile solute B)

  $\chi_A + \chi_B = 1$ (for a 2-component mix)

- **Now it gets interesting!**

  Suppose we have a solution with a composition such that: $\mathbf{c_A = c_B = 0.5}$

  Question: ***What are*** χ_A and χ_B *in the* ***vapor*** if **A** is 2x as volatile as **B** ($P^o_A = 2\ P^o_B$)?

22

The Solution (or is it the vapor?!)

$P_A = \chi_A P^o_A$

Substituting:

$P_A = (0.5)\ 2P^o_B$

Giving:

$P_A = P^o_B$

Also:

$P_B = \chi_B P^o_B$

So:

$P_B = (0.5)\ P^o_B$

So, in the *vapor:*

χ_A (vapor) $= P_A / (P_A + P_B)$

Substituting:

χ_A (vapor) $= P^o_B / (P^o_B + (0.5)\ P^o_B)$

c_A (vapor) = 2/3

And, since $\chi_A + \chi_B = 1$:

c_B (vapor) = 1/3

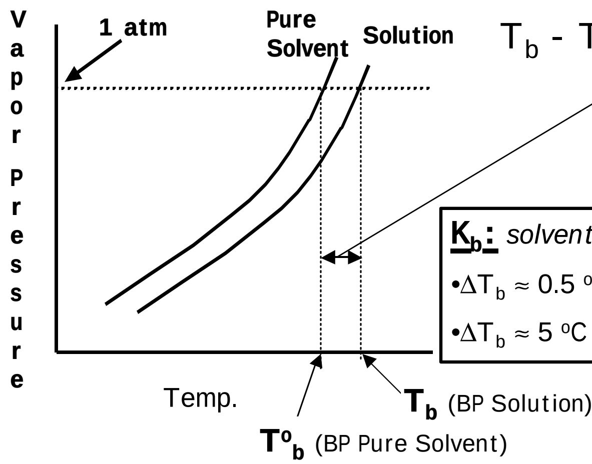
23

Why so interesting?

- **Notice:** the *vapor is enriched in the more volatile component (A)*
- **So, to separate a mixture of *A* and *B*:**
  - ✓ Collect and condense vapor above liquid
  - ✓ Repeat process with condensed vapor
  - ✓ The *new* vapor phase will be: $\chi_A = 0.80$
  - ✓ Repeat, repeat, repeat!
  - Perform at or near *boiling point* to maximize amounts of compounds in vapor phase (distillation)

24

Boiling Point Elevation



$T_b - T^o_b = \Delta T_b = K_b\, m$

BP Elevation Constant
(*Ebulioscopic Constant*)

K_b: *solvent specific*

- $\Delta T_b \approx 0.5\ ^oC$ for 1 *m* sol'n in water
- $\Delta T_b \approx 5\ ^oC$ for 1 *m* sol'n in CCl_4

Freezing Point Depression

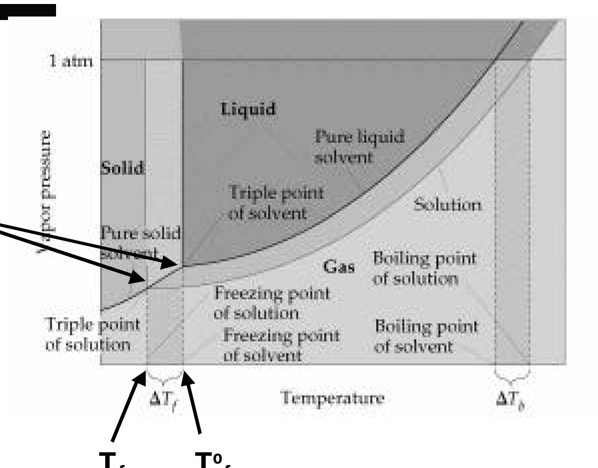
- **Freezing Point:** the temperature at which the VP of the *Liquid* and *Solid* phases are the same

So:

$T^o_f - T_f = \mathbf{DT_f}$

$\mathbf{DT_f = K_f}\ m$

FP Depression Constant
(Cryoscopic Constant)



How Depressed?

- K_f is usually *larger* than K_b:
  - $\Delta T_f \approx 2\ ^oC$ for 1 *m* sol'n in water
  - $\Delta T_b \approx 32\ ^oC$ for 1 *m* sol'n in CCl_4
- **Uses for FP Depression:**
  - Melting Ice
  - Auto Antifreeze
  - Solvent Purification
  - Molecular Weight Determination

27

MW Determination via FP Depression

- ✓ Add a *known amount* of compound to *known amount* of solvent
  - Weigh compound and solvent *accurately*
  - Use solvent with a **large** K_f
- ✓ Measure $\mathbf{DT_f}$
- ✓ Determine *molality*: $\mathbf{DT_f = K_f}\ \boldsymbol{m}$
- ✓ Use *m* to solve for n_{cmpd}: $\boldsymbol{m} \mathbf{= n_{cmpd}/kg\ solvent}$
- ✓ Finally, calculate MW: $\mathbf{MW = g\ cmpd/n_{cmpd}}$

