

Stoichiometry

- **Limiting Reagents:**

The extent to which a reaction takes place depends on the reactant that is present in limiting amounts—the limiting reagent.

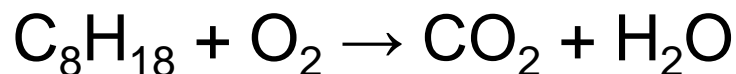


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Stoichiometry

Limiting Reagent: The reactant that governs the maximum amount of product that can be formed.

Ex: Combustion of Octane

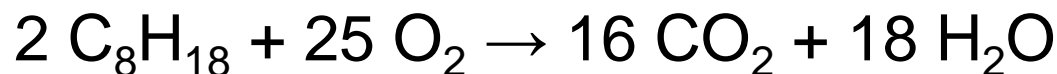


If 100 g octane and 150 g oxygen are supplied for combustion, which is the limiting reagent?

Stoichiometry

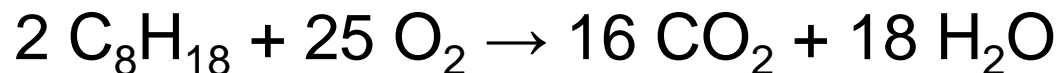
Limiting Reagent: The reactant that governs the maximum amount of product that can be formed.

Ex: Combustion of Octane



If 100 g octane and 150 g oxygen are supplied for combustion, which is the limiting reagent?

Stoichiometry



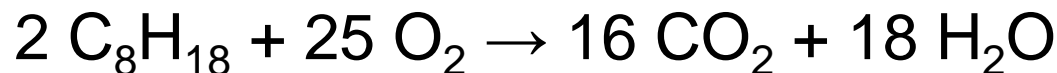
Moles octane: $100 \text{ g} \times \text{mole}/114.22 \text{ g} = 0.876 \text{ moles}$

Moles oxygen: $150 \text{ g} \times \text{mole}/32.00 \text{ g} = 4.69 \text{ moles}$

Moles oxygen needed: $0.876 \times 25/2 = 11.0 \text{ moles}$

Moles octane needed: $4.69 \times 2/25 = 0.375 \text{ moles}$

Stoichiometry



0.976 moles octane available and 0.375 moles needed

4.69 moles oxygen available and 11.0 moles needed

So OXYGEN is the limiting reagent

We won't burn all of the octane

Solution Concentrations

- **Concentrations**

allow us to measure out a specific number of moles of a compound by measuring the mass or volume of a solution.



Solution Concentrations

- **Molarity:** The most useful way of expressing the amount of a substance dissolved in a solution is with molarity.

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

- It is important to note that the final volume of solution must be used, not volume of solvent.

Solution Concentrations

Preparing an aqueous solution of known concentration.

1. Transfer a known amount of solute into a graduated flask.
2. Add enough water to dissolve the solute.
3. After solute dissolves, add water up to the mark on the flask.

$$M_{\text{solute}} = \text{moles}_{\text{solute}} / \text{Liters}_{\text{flask}}$$

Solution Concentrations

How many grams of solute would you use to prepare 500.0 mL of 1.25 M NaOH?

$$0.500 \text{ L} \times 1.25 \text{ moles/L} \times 40.00 \text{ g/mole} = 25.0 \text{ g NaOH}$$

Solution Concentrations

How many moles of solute are present in 125 mL of
0.20 M NaHCO_3 ?

$$0.20 \text{ moles/L} \times 0.125 \text{ L} = 0.025 \text{ moles NaHCO}_3$$

Solution Concentrations

To transfer a specified amount of solute, remove a given volume of a solution with known concentration.

Transfer 0.00100 mole of NaCl from a 0.0500 M solution

(20.0 mL)

Solution Concentrations

- **Dilution:**
- Is the process of reducing a solution's concentration by adding more solvent.



Solution Concentrations

Initial moles of solute = Final moles of solute

Initial Concentration x Initial Volume =

Final Concentration x Final Volume

$$M_i \times V_i = M_f \times V_f$$

Solution Concentrations

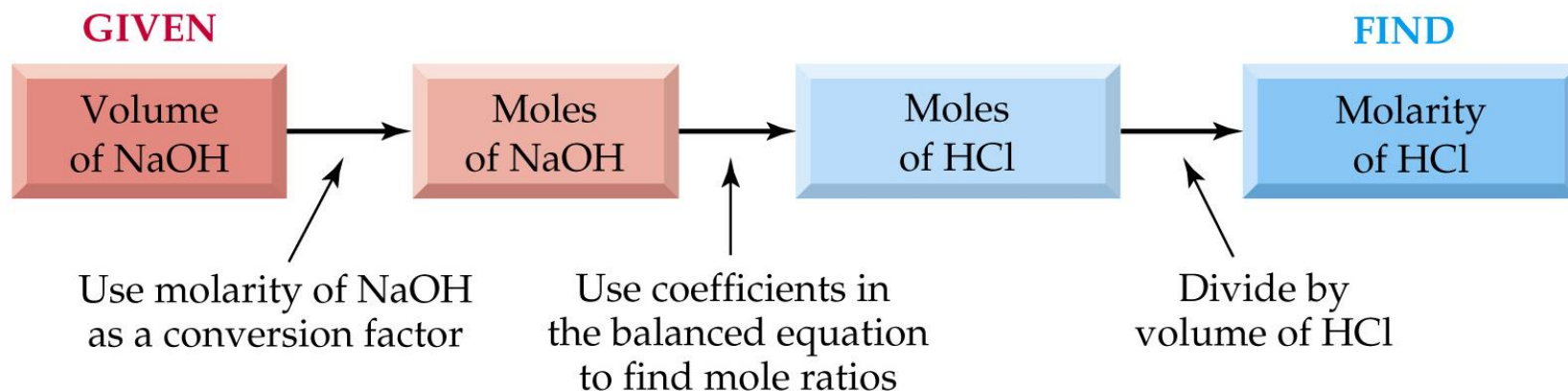
- What volume of 18.0 M H_2SO_4 is required to prepare 250.0 mL of 0.500 M aqueous H_2SO_4 ?

$$M_i \times V_i = M_f \times V_f$$

(6.94 mL)

