CHEM 116
Concentrations and Colligative Properties

Lecture 10
Prof. Sevian

FSG is
Mondays 11:00 am
and
Tuesdays 3:30 pm
both in
S-1-89

Today's agenda

- Ways of expressing concentration
- Colligative properties
  - 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
- Return Exam #1 and go over it

Clicker question about solutions

In a saline solution (for contact lenses), which of the following correctly identifies the components of the solution?

	Solute	Solvent
(A)	Na^+ and Cl^- ions	Water
(B)	Water	Na^+ and Cl^- ions
(C)	NaCl (*s*)	Water
(D)	Water	NaCl (*s*)

Know the difference between mass and moles

Three inert gases are placed in the same container: 3.00 g of He, 3.00 g of Ne, and 3.00 g of Ar. The total pressure in the container is 22.2 atm.

(a) What is the partial pressure of He in the container?

(b) What is the weight % of He?

(c) What is the mole fraction of He?

$$\text{mole fraction of He} = \frac{\text{moles of He}}{\text{total moles}} = \frac{\left(\dfrac{3.00g\ \text{He}}{4.00\,{}^{g}\!/_{mol}}\right)}{\left(\dfrac{3.00g\ \text{He}}{4.00\,{}^{g}\!/_{mol}}\right)+\left(\dfrac{3.00g\ \text{Ne}}{20.18\,{}^{g}\!/_{mol}}\right)+\left(\dfrac{3.00g\ \text{Ar}}{39.95\,{}^{g}\!/_{mol}}\right)} \quad \text{as a decimal} = 0.770$$

3.00 g He

3.00 g Ne

3.00 g Ar

all mixed together

$$\%\ \text{wt. of He} = \frac{\text{mass of He}}{\text{total mass}} = \frac{3.00g}{9.00g} \quad \text{as a } \% = 33.3\%$$

What causes pressure?

Collisions of gas particles with the sides of the container.

If the gases are ideal, what does this mean?

The identities of the gases do not matter.

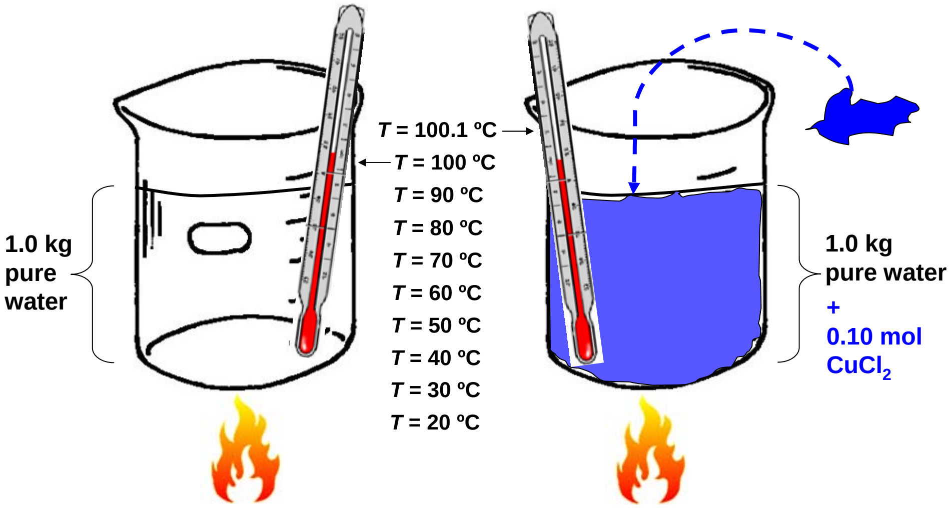
What does the "partial pressure of He" mean?

The portion of the total pressure that is caused by He.

How does chemistry explain the ways in which solutions are different than pure solvents? Example: Boiling point of a solution vs. pure solvent

- 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?
- Once we understand the basic model, we will discuss “non-ideal” behavior – that is, how the model doesn’t quite fit reality

Compare boiling points: pure solvent vs. a solution



Boils at 100.000 ºC

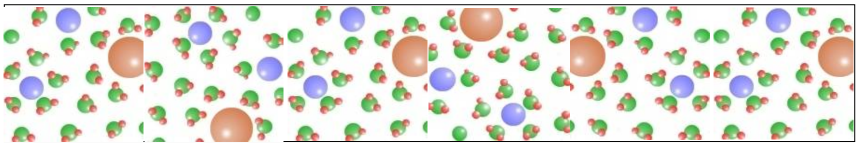
Boils at 100.102 ºC

ΔT_{bp} = 0.102 ºC

What does the boiling point elevation depend on?

