# CHEM 116

## Colligative Properties and Intro to Rates of Reaction

Lecture 11
Prof. Sevian

Note: Some of the slides here were in Lecture 10 but we didn't get to them, so we will begin with those. They are repeated here, but if you already printed out Lecture 10, then you can bring your Lecture 10 notes to lecture with you and print just pages 8 to 11 of this Lecture 11.

## Today's agenda

- Finish colligative properties (ch. 13)
  - Volatility
    - Decrease when a solute is present
    - Composition of vapor when both components are volatile (Raoult's law for ideal solutions)
  - Boiling point elevation
  - Freezing point depression
  - Osmotic pressure
  - Henry's law for gas solubility in a liquid solvent
- Introduce reaction rates (ch. 14)

## Summary of equations for BPE, FPD and Osmotic pressure

- Boiling point elevation (BPE)

$$\Delta T_{bp} = i\, m_{solute} K_{solvent,bp}$$

- Freezing point depression (FPD)

$$\Delta T_{fp} = i\, m_{solute} K_{solvent,fp}$$

- Osmotic pressure

$$(\text{osmotic pressure}, \pi)V = nRT$$

$$\pi = \frac{n}{V}RT = \left(\text{effective molarity in } \frac{mol}{L}\right)RT$$

$$\pi = i\left(\text{molarity in } \frac{mol}{L}\right)RT$$

Note: text book uses *M* to represent molarity, p. 554

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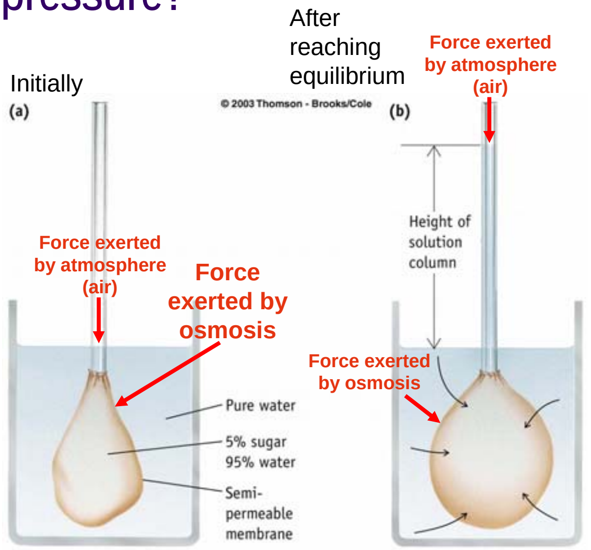
## What is osmotic pressure?

- Process of osmosis through a semipermeable membrane separating solutions of different concentrations
- Osmosis continues until downward force exerted by air on solution equals upward force exerted by osmosis

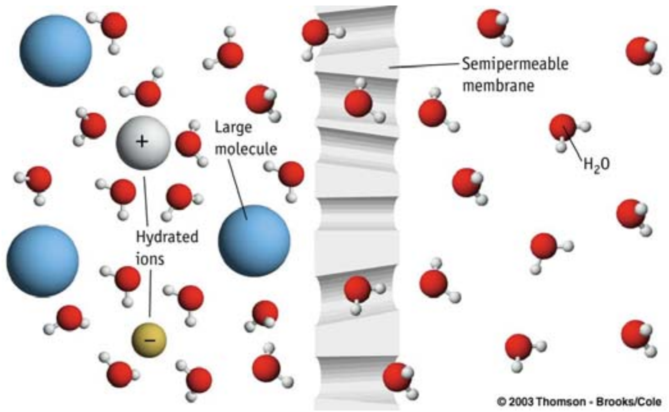


Note: lengths of arrows here are intended to represent strengths of forces

## Where osmotic pressure comes from

Solution on the inside
of the bag

Pure water on the
outside of the bag



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**Net direction of flow of water**

## Many (most) solutes are not ideal

- Ideal behavior of solutes (pretend)
  - Ionic compounds dissociate completely in water; molecular compounds do not dissociate in water
  - van’t Hoff factor for a molecular solute equals 1
  - van’t Hoff factor for an ionic solute equals number of ions that an ionic unit theoretically breaks into
- Non-ideal behavior of solutes (reality)
  - Some ionic compounds are only partially dissociated in water; some molecular compounds dissociate a tiny bit
  - van’t Hoff factor for a molecular solute can be > 1
  - van’t Hoff factor for an ionic solute can be < number of ions that an ionic unit theoretically breaks into

## Ideal vs. Non-ideal behavior in colligative properties

<u>Ideal behavior</u>

- Strong electrolytes dissociate completely in water, especially if they are at very low concentrations
- Examples (solutions at very low concentrations)