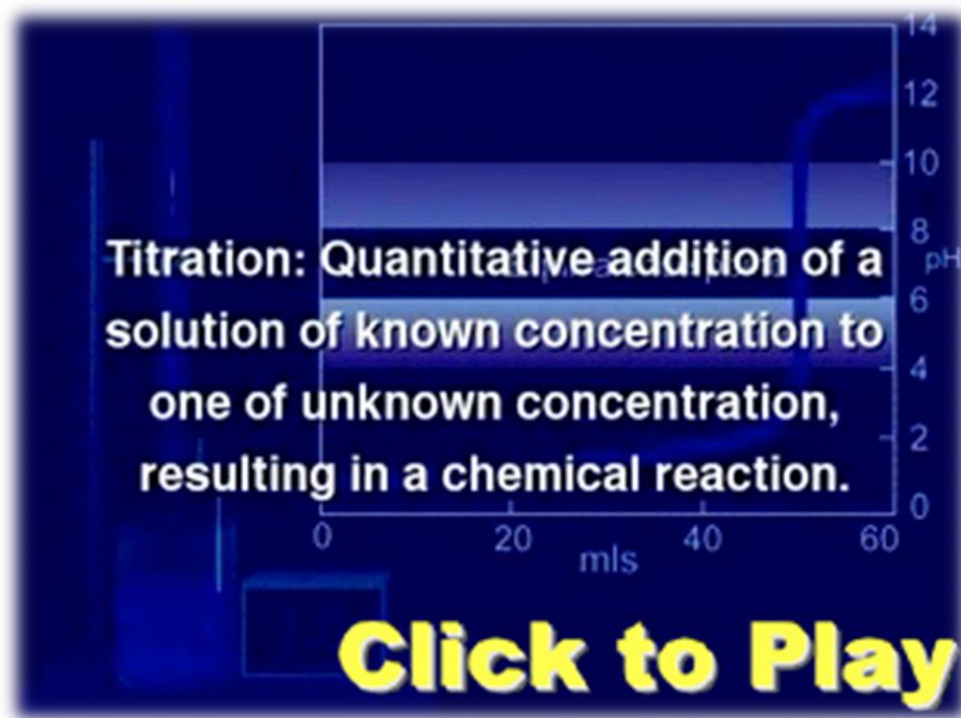
Solution Stoichiometry

- **Solution Stoichiometry** uses molarity as a conversion factor between volume and moles of a substance in a solution.



Solution Stoichiometry

- **Titration:**
- A technique for determining the concentration of a solution.



Titration

Titration: the process of analyzing composition by measuring the volume of one solution needed to completely react with another solution.

This is a special case of a *Limiting Reagent*!

Usually the reaction of an acid with a base.

Titration

Analyte: the solution of unknown concentration but known volume.

Titrant: the solution of known concentration.



Add titrant until all of the analyte has reacted, then detect the excess of titrant.

Titrations

Equivalence Point: the point at which exactly the right volume of titrant has been added to complete the reaction.

Indicator: substance that changes color when an excess of titrant has been added.

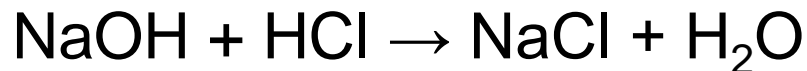
Titration

Titration Calculations:

1. Find the number of moles of titrant added to reach the endpoint.
2. Determine the moles of analyte that must have been present (use stoichiometric coefficients).
3. Determine the concentration of analyte that must have been present (use the volume of analyte).

Titration

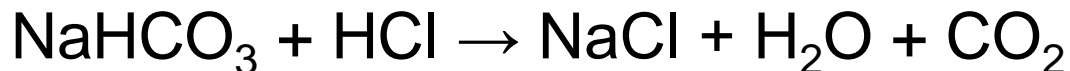
Example #1: 14.84 mL of an HCl solution of unknown concentration is titrated with standard NaOH solution. At the equivalence point, 25.0 mL of the 0.675 M NaOH has been added. Calculate the concentration of the HCl solution.



Titrant = ? Analyte = ? (1.14 M)

Titration

Example #2: An antacid tablet containing sodium bicarbonate (NaHCO_3) and weighing 4.00 g is dissolved in water. The solution is titrated to the equivalence point with 50.0 mL of 0.200 M HCl. Calculate the mass% of sodium bicarbonate in the tablet.



Titrant = ? Analyte = ? (21.0%)

$$\text{Mass \% of A} = \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 100$$

Mass Percentage



Parts per Million (ppm)

$$\text{ppm} = \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 10^6$$

Parts per Billion (ppb)

$$\text{ppb} = \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 10^9$$

**Parts per Million and
Parts per Billion**



$$X_A = \frac{\text{moles of A}}{\text{total moles in solution}}$$

$$X_A = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}}$$

In some applications, one needs the •
mole fraction of *solvent*, not solute—
make sure you find the quantity you
need!

Mole Fraction (X)



$$M = \frac{\text{mol of solute}}{\text{L of solution}}$$

You will recall this concentration •
measure from Chapter 4.

Because volume is temperature •
dependent, molarity can change with
temperature.

Molarity (*M*)



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

Because neither moles nor mass change with temperature, molality (unlike molarity) is *not* temperature dependent.

Molality (*m*)



$$\text{Mass}\% = \frac{\text{mass } A}{\text{total mass of solution}} \times 100$$

$$\text{ppm} = \frac{\text{mass } A}{\text{total mass of solution}} \times 10^6$$

$$\text{ppb} = \frac{\text{mass } A}{\text{total mass of solution}} \times 10^9$$

$$X_A = \frac{\text{moles of solute}}{\text{total moles}}$$

$$M = \frac{\text{moles of solute}}{\text{L of solution}}$$

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

Mass/Mass

Moles/Moles

Moles/L

Moles/Mass

SAMPLE EXERCISE 13.4 Calculation of Mass-Related Concentrations

(a) A solution is made by dissolving 13.5 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in 0.100 kg of water. What is the mass percentage of solute in this solution? (b) A 2.5-g sample of groundwater was found to contain $5.4 \mu\text{g}$ of Zn^{2+} . What is the concentration of Zn^{2+} in parts per million?

PRACTICE EXERCISE

(a) Calculate the mass percentage of NaCl in a solution containing 1.50 g of NaCl in 50.0 g of water. (b) A commercial bleaching solution contains 3.62 mass % sodium hypochlorite, NaOCl. What is the mass of NaOCl in a bottle containing 2500 g of bleaching solution?

PRACTICE EXERCISE

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

Colligative properties depend only on •
the *number* of solute particles present,
not on the *identity* of the solute
particles.