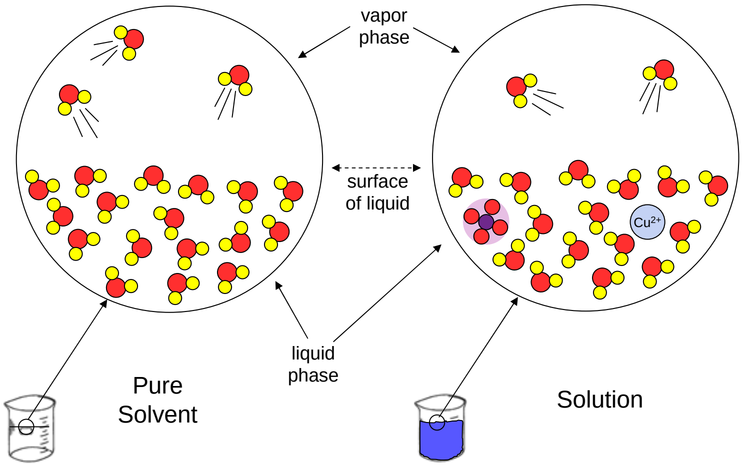
To make sense of this, we need to picture what is happening at the particle level

- Comparing solution to solvent at the same temperature: fewer solvent particle in the vapor phase, because solute particles are in the way
- Think about volatility of the solvent – pure solvent has a vapor pressure
- Assume that solute does <u>not</u> have vapor pressure



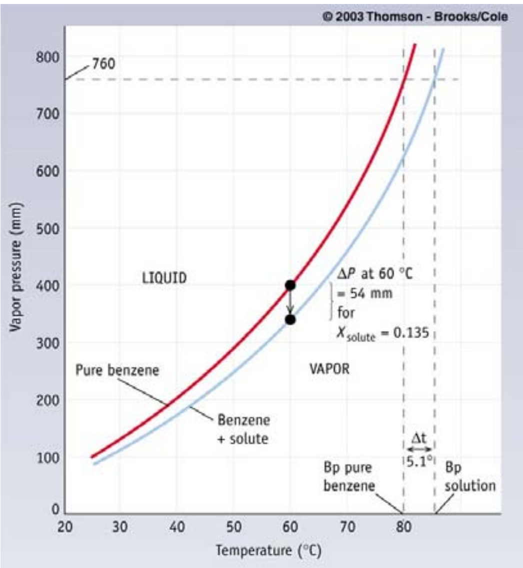
Particle level model of boiling point elevation

Which has lower vapor pressure at the same temperature? Why?



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

- In this case, benzene is the solvent
- Red line is the L-G portion of the phase diagram for pure benzene (vapor pressure curve)
- Compare curves at the same temperature (60ºC)
  - 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?



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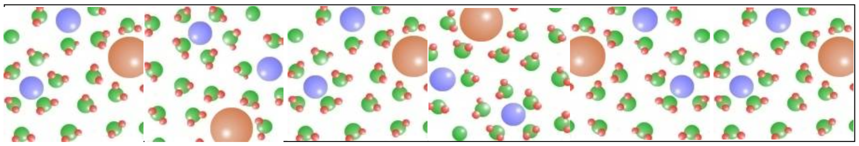
What does the boiling point elevation depend on?

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 and/or holding the solvent in the liquid phase
- Also would depend on what solvent it is, because different solvents have different vapor pressures

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



An example: boiling point elevation in a solution

Example (from p. 552)

Antifreeze, ethylene glycol, $HOCH_2CH_2OH$, 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?

Key points so far about solutions

- 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 boiling point is elevated
- The equation to describe this is

  $$\Delta T_{\text{bp}} = (i\, m_{\text{solute}})\, K_{\text{bp}}$$

- Because colligative properties depend on the concentration of solute dissolved in a solvent, colligative properties can be used to determine molecular weights of solutes

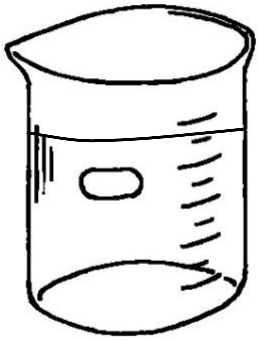
Vapor pressure

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

$$p_{solvent} = \chi_{solvent} \, p^{o}_{solvent}$$

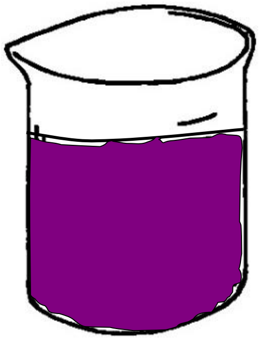
- Simplest version of Raoult's law: only the solvent is volatile (*i.e.*, solute is not volatile)
- Raoult's law can be extended to situation where solute is volatile (*e.g.*, ethanol and water mixed together)

