

CHEM 116

Colligative Properties of Solutions

October 5, 2006
Prof. Sevian



1

Agenda

Properties of solutions that we can measure in the lab:

1. Vapor pressure decrease
 - In a solution that has a non-volatile solute dissolved, the solvent always has a lower vapor pressure than it would in the pure solvent at the same temperature
2. Boiling point elevation
 - Solutions always boil at higher temperatures than pure solvent – how much higher?
3. Freezing point depression
 - Solutions always freeze at lower temperatures than pure solvent
4. Osmotic pressure existence
5. Increased solubility of gases (solute) in a liquid solvent when the pressure increases or temperature decreases

When the model breaks down: Non-ideal (real or actual) behavior of solutions

2

Announcement

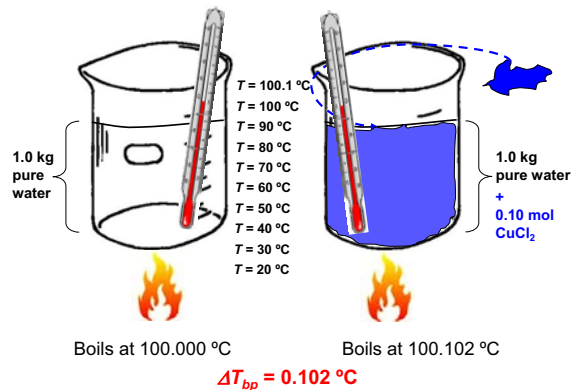
- On Tuesday of next week, the class that meets in here before us will be taking an exam.
- The instructor of that class has asked that students in our class please remain in the hallway outside the lecture hall until 2:25 so as not to disturb students who are finishing their exams.

3

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?

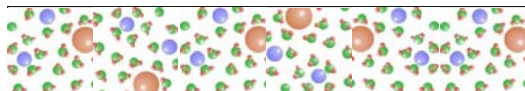
Compare boiling points: pure solvent vs. a solution



What does the boiling point elevation depend on?

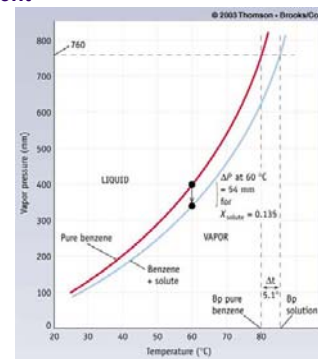
To make sense of this, we need to picture what is happening at the particle level

- Comparing solution to solvent at the same temperature: fewer solvent particle 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?

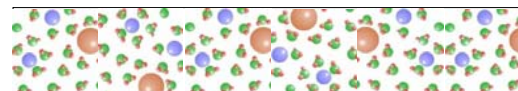
To make sense of this, we need to picture what is happening at the particle level

- Comparing solution to solvent at the same temperature: fewer solvent particle 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?

Vapor pressure


- Vapor pressure of the solvent decreases as more solute dissolves (as compared to pure solvent)
- Raoult's law describes the behavior for "ideal" behavior

$$P_{\text{solvent}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

- Simplest version of Raoult's law: only the solvent is volatile (i.e., solute is not volatile)
- Raoult's law can be extended to situation where solute is volatile (e.g., ethanol and water mixed together)

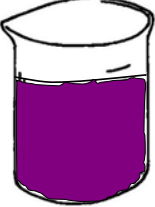
10

At a given temperature, how much lower is the vapor pressure of a solution than the pure solvent?



Same T
Solute has no vapor pressure (nonvolatile)



Fraction of surface occupied by solvent particles is 1.0
Vapor pressure of solvent is $P_{\text{solvent}}^{\circ}$



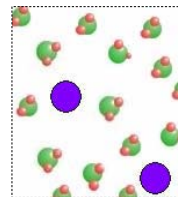
Fraction of surface occupied by solvent particles is χ_{solvent}
Vapor pressure of solvent is $\chi_{\text{solvent}} \times P_{\text{solvent}}^{\circ}$

11

The mathematics of solution in pictures

One (nonvolatile) solute unit =  One solvent unit = 

$$\text{mole fraction of solvent} = \frac{\text{moles of units}}{\text{total moles of units in entire solution}}$$



Mole fraction must be a number between 0 and 1.

$$\chi_A = \frac{\text{moles of } A}{\text{moles of } A + \text{moles of } B}$$

$$\chi_B = \frac{\text{moles of } B}{\text{moles of } A + \text{moles of } B}$$

All the mole fractions must sum to 1.

$$\chi_A + \chi_B = 1, \text{ and generally } \sum_i \chi_i = 1$$

An example: vapor pressure in a solution

Practice Exercise, p. 550

The vapor pressure of pure water at 110°C is 1070 torr. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at 110°C. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in the solution?

