

CHEM 116
Predicting Properties of Solutions (Math)

September 28, 2006
 Prof. Sevian



1

Agenda

- Re-iterate why solutes dissolve in solvents
- Basics about solutions
 - What is a solution? (last lecture)
 - Why study the properties of solutions?
 - What properties are most interesting about solutions, and how do we measure these properties?
 - Predicting properties of solutions (math)

Properties of solutions that we can measure in the lab:

1. Boiling point elevation

- Solutions always boil at higher temperatures than pure solvent – how much higher?

2

**Is a particular solution process
 endothermic or exothermic?**

<p style="text-align: center;"><u>Endothermic</u></p> <p style="text-align: center;">Ex: $\text{NH}_4\text{NO}_3 (s) \rightarrow \text{NH}_4\text{NO}_3 (aq)$</p> <div style="text-align: center;"> </div> <table border="0" style="width: 100%; margin-top: 10px;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>Magnitude of $\Delta H_1 + \Delta H_2$</p> <p>Energy input needed to separate solute particles + Energy input needed to separate solvent particles</p> </td> <td style="width: 50%; vertical-align: top;"> <p>Magnitude of ΔH_3</p> <p>Energy released when attractions form between solvent molecules and solute particles</p> </td> </tr> </table>	<p>Magnitude of $\Delta H_1 + \Delta H_2$</p> <p>Energy input needed to separate solute particles + Energy input needed to separate solvent particles</p>	<p>Magnitude of ΔH_3</p> <p>Energy released when attractions form between solvent molecules and solute particles</p>	<p style="text-align: center;"><u>Exothermic</u></p> <p style="text-align: center;">Ex: $\text{NaOH} (s) \rightarrow \text{NaOH} (aq)$</p> <div style="text-align: center;"> </div> <table border="0" style="width: 100%; margin-top: 10px;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>Magnitude of $\Delta H_1 + \Delta H_2$</p> <p>Energy input needed to separate solute particles + Energy input needed to separate solvent particles</p> </td> <td style="width: 50%; vertical-align: top;"> <p>Magnitude of ΔH_3</p> <p>Energy released when attractions form between solvent molecules and solute particles</p> </td> </tr> </table>	<p>Magnitude of $\Delta H_1 + \Delta H_2$</p> <p>Energy input needed to separate solute particles + Energy input needed to separate solvent particles</p>	<p>Magnitude of ΔH_3</p> <p>Energy released when attractions form between solvent molecules and solute particles</p>
<p>Magnitude of $\Delta H_1 + \Delta H_2$</p> <p>Energy input needed to separate solute particles + Energy input needed to separate solvent particles</p>	<p>Magnitude of ΔH_3</p> <p>Energy released when attractions form between solvent molecules and solute particles</p>				
<p>Magnitude of $\Delta H_1 + \Delta H_2$</p> <p>Energy input needed to separate solute particles + Energy input needed to separate solvent particles</p>	<p>Magnitude of ΔH_3</p> <p>Energy released when attractions form between solvent molecules and solute particles</p>				

Remember the solubility rules? (from p. 127 in text)

TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water	
Soluble Ionic Compounds	Important Exceptions
Compounds containing NO_3^-	None
$\text{C}_2\text{H}_3\text{O}_2^-$	None
Cl^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
Br^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
I^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
SO_4^{2-}	Compounds of Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}
Insoluble Ionic Compounds	Important Exceptions
Compounds containing S^{2-}	Compounds of NH_4^+ , the alkali metal cations, and Ca^{2+} , Sr^{2+} , and Ba^{2+}
CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
OH^-	Compounds of the alkali metal cations, and NH_4^+ , Ca^{2+} , Sr^{2+} , and Ba^{2+}

Copyright © 2006 Pearson Prentice Hall, Inc.

Solubility of Some Common Sulfate Compounds (at 25°C)

Formula	Solubility (g/100 g H ₂ O)	Solubility (mol/L)
BaSO ₄	0.00246	0.00010
PbSO ₄	0.00425	0.00014
SrSO ₄	0.0113	0.00060
Hg ₂ SO ₄	0.060	0.0012
CaSO ₄	0.209	0.0150
Ag ₂ SO ₄	0.57	0.018
Na ₂ SO ₄	4.76	0.335
MgSO ₄	26.0	2.16

5

What affects solubility?

- Of an ionic compound dissolving in water
- Of a solute whose molecules have polar parts dissolving in a polar solvent (like water)
- Of a nonpolar solute dissolving in a polar liquid (like water)
- Of a nonpolar solute dissolving in a nonpolar solvent

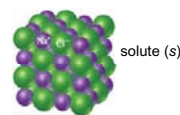
In all these cases, it's a balancing act.