Among colligative properties are •

Vapor pressure lowering ➤

Boiling point elevation ➤

Melting point depression ➤

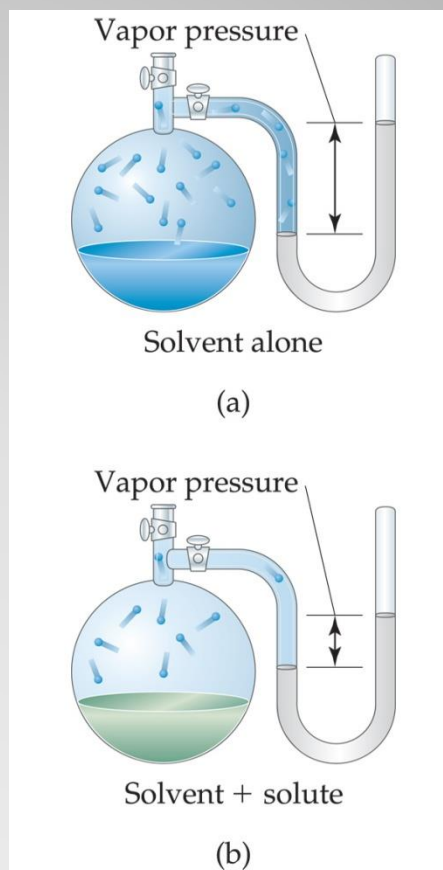
Osmotic pressure ➤

Colligative Properties



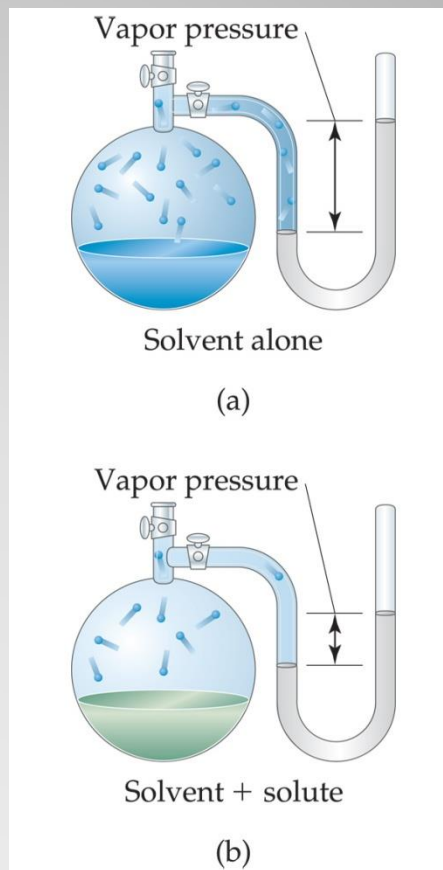
Vapor Pressure

As solute molecules are added to a solution, the solvent become less volatile (=decreased vapor pressure). Solute-solvent interactions contribute to this effect.



Vapor Pressure

Therefore, the vapor pressure of a solution is lower than that of the pure solvent.



$$P_A = X_A P_A^\circ$$

where

X_A is the mole fraction of compound A •

P_A° is the normal vapor pressure of A at that •
temperature

NOTE: This is one of those times when you want to make sure you have the vapor pressure of the *solvent*.

Raoult's Law



SAMPLE EXERCISE 13.8 Calculation of Vapor-Pressure Lowering

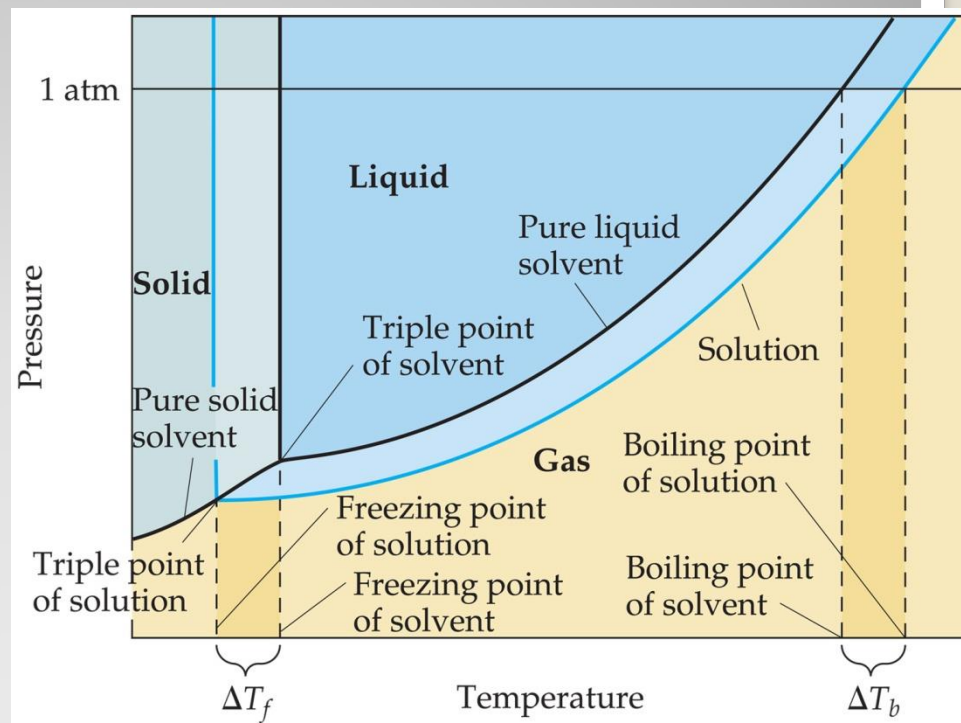
Glycerin ($\text{C}_3\text{H}_8\text{O}_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25°C. Calculate the vapor pressure at 25°C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25°C is 23.8 torr (Appendix B).

PRACTICE EXERCISE

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?

Boiling Point Elevation and Freezing Point Depression

Solute-solvent interactions also cause solutions to have higher boiling points and lower freezing points than the pure solvent.



Boiling Point Elevation

The change in boiling point is proportional to the molality of the solution:

$$\Delta T_b = K_b \cdot m$$

where K_b is the molal boiling point elevation constant, a property of the solvent.

ΔT_b is added to the normal boiling point of the solvent.

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water, H ₂ O	100.0	0.51	0.0	1.86
Benzene, C ₆ H ₆	80.1	2.53	5.5	5.12
Ethanol, C ₂ H ₅ OH	78.4	1.2	-114.6	.99
Carbon tetrachloride, CCl ₄	76.8	5.02	-22.3	29.8
Chloroform, CHCl ₃	61.2	3.6	-63.5	.68



Freezing Point Depression

The change in freezing point can be found similarly:

$$\Delta T_f = K_f \cdot m$$

Here K_f is the molal freezing point depression constant of the solvent.

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
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Chloroform, CHCl ₃	61.2	3.6	-63.5	.68

ΔT_f is subtracted from the normal freezing point of the solvent.



In both equations, ΔT does not depend on *what the solute is*, but only on *how many particles* are dissolved.

$$\Delta T_b = K_b \cdot m$$

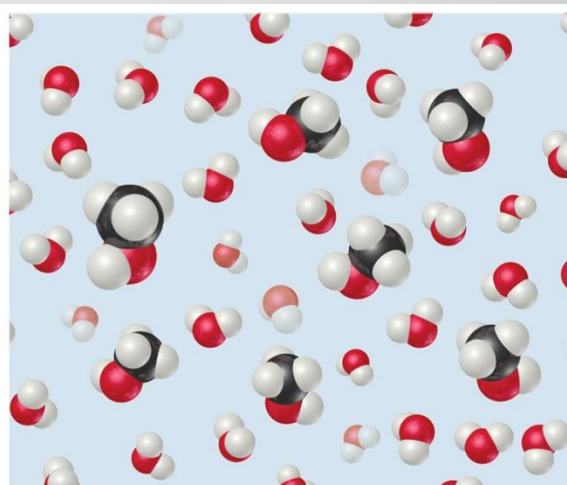
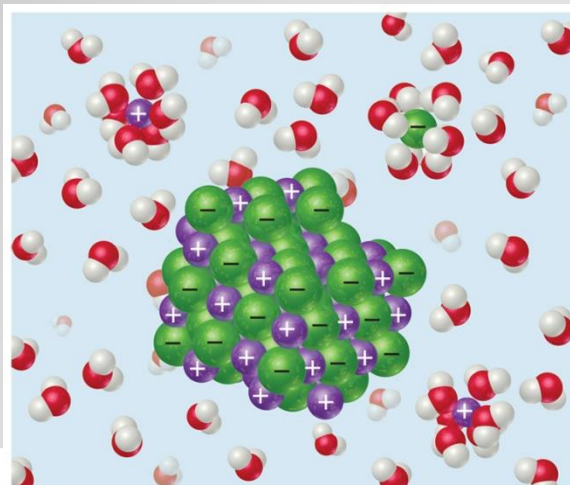
$$\Delta T_f = K_f \cdot m$$