13

Raoult's law (ideal behavior) when two components are volatile

Consider water and ethanol as an example

- For water

$$P_{\text{water}} = \chi_{\text{water}} P_{\text{water}}^{\circ} \quad \text{with } P_{\text{water}}^{\circ} = \text{vapor pressure of pure water at that temperature}$$

- For ethanol (EtOH for brevity)

$$P_{\text{EtOH}} = \chi_{\text{EtOH}} P_{\text{EtOH}}^{\circ} \quad \text{with } P_{\text{EtOH}}^{\circ} = \text{vapor pressure of pure ethanol at that temperature}$$

- But mole fractions must sum to 1, so

$$\chi_{\text{water}} + \chi_{\text{EtOH}} = 1$$

- Therefore, ethanol vapor pressure can be expressed in terms of water mole fraction

$$P_{\text{EtOH}} = (1 - \chi_{\text{water}}) P_{\text{EtOH}}^{\circ}$$

- Generalize to two components A and B

$$P_A = \chi_A P_A^{\circ} \quad \text{with } P_A^{\circ} = \text{vapor pressure of A at that temperature}$$

$$P_B = (1 - \chi_A) P_B^{\circ} \quad \text{with } P_B^{\circ} = \text{vapor pressure of B at that temperature}$$

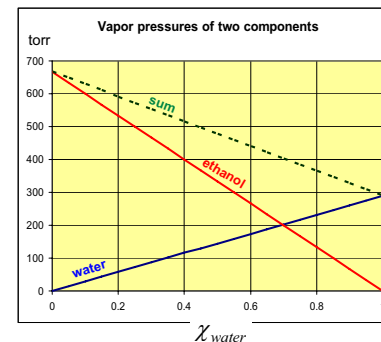
Vapor pressure when two components are volatile

Ideal behavior predicted by Raoult's law

Pure water
 $T_{\text{boil}} = 100 \text{ }^{\circ}\text{C}$
 $P_{\text{water}}^{\circ} = 289 \text{ torr}$
 at 75 °C

Pure ethanol
 $T_{\text{boil}} = 78 \text{ }^{\circ}\text{C}$
 $P_{\text{water}}^{\circ} = 665 \text{ torr}$
 at 75 °C

- Water mole fraction is opposite ethanol mole fraction
- Extremes
 - All water
 - All ethanol
- In between



Raoult's law applied to two components

The mixture contains both A and B molecules. Therefore, there are three kinds of interactions to overcome when molecules change from liquid to vapor phase: A-A, B-B and A-B.

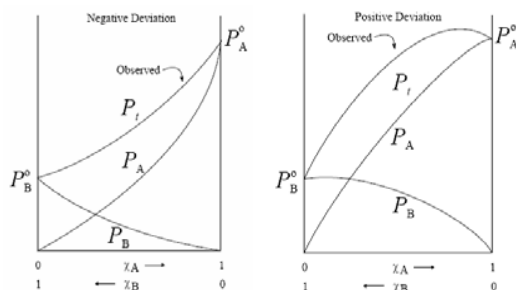
- Assumption in ideal (pretend) case: intermolecular attractions are predictable
 - A-A attractions may be different from B-B attractions, leading to different pure vapor pressures at the same temperature (which results in the two components having different boiling points)
 - A-B attractions assumed to be the average of A-A and B-B interactions
- When this assumption is not true (reality)
 - A-B attractions are greater than the average of A-A and B-B \Rightarrow results in molecules entering vapor phase less easily than Raoult's law predicts
 - A-B attractions are smaller than the average of A-A and B-B \Rightarrow results in molecules entering vapor phase more easily than Raoult's law predicts