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

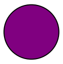
$$P^{o}_{solvent}$$

Fraction of surface occupied by solvent particles is $\chi_{solvent}$

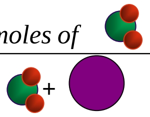
Vapor pressure of solvent is

$$\chi_{solvent} \times P^{o}_{solvent}$$

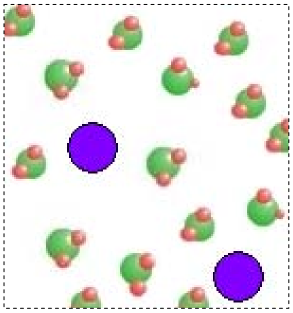
The mathematics of solution in pictures

One (nonvolatile) solute unit = 

One solvent unit = 



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



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.

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

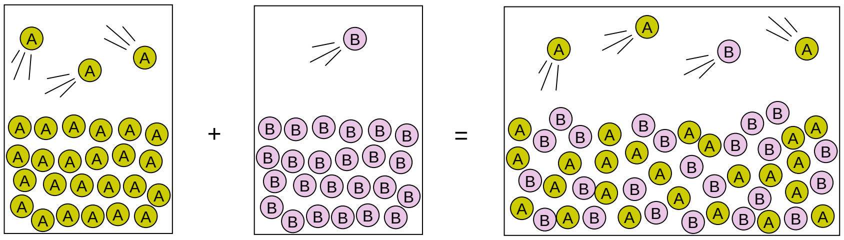
An example: vapor pressure in a solution

Practice Exercise, p. 550

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

Vapor pressure when two components are both volatile

At 20ºC the vapor pressure of pure benzene is 75 mmHg and the vapor pressure of pure toluene is 22 mmHg. If equal moles of benzene and toluene are mixed and then allowed to achieve equilibrium vapor pressure in a container at 20ºC, how would the mole fractions of the two components in the vapor phase compare?



Pure benzene

Vapor pressure
75 mmHg

Pure toluene

Vapor pressure
22 mmHg

50/50 mixture of benzene & toluene

What is the composition of the vapor?

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

Consider water and ethanol as an example

- For water

$$p_{water} = \chi_{water}\, p^o_{water} \quad \text{with } p^o_{water} = \text{vapor pressure of pure water at that temperature}$$

- For ethanol (EtOH for brevity)

$$p_{EtOH} = \chi_{EtOH}\, p^o_{EtOH} \quad \text{with } p^o_{EtOH} = \text{vapor pressure of pure ethanol at that temperature}$$

- But mole fractions must sum to 1, so

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

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

$$p_{EtOH} = (1 - \chi_{water})\, p^o_{EtOH}$$

- Generalize to two components A and B

$$p_A = \chi_A\, p^o_A \quad \text{with } p^o_A = \text{vapor pressure of A at that temperature}$$

$$p_B = (1 - \chi_A)\, p^o_B \quad \text{with } p^o_B = \text{vapor pressure of B at that temperature}$$