Boiling Point Elevation and Freezing Point Depression



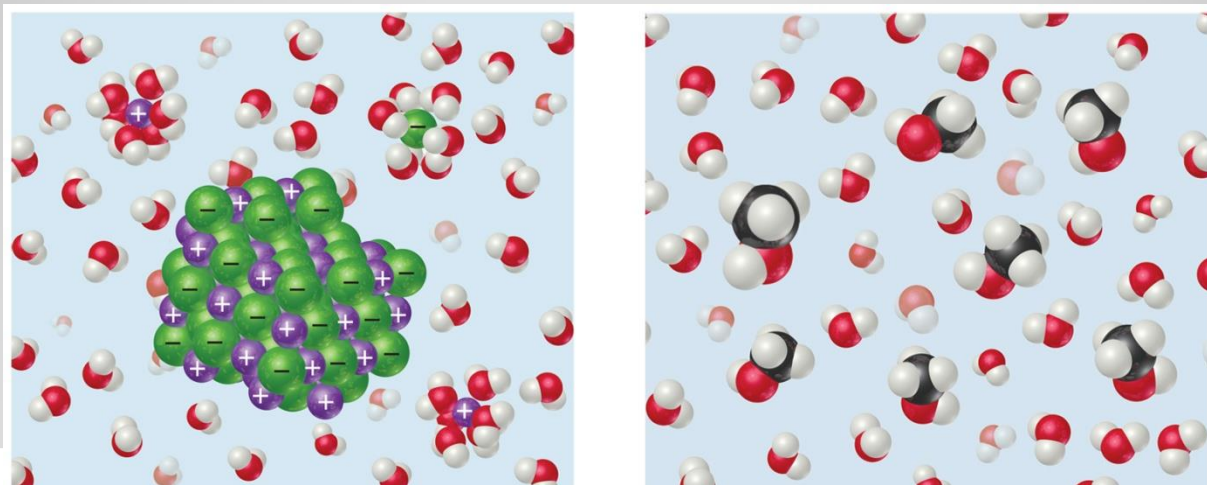
Colligative Properties of Electrolytes

Because these properties depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) show greater changes than those of nonelectrolytes.
e.g. NaCl dissociates to form 2 ion particles; its limiting van't Hoff factor is 2.

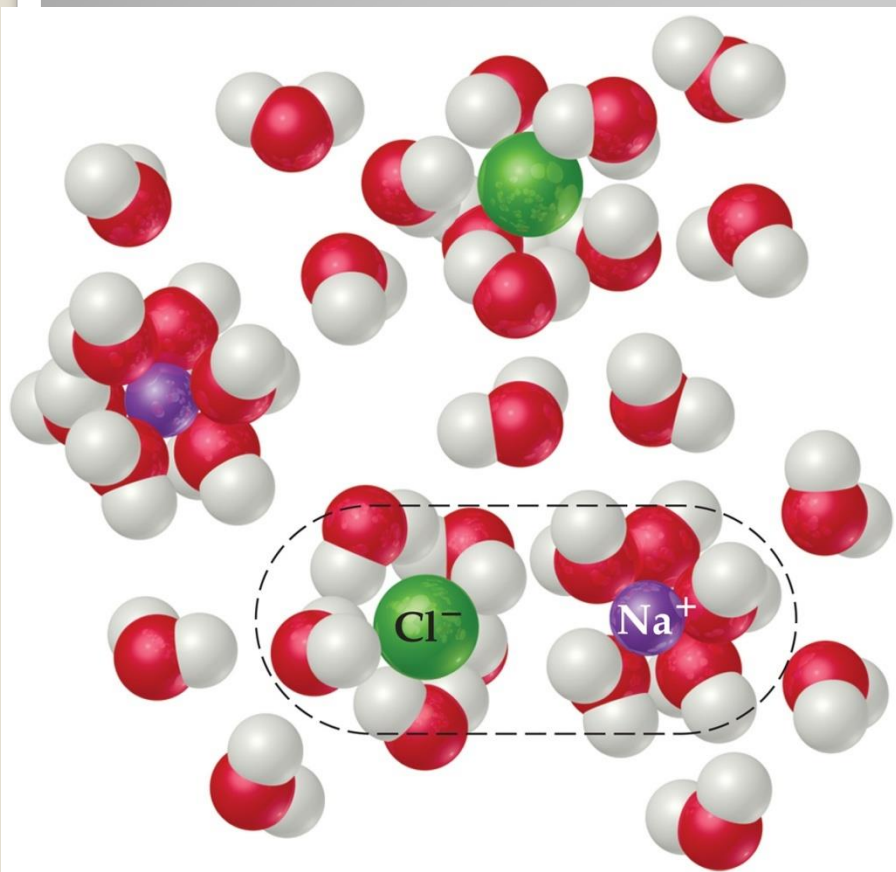


Colligative Properties of Electrolytes

However, a 1 *M* solution of NaCl does not show twice the change in freezing point that a 1 *M* solution of methanol does. It doesn't act like there are really 2 particles.

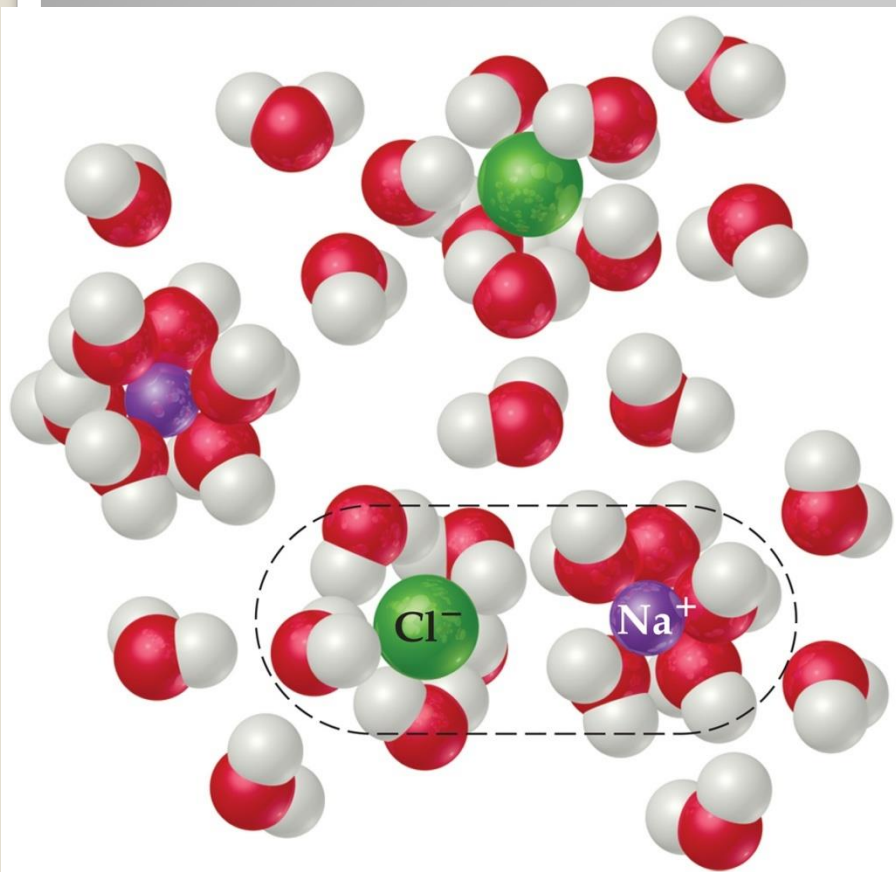


van't Hoff Factor



One mole of NaCl
in water does not
really give rise to
two moles of
ions.

van't Hoff Factor



Some Na^+ and Cl^- reassociate as hydrated ion pairs, so the true concentration of particles is somewhat less than two times the concentration of NaCl.