- Energy given off (becoming dispersed) vs. energy input (becoming more organized)
- Organization of particles (solutions are always more dispersed than the original pure solute plus pure solvent)

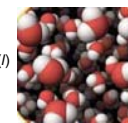
6

Spontaneity: Which is more favorable?

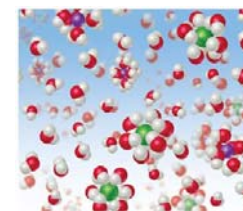
Particles in their undissolved state



and



Particles in their dissolved state



7

Key points so far about solutions

- Solutions are mixtures (two or more pure substances mixed together uniformly)
- Solvent is the medium in which a solute gets dissolved
- Saturation is the point at which no more solute can dissolve in the solvent
- "Solubility" is the maximum amount of solute that can dissolve in a given amount of solvent (usually measured in grams of solute per 100 g of solvent)
- Particle-level model/understanding: Solutions form when attractions between solute and solvent are stronger than solute-solute and solvent-solvent attractions

8

What solutions can do, practical uses

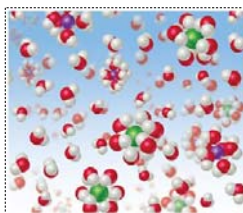
- Boil at higher temperature than the pure solvent
 - Cooking
 - Keeps things in the liquid phase
- Freeze at lower temperature than the pure solvent
 - Making ice cream
 - Melting ice on sidewalks and streets in winter
 - Keeps your radiator liquid from freezing in winter
 - Keeps things in the liquid phase
- Create osmotic pressure
 - Dialysis
 - Cell assays
- Nature figured out a long time ago how to take advantage of these properties

9

What's significant about how particles are arranged inside a solution?

In the bulk

- Solute particles surrounded by solvent particles
- Solute-solvent attraction is stronger than a solvent-solvent attraction



At the surface

- Phase changes occur at surfaces
- Only solvent particles change phase (solute particles remain dissolved)
- As solvent particles leave the liquid phase, the solution becomes more concentrated in solute

10

What kind of concentration do we need in order to explain the behavior of solutions?

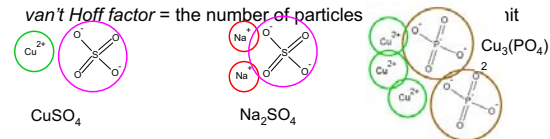
- A measure of how many solute particles are dissolved in a given amount of solvent

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

Molality = the number of moles of solute per kilogram of solvent

- But, what we really need to know is how many particles are dissolved separately, not how many moles of solute units

van't Hoff factor = the number of particles



What kind of concentration do we need in order to explain the behavior of solutions?

- Effective molality

$$\text{Effective molality} = (\text{van't Hoff factor}) \times \left(\frac{\text{moles of solute units}}{\text{kg of solvent}} \right)$$

- All interesting behaviors of solutions scale linearly with the effective molality
 - How much the boiling point rises (as compared to pure solvent)
 - How much the freezing point is lowered (as compared to pure solvent)
 - How much pressure a solution exerts across a semipermeable membrane (through which the solvent can cross but the solute cannot)

12

Concept check

All of these aqueous solutions boil at a temperature higher than 100°C. Which one is expected to have the highest boiling point? Which one should have a boiling point closest to 100°C?

- 0.10-molal sugar solution
- 0.20-molal sugar solution
- 0.10-molal NaCl solution
- 0.10-molal Na₂SO₄ solution

13

The mathematics of concentrations

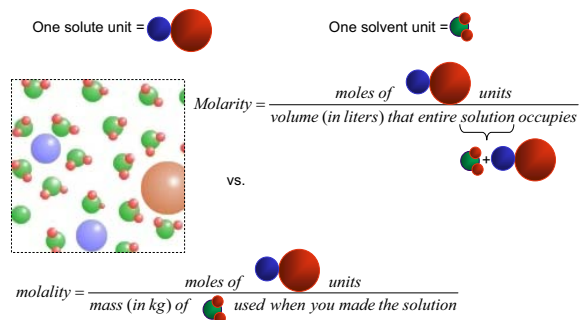
Many ways to express concentration mathematically

- Molarity = moles of solute per liter of solution
- Molality = moles of solute per kg of solvent
- Mole fraction = moles of component per total moles (expressed as a value between 0 and 1)
- Weight percent = mass of component per total mass (expressed as a percentage)

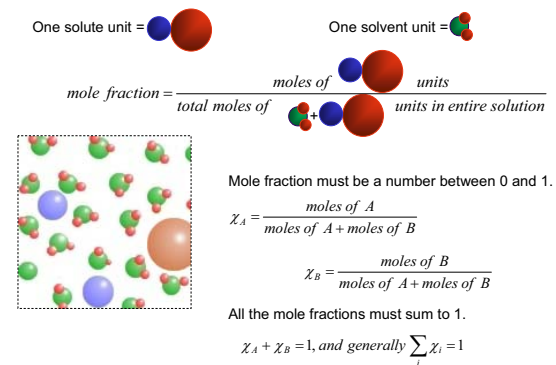
You need to know how to convert between them because – just like quantity of matter as mass vs. moles – some measures of concentration are easier to measure in lab, and other measures are necessary to use in calculations to predict properties