28

Solvent Purification

Freezing *process* often involves **solvent freezing first**

- Solid, initially, is ***pure***
  (zone refining, water purification)
- Solute concentration in remaining solution *increases* as solvent freezes
  (FP is lowered even more)

29

Automobile Antifreeze

- Add *Ethylene Glycol* ($C_2H_6O_2$) to water in radiator:

```
         H    H
         |    |
HO  -  C  -  C  -  OH
         |    |
         H    H
```

MW = 62.0 g/mol

d = 1.12 g/mL

30

How Much EG to Add?

- **Calculate the FP of a solution made by mixing 50.0 mL of EG with 50.0 g of H_2O.**

1) Calculate *molality* of resulting solution.

$$50.0 \text{ mL EG} \times \frac{1.12 \text{ g EG}}{\text{mL EG}} \times \frac{1 \text{ mol EG}}{62.0 \text{ g EG}} = \mathit{0.90323\ mol\ EG}$$

So: $m = \frac{0.90323 \text{ mol EG}}{0.0500 \text{ kg } H_2O}$ = ***18.06 mol EG/kg H_2O***

How does this compare with solution *molarity*?

31

On to the solution!

2) Substitute and solve:

$\Delta T_f = m\,K_f$ = (18.06 mol/kg)(1.86 K-kg/mol)

ΔT_f =33.6 K ≈ *34 °C*

So:

$T_f = T^o_f - \Delta T_f$ = 0 °C - 34 °C = **-34 °C**

-29 °F

Reality Check! Why is the *actual* FP between -35 °C and -37 °C?

32

Melting the Ice

- **"Salt" is added to icey roads to melt the ice**
  - FP of H_2O lowered, so ice melts
  - $CaCl_2$ more effective than NaCl . . . . ***Why?***
- **How many ions released per mol of compound?**

$NaCl (s) \rightarrow Na^+ (aq) + Cl^- (aq)$ 2 ions/mol

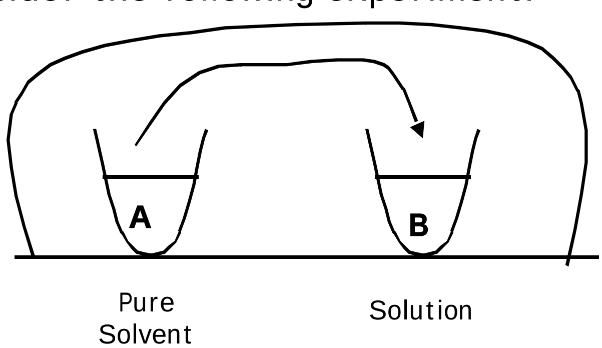
$CaCl_2 (s) \rightarrow Ca^{2+} (aq) + 2Cl^- (aq)$ 3 ions/mol

Need to consider *dissociation* of ionic compounds and the *total number* of species dissolved in solution.

33

Osmosis

Consider the following experiment:



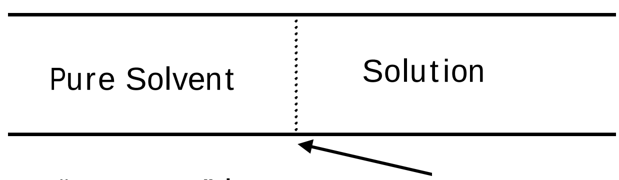
Recall that: $P_A > P_B$

So: net transfer of solvent from A to B

34

Osmosis . . . *Really!*

Now, consider the following:



Semi-permeable membrane (solvent only can pass through)

•Solvent "pressure" is greatest for pure solvent, so solvent flows into solution.

35

Quantifying Osmosis

- "Pressure" of pure solvent = **<u>Osmotic Pressure (P)</u>**
- Magnitude will depend on *solution concentration:*

$$P = M RT$$

- P: Osmotic Pressure (atm)
- M: Molarity (mol/L)
- R: Gas Constant (0.08206 L-atm/mol-K)
- T: Absolute Temp (K)

Why can we use *molarity* here instead of **molality**?

36

Osmosis: What is it good for?

- **Biological Systems**
  - Cell membranes
- **Water Desalinization**
  - *Reverse* Osmosis
- **MW Determination**
  - No solvent dependence of effect
  - Easier to measure:

e.g., *30 g of a 10,000 g/mol protein in 1.00 L* H_2O

$\Delta VP = 10^{-7}$ atm

$\Delta T_b = 10^{-4}$ °C $\Delta T_f = 10^{-3}$ °C

$\Pi = 10^{-2}$ atm (~10 torr)

37