The van't Hoff Factor

Reassociation is more likely at higher concentration. Therefore, the number of particles present is concentration dependent.

Compound	Concentration			Limiting Value
	0.100 <i>m</i>	0.0100 <i>m</i>	0.00100 <i>m</i>	
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K ₂ SO ₄	2.32	2.70	2.84	3.00
MgSO ₄	1.21	1.53	1.82	2.00



The van't Hoff Factor

We modify the previous equations by multiplying by the van't Hoff factor, i

$$\Delta T_f = K_f \cdot m \cdot i$$

$i = 1$ for non-electrolytes

Compound	Concentration			Limiting Value
	0.100 <i>m</i>	0.0100 <i>m</i>	0.00100 <i>m</i>	
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K ₂ SO ₄	2.32	2.70	2.84	3.00
MgSO ₄	1.21	1.53	1.82	2.00



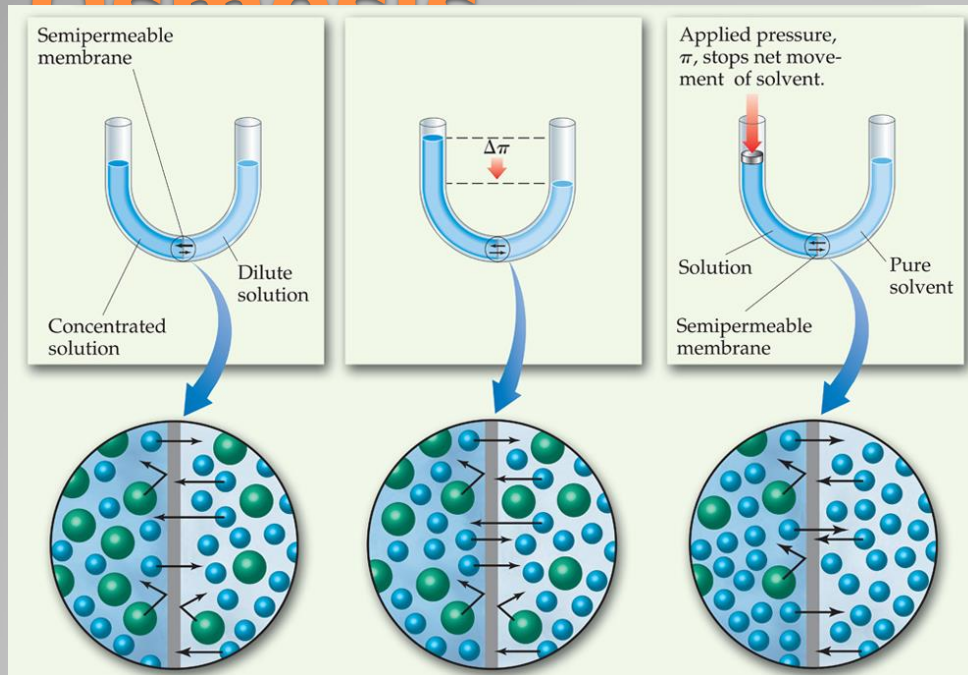
Semipermeable membranes allow some •
particles to pass through while blocking
others.

In biological systems, most •
semipermeable membranes (such as
cell walls) allow water to pass through,
but block solutes.

Osmosis



Osmosis



In osmosis, there is net movement of solvent from the area of **higher solvent concentration** (*lower solute concentration*) to the area of **lower solvent concentration** (*higher solute concentration*).

Water tries to equalize the concentration on both sides until pressure is too high.



The pressure required to stop osmosis, •
known as **osmotic pressure**, π , is

$$\pi = \left(\frac{n}{V} \right) RT = MRT$$

where M is the molarity of the solution

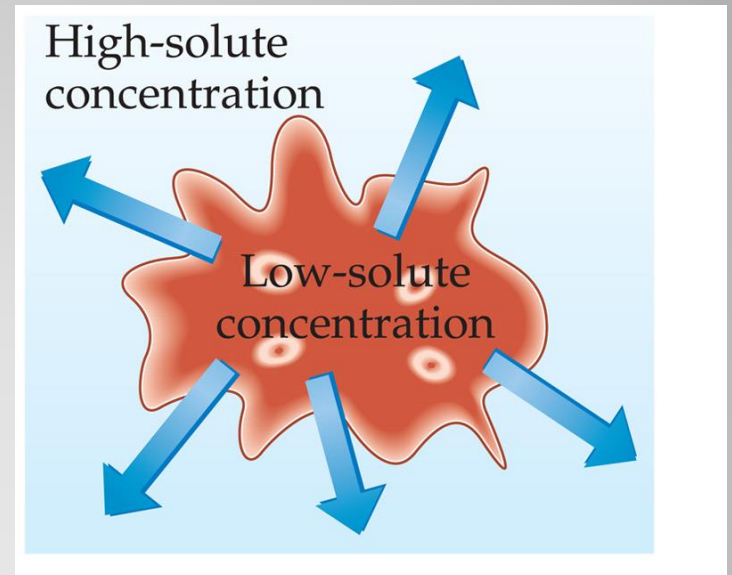
Osmotic Pressure
If the osmotic pressure is the same on both sides of a membrane (i.e., the concentrations are the same), the solutions are **isotonic**.



Osmosis in Blood Cells

If the solute concentration outside the cell is greater than that inside the cell, the solution is **hypertonic**.

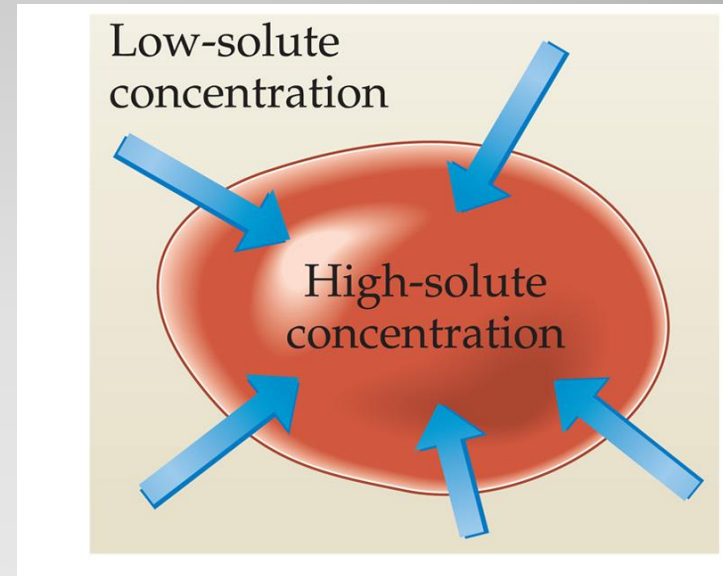
Water will flow out of the cell, and **crenation** results.