14



The mathematics of solutions in pictures

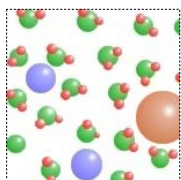


The mathematics of solutions in pictures



The mathematics of solutions in pictures

One solute unit =  One solvent unit = 

$$\text{wt}\% = \frac{\text{mass of } \text{units}}{\text{total mass of } \text{units}} \times 100\%$$


Alternative concept of weight percent if you have exactly 100 grams of the mixture:

$$\text{wt}\% = \frac{\text{part of mass that is } \text{units}}{100 \text{ grams total mass of } \text{units}} \times 100\%$$

For example, if a particular aqueous solution were 3.2% acetic acid by mass, and if you had exactly 100 grams of the solution, then 3.2 grams would be acetic acid and the remainder (96.8 g) would be water.

Ways of expressing concentration

Example (from p. 546)

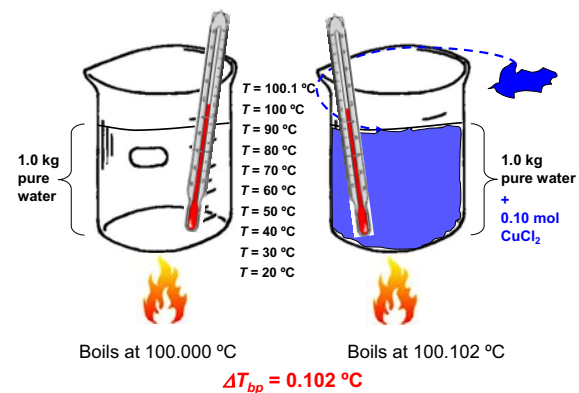
A commercial bleach solution contains 3.62 mass % NaOCl in water. Calculate (a) the molality, (b) the mole fraction of NaOCl, (c) the mole fraction of H₂O in the solution.

18

How does chemistry explain the ways in which solutions are different than pure solvents?

- In the lab, we find that solutions always boil at higher temperatures than the pure solvent (we call this Boiling Point Elevation)
- We know that "boiling" is the physical phenomenon that happens when the vapor pressure of the liquid (solvent) reaches atmospheric pressure
- Therefore, the cause for the BPE must have to do with the presence of the solute causing a change in the solvent's vapor pressure
- What is going on at the particle level that could be causing this vapor pressure difference?

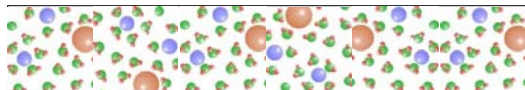
Compare boiling points: pure solvent vs. a solution



What does the boiling point elevation depend on?

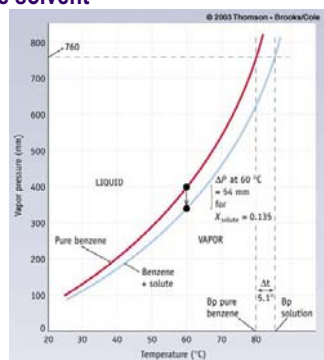
To make sense of this, we need to picture what is happening at the particle level

- Comparing solution to solvent at the same temperature: fewer solvent particles in the vapor phase, because solute particles are in the way



Vapor pressure of solvent over solution vs. vapor pressure of pure solvent

- Benzene is the solvent
- Red line is the L-G portion of the phase diagram for pure benzene
- Compare curves at the same temperature (60°C)
 - Solution vapor pressure is _____ than solvent vapor pressure. Why?
- Compare curves at the same pressure (760 torr)
 - Boiling point of solution is _____ than boiling point of solvent. Why?



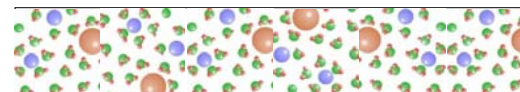
What does the boiling point elevation depend on?

To make sense of this, we need to picture what is happening at the particle level

- Comparing solution to solvent at the same temperature: fewer solvent particles in the vapor phase, because solute particles are in the way
- Also would depend on what solvent it is, because different solvents have different vapor pressures

$$\Delta T_{bp} = (\text{effective molality}) \times (\text{solvent factor}) = i m_{\text{solute}} K_{bp}$$

solvent factor
effective molality



An example: boiling point elevation in a solution

Example (from p. 552)

Antifreeze, ethylene glycol, HOCH₂CH₂OH, is added to water to raise its boiling point (and also lower its freezing point). What would be the boiling point temperature of a 25.0 mass % solution of ethylene glycol in water?