  NaCl $i = 2$

  $K_2SO_4$ $i = 3$

  $(NH_3)_3PO_4$ $i = 4$

<u>Non-ideal behavior</u>

- Real solutions of ionic compounds have van't Hoff factors that are not integers because of ion-ion interactions while dissolved in solution
- As the concentration of ionic solute increases, ions interact more with each other, and *i*-value decreases
- Examples

  $K_2SO_4$ at 0.00100 *m* $i = 2.84$

  $K_2SO_4$ at 0.0100 *m* $i = 2.69$

  $K_2SO_4$ at 0.100 *m* $i = 2.32$

## More on non-ideal van't Hoff factors

- Some substances that appear (from their chemical composition) to be molecular actually dissociate partially when dissolved in water – this is most important for organic acids
- As with ionic compounds, the higher the concentration of the substance, the less dissociated it will be
- Example: acetic acid reacts with water to a small extent

  $CH_3COOH\ (aq) + H_2O\ (l) \rightarrow CH_3COO^-\ (aq) + H_3O^+\ (aq)$

  As you will learn to calculate when we get to chapter 16, when the concentration of the acid decreases, the % dissociation increases

  0.010 *m* $CH_3COOH$ solution $i = 1.04$ (4% dissociated)

  0.0010 *m* $CH_3COOH$ solution $i = 1.13$ (13% dissociated)

  0.00010 *m* $CH_3COOH$ solution $i = 1.34$ (34% dissociated)

  (The main point here is that the van't Hoff factor for acetic acid can be greater than 1, but only at very low concentrations.)

# How do pressure of gas and temperature of the solution affect solubility?

## Solids and liquids

- Increasing the gas pressure over the liquid has no effect on how much solid or liquid can dissolve in a liquid solvent
- Increasing the temperature *usually* has the effect of causing greater solubility, but there are some exceptions

## Gases that do not react with a solvent (“ideal” situation)

- Increasing the gas pressure results in greater solubility of the gas in the liquid solvent
- Increasing the temperature of the solution results in lower solubility of the gas in the liquid solvent

## Gases that react with solvent (*e.g.*, $CO_2$ reacts with water)

- If some of the gas molecules react with water, more molecules move into the liquid from the gas phase, to compensate and re-establish equilibrium

# Gases dissolved in liquids: Henry’s law

- How much gas can dissolve in a liquid depends on the partial pressure of the gas above the liquid

$$\text{gas solubility} = k_H P_{gas}$$

**Partial pressure of the gas above the liquid solvent**

**Maximum concentration of gas that can dissolve (in moles of gas per liter of solvent)**

**Henry’s law gas constant (dependent on strength of solute-solvent attractions)**

- Different gases can dissolve to different extents, owing to the dipole (water) – induced dipole (solute) interactions

| Gas | Molecular mass | Henry’s law constant ($k_H$) at 25ºC |
|---|---|---|
| $N_2$ | 28.0 g/mol | 0.000000842 M/mmHg |
| $O_2$ | 32.0 g/mol | 0.00000166 M/mmHg |
| $CO_2$ | 44.0 g/mol | 0.0000448 M/mmHg |

## The most useful use of colligative properties: identifying unknown substances by their molar mass

Basic strategy:

- All colligative properties depend on the concentration of solute in a solvent
- Make a solution and measure a colligative property, then calculate concentration of solute that must be in the solvent
- From concentration of solute, if you know how much solvent there is, you can figure out the moles of solute
- If you independently know the mass of solute that was used to create the solution, then you can get the molar mass of the solute

$$M_w = \frac{mass\ of\ solute\,(g)}{moles\ of\ solute\,(mol)}$$

## Example: Molecular formula determination by boiling point elevation

*Similar to FPD Practice Exercise, p. 556*

0.640 g of azulene are dissolved in 99.0 g of benzene. The boiling point of the solution is 80.23 ºC. If the empirical formula of azulene is $C_5H_4$, what is its molecular formula? The normal boiling point of pure benzene is 80.10 ºC, and the boiling point constant, $K_{bp}$ = 2.53 ºC/*m*.

# Key points about colligative properties

- Colligative properties are properties of a solution compared to the pure solvent
- Colligative properties are caused by the presence of the solute
- When solute is present, the vapor pressure is lower, boiling point is elevated and freezing point is depressed (the liquid phase of a solution is extended at both ends over the pure solvent)
- Real solutions have van't Hoff factors that are larger when less solute is dissolved. This is because at lower concentrations, dissolved + and – solute particles cannot pair as easily.
- Because colligative properties depend on the concentration of solute dissolved in a solvent, colligative properties can be used to determine molecular weights of solutes

# Clicker question about solutions

Which solution should have the highest boiling point?

(A) 1 gram of $CaCO_3$ (f.w. 100. g/mol) in 100 mL of solution

(B) 2 moles of $CaCO_3$ in 1 kg of water

(C) A 2.0 wt% aqueous solution of $CaCO_3$

(D) A 0.003 *m* aqueous solution of $CaCO_3$

# Kinetics: Key terms

What makes kinetics difficult is that there are a lot of new ideas and new vocabulary all introduced at the same time. Becoming familiar with the vocabulary will help immensely.