Osmosis in Cells

If the solute concentration outside the cell is less than that inside the cell, the solution is **hypotonic**.

Water will flow into the cell, and **hemolysis** results.



$$\Delta T_f = K_f \times m \times i$$

$$\Delta T_b = K_b \times m \times i$$

$$P_A = X_A P_A^\circ$$

$$\Pi = \left(\frac{n}{V} \right) RT = MRT$$

Molar Mass from Colligative Properties



125 mg of an alkaline earth metal chloride (XCl_2) dissolved in enough water to make 50.0 mL of solution at 298°C has an osmotic pressure of 1.16 atm. Identify the alkaline earth metal.

Use the measured osmotic pressure to determine the molar concentration of dissolved particles.

Use the molarity of dissolved particles, and knowledge of the compound formula, to determine the molarity of the *compound*.

Use the molarity of the compound and the volume of solution to determine the number of moles of compound in solution.

Use the number of moles of compound and the number of grams of compound in solution to determine molar mass.

Knowing molar mass, determine the identity of the alkaline earth chloride.

We can use the effects of a colligative property such as osmotic pressure to determine the molar mass of a compound.



Colloids:

Suspensions of particles larger than individual ions or molecules, but too small to be settled out by gravity.

Phase of Colloid	Dispersing (solventlike) Substance	Dispersed (solutelike) Substance	Colloid Type	Example
Gas	Gas	Gas	—	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass



Tyndall Effect



- Colloidal suspensions can scatter rays of light.
- This phenomenon is known as the Tyndall effect.

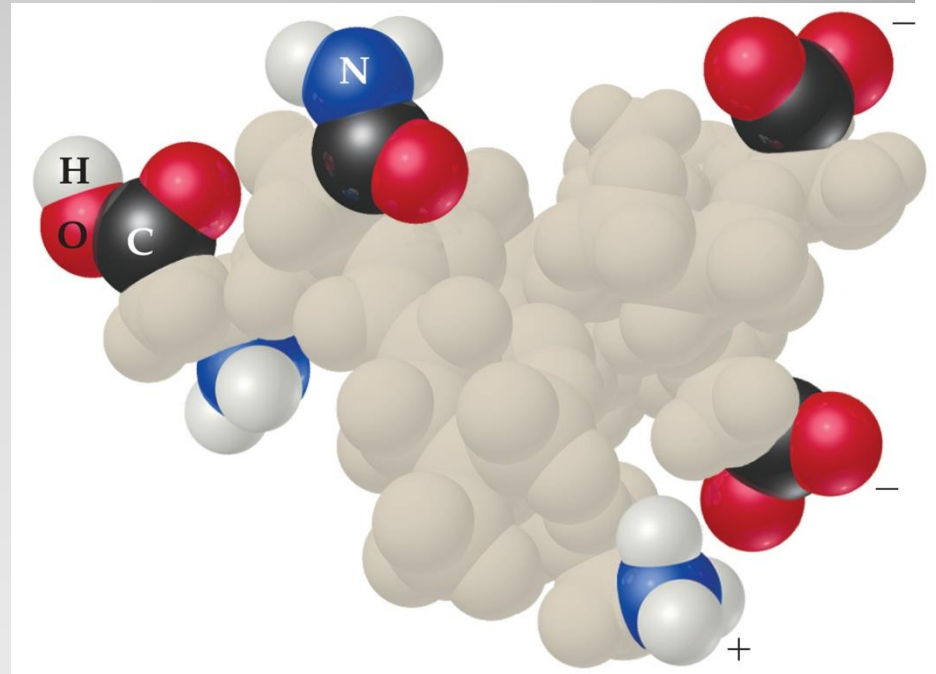


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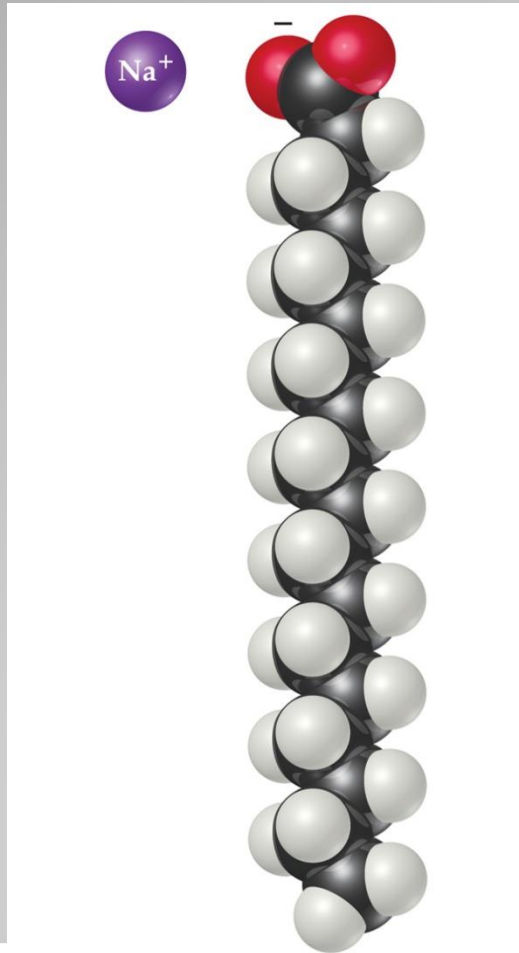


Colloids in Biological Systems

Some molecules have a polar, **hydrophilic** (*water-loving*) end and a nonpolar, **hydrophobic** (*water-hating*) end.



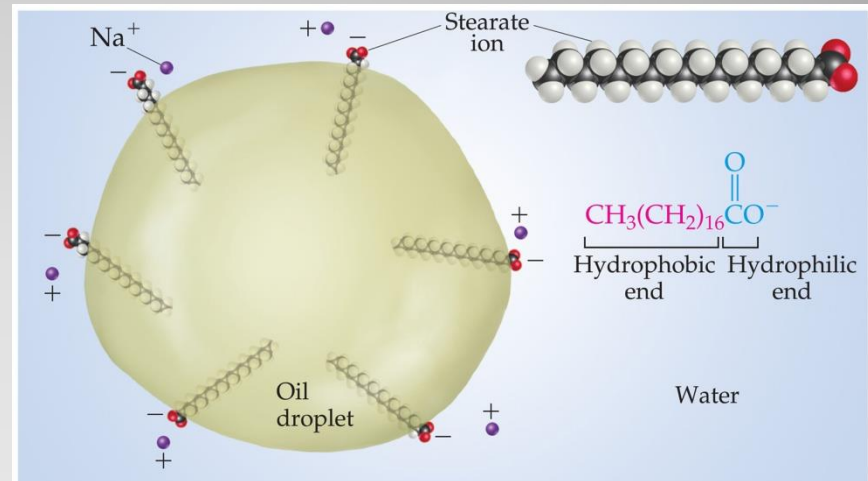
Colloids in Biological Systems



Sodium
stearate is one
example of
such a
molecule.