16

Non-ideal behavior with two volatile components

When A-B attractions are stronger than the average of A-A and B-B

When A-B attractions are weaker than the average of A-A and B-B



Source of graphs: R. Carter (UMass Boston)

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

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

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

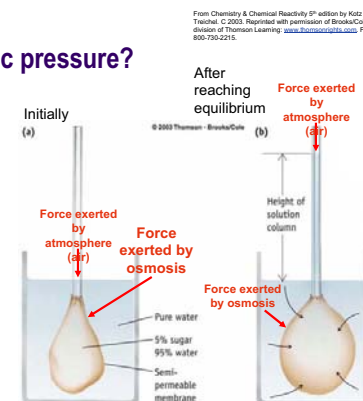
$$\pi = i \left(\text{molarity in } \frac{\text{mol}}{L} \right) RT$$

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

18

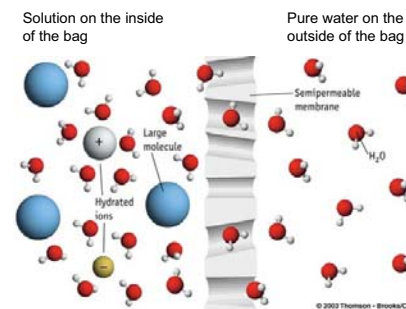
What is osmotic pressure?

- 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



Net direction of flow of water

20

Some 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 < number of ions that an ionic unit theoretically breaks into

21

Ideal vs. Non-ideal behavior in colligative properties

Ideal behavior

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

NaCl	$i = 2$
K ₂ SO ₄	$i = 3$
(NH ₃) ₃ PO ₄	$i = 4$

Non-ideal behavior

- 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 ₂ SO ₄ at 0.00100 <i>m</i>	$i = 2.84$
K ₂ SO ₄ at 0.0100 <i>m</i>	$i = 2.69$
K ₂ SO ₄ at 0.100 <i>m</i>	$i = 2.32$

22

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

$$\text{CH}_3\text{COOH} (aq) + \text{H}_2\text{O} (l) \rightarrow \text{CH}_3\text{COO}^- (aq) + \text{H}_3\text{O}^+ (aq)$$

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

0.010 <i>m</i> CH ₃ COOH solution	$i = 1.04$ (4% dissociated)
0.0010 <i>m</i> CH ₃ COOH solution	$i = 1.13$ (13% dissociated)
0.00010 <i>m</i> CH ₃ COOH 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.)

23

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., CO₂ 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

24

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

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

Partial pressure of the gas above the liquid solvent
 Henry's law gas constant (dependent on strength of solute-solvent attractions)
 Maximum concentration of gas that can dissolve (in moles of gas per liter of solvent)

- 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 25°C
N ₂	28.0 g/mol	0.00000842 M/mmHg
O ₂	32.0 g/mol	0.0000166 M/mmHg
CO ₂	44.0 g/mol	0.000448 M/mmHg

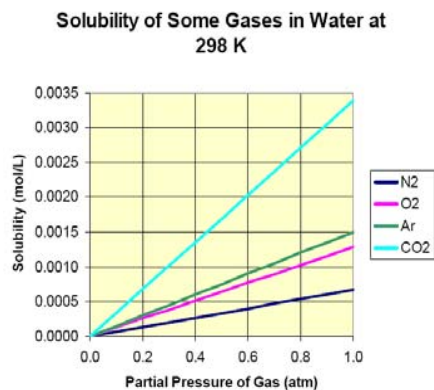
25

An example: A gas dissolved in water

Practice Exercise, p. 542

Calculate the concentration of CO₂ in a soft drink after the bottle is opened and equilibrates at 25°C under a CO₂ partial pressure of 3.0×10^{-4} atm. Assume CO₂ reacts negligibly.

27



Source of graph: R. Carter (UMass Boston)

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

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

28

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 °C. If the empirical formula of azulene is C_2H_4 , what is its molecular formula? The normal boiling point of pure benzene is 80.10 °C, and the boiling point constant, $K_{bp} = 2.53 \text{ }^\circ\text{C}/m$.

29

Key points from today

- 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

30