Vapor pressure when two components are volatile

Ideal behavior predicted by Raoult's law

Pure water

T_{boil} = 100 ºC

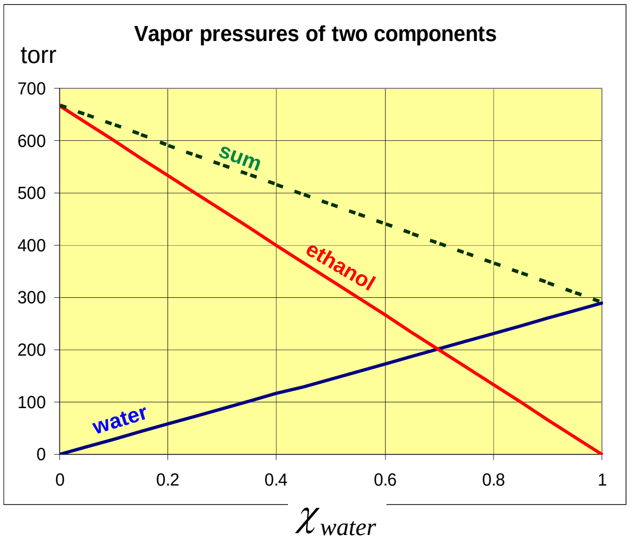
P^o_{water} = 289 torr at 75 ºC

Pure ethanol

T_{boil} = 78 ºC

P^o_{water} = 665 torr at 75 ºC

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



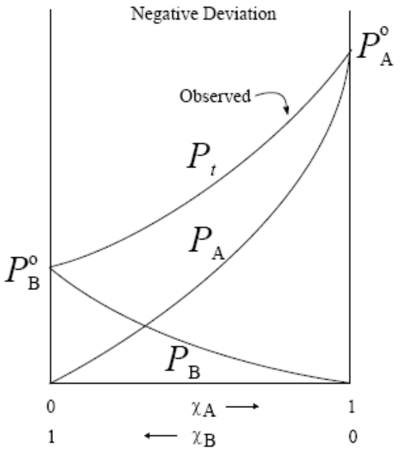
Raoult's law applied to two components

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.

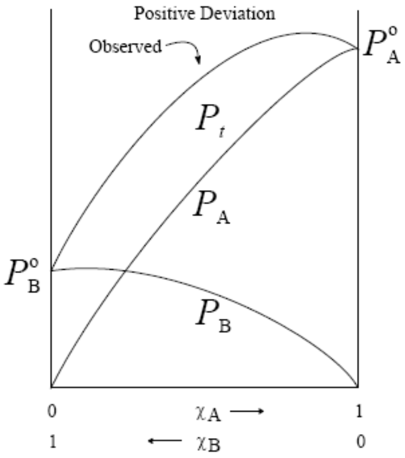
- Assumption in ideal (pretend) case: intermolecular attractions are predictable
  - A-A attractions may be different from B-B attractions, leading to different pure vapor pressures at the same temperature (which results in the two components having different boiling points)
  - A-B attractions assumed 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 ⇒ 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 ⇒ results in molecules entering vapor phase more easily than Raoult's law predicts

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

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

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

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

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

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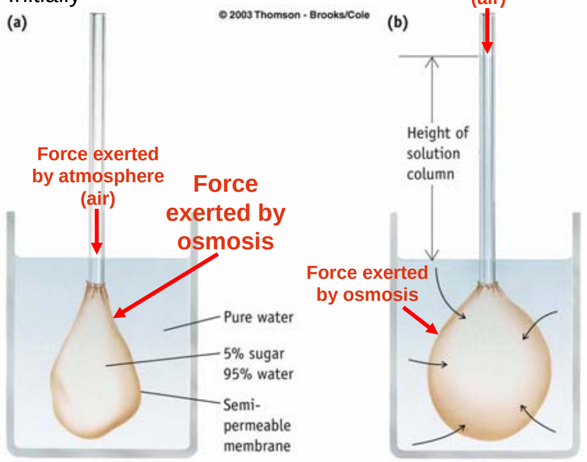
What is osmotic pressure?

- 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

Initially

After reaching equilibrium



Force exerted by atmosphere (air)

Force exerted by osmosis

Force exerted by atmosphere (air)

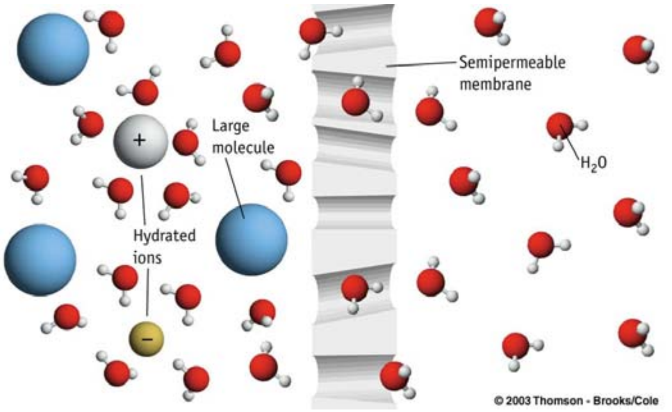
Force exerted by osmosis

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 < number of ions that an ionic unit theoretically breaks into

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_2SO_4	$i = 3$
$(NH_3)_3PO_4$	$i = 4$

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_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 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

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 $CaCO_3$

Only one other major difficulty on Exam 1 besides the two problems already addressed in today's lecture

Compound	#1	#2	#3
Lattice energy (kJ/mol)	3795	3414	3217
(A)	MgO	CaO	SrO
(+2) (-2) where +2's are increasingly larger in radius			
(B)	KCl	K_2S	CaS
same period so approx. same radius, comparing (+1)(-1)… (+1)(-2)… (+2)(-2)			
(C)	LiBr	NaCl	KF
(+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)	NaBr	NaCl	NaF
(+1)(-1) where -1's are decreasing in radius			