Colloids in Biological Systems

These molecules can aid in the emulsification of fats and oils in aqueous solutions.



Concentration Units

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

Percent by Mass

$$\begin{aligned}\% \text{ by mass} &= \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\% \\ &= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%\end{aligned}$$

Mole Fraction (X)

$$X_A = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

Concentration Units Continued

Molarity (M)

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Molality (m)

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$





What is the molality of a 5.86 *M* ethanol (C₂H₅OH) solution whose density is 0.927 g/mL?

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Assume 1 L of solution:

5.86 moles ethanol = 270 g ethanol

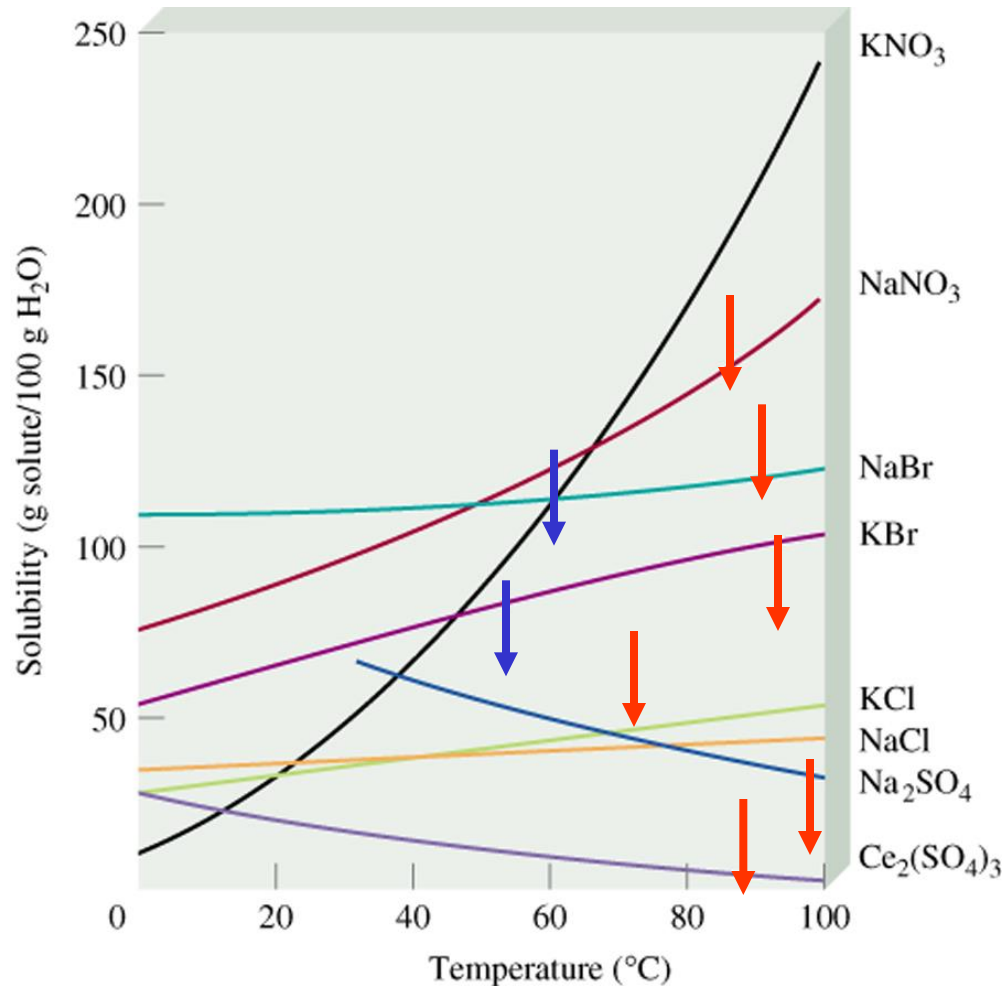
927 g of solution (1000 mL x 0.927 g/mL)

$$\begin{aligned}\text{mass of solvent} &= \text{mass of solution} - \text{mass of solute} \\ &= 927 \text{ g} - 270 \text{ g} = 657 \text{ g} = 0.657 \text{ kg}\end{aligned}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles C}_2\text{H}_5\text{OH}}{0.657 \text{ kg solvent}} = 8.92 \text{ } m$$