Rate law
Concentration
Catalyst
Overall order of reaction
Order with respect to a particular reactant
Rate constant
Half-life
Collision model
Activated complex/transition state
Activation energy
Arrhenius equation
Reaction mechanism
Elementary step in reaction mechanism
Rate-determining step
Molecularity of a step
Equilibrium

# Kinetics

- *The study of how quickly (or slowly) reactions occur*

Using chemistry in the world:

- How do you produce chemicals?
  - What kinds of chemical reactions are there?
- What properties do materials have and why do they have those properties?
- How much of a given chemical can you produce? How can you control it?
  - Stoichiometry
  - **How fast do reactions occur?**
  - How much energy does it take to make a reaction occur, or how much energy does a reaction give off?
  - How pure can you make the chemical? (Are there competing reactions?)
  - Scaling up reactions to useful proportions
- How dangerous are specific chemicals?
  - LD50 of the desired products
  - Are there any byproducts or left over reactants? Are these dangerous?

## What factors can affect the speed of a reaction?

- Everyone is comparing to the same control
  React Alka-Seltzer in water at room temperature
  How much time does it take to react?
  What could we vary?

- Send one person from your group to get materials
- Do the experiment (5 minutes)
- Report what you learned to the class
- Clean up at end of class

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## Four different experiments

Control (same for everyone): 1 tablet Alka-Seltzer in a ¾ full cup (approx. 100 mL) of room temperature water

- Send a member of your group to pick up a set of materials, note the Group #
- Set contains: 2 cups, water, Alka-Seltzer tablets
- Measure time in seconds (digital watch or second hand on clock in front)

| | |
|---|---|
| A)<br>Groups 1, 2, 3 and 4<br>● Same control<br>● Experiment: 2 tablets instead of 1 tablet | B)<br>Groups 5, 6, 7 and 8<br>● Same control<br>● Experiment: 1 tablet A-S in a ¾ full cup of very warm water |
| C)<br>Groups 9, 10, 11 and 12<br>● Same control<br>● Experiment: 1 crushed A-S tablet in same amount of room temp water | D)<br>Groups 13, 14, 15 and 16<br>● Same control<br>● Experiment: 1 tablet A-S in twice as much water as the control |

## What is rate of a reaction?

- Comparison: What is rate of travel? How fast you travel.

$$\text{rate of travel } (\textit{speed}) = \frac{\text{distance traveled}}{\text{time of travel}} = \frac{\Delta d}{\Delta t} = \frac{d_2 - d_1}{t_2 - t_1}$$

- Rate of a reaction is how fast the reaction happens
- Measured mathematically as

$$\text{rate of reaction } (\textit{rate}) = \frac{\text{change of chemical concentration}}{\text{time elapsed}} = \frac{\Delta[\mathrm{A}]}{\Delta t} = \frac{[\mathrm{A}]_2 - [\mathrm{A}]_1}{t_2 - t_1}$$

- What if you couldn't measure reactant concentration but you could measure how much product is created?

## What factors can affect the speed of a reaction?

- Everyone compared to the same control
  React 1 tablet of Alka-Seltzer in water at room temperature
  How much time does it take for the reaction to appear to finish?

- We looked at how the reaction rate changed for four variations
  Experiment 1: 2 tablets instead of 1
  Experiment 2: higher temperature
  Experiment 3: powdered tablet
  Experiment 4: increase volume of water

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## Extra credit assignment (turn in at 2:00 next class)

- Make a table like the following and fill it out
- Your answers in the "Why I think that happened" column do not need to be correct, but they do need to be what you think.

| | Results of this experiment in class | Why I think that happened |
|---|---|---|
| A) *Increase reactant concentrations* | | |
| B) *Raise temperature* | | |
| C) *Increase surface area of reaction* | | |
| D) *Decrease reactant concentrations* | | |

## Slide about one of the questions on Exam 1 that was shown at the end of Lecture 10 but wasn't on the website version of the lecture slides

| Compound | #1 | #2 | #3 |
|---|---|---|---|
| Lattice energy (kJ/mol) | 3795 | 3414 | 3217 |
| (A) | MgO | CaO | SrO |
| (B) | KCl | $K_2S$ | CaS |
| (C) | LiBr | NaCl | KF |
| (D) | NaBr | NaCl | NaF |

(A) (+2) (-2) where +2's are increasingly larger in radius

(B) same period so approx. same radius, comparing (+1)(-1)… (+1)(-2)… (+2)(-2)

(C) (+1 in Pd 2)(-1 in Pd 4)…. (+1 in Pd 3)(-1 in Pd 3)…. (+1 in Pd 4)(-1 in Pd 2)

(D) (+1)(-1) where -1's are decreasing in radius