Temperature and Solubility

Solid solubility and temperature

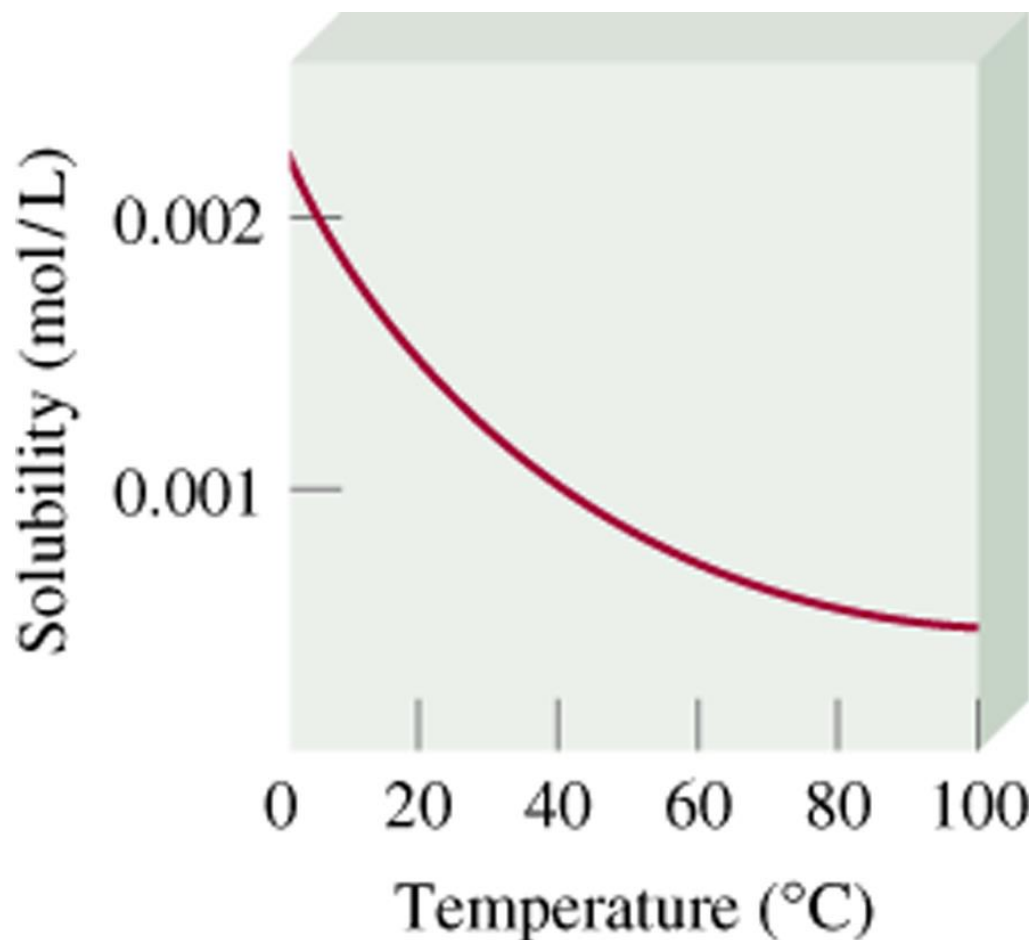


solubility decreases with increasing temperature

solubility increases with increasing temperature

Temperature and Solubility

Gas solubility and temperature



solubility usually
decreases with
increasing temperature

Pressure and Solubility of Gases

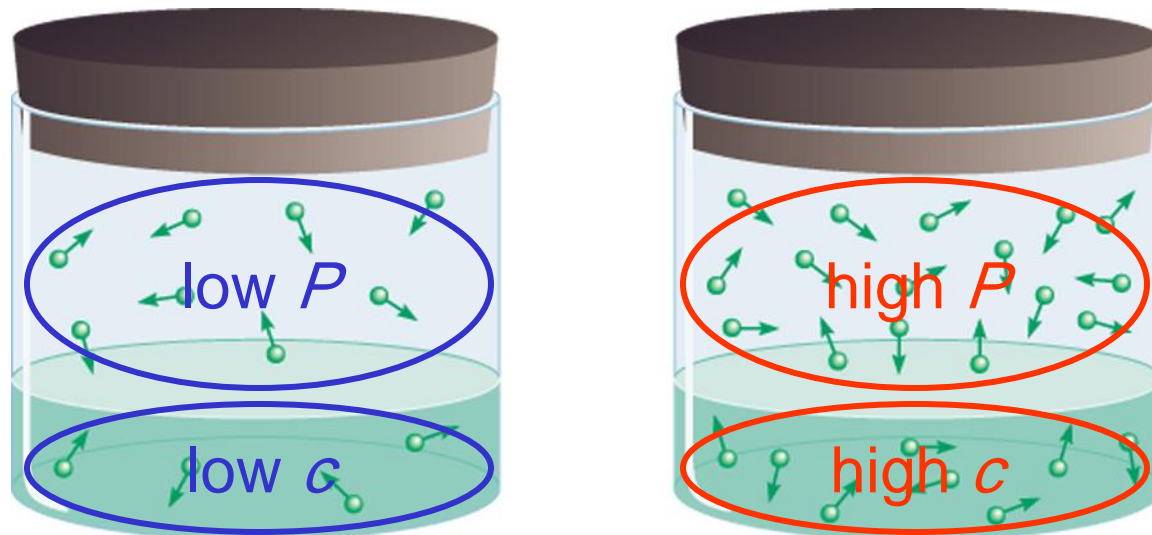
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (***Henry's law***).

$$c = kP$$

c is the concentration (M) of the dissolved gas

P is the pressure of the gas over the solution

k is a constant ($\text{mol/L}\cdot\text{atm}$) that depends only on temperature



Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend **only on the number of solute particles** in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering

$$P_1 = X_1 P_1^0$$

Raoult's law

P_1^0 = vapor pressure of **pure** solvent

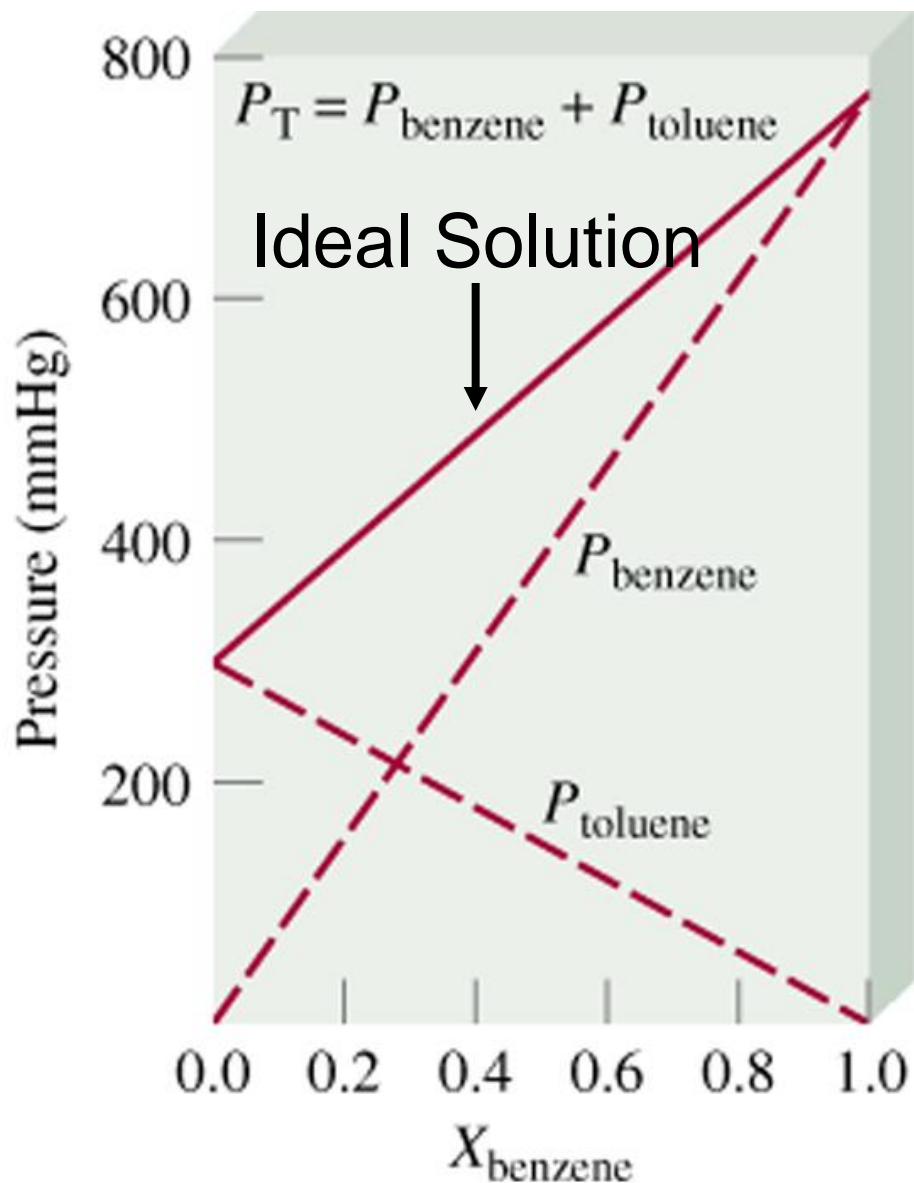
X_1 = mole fraction of the solvent

If the solution contains only one solute:

$$X_1 = 1 - X_2$$

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0$$

X_2 = mole fraction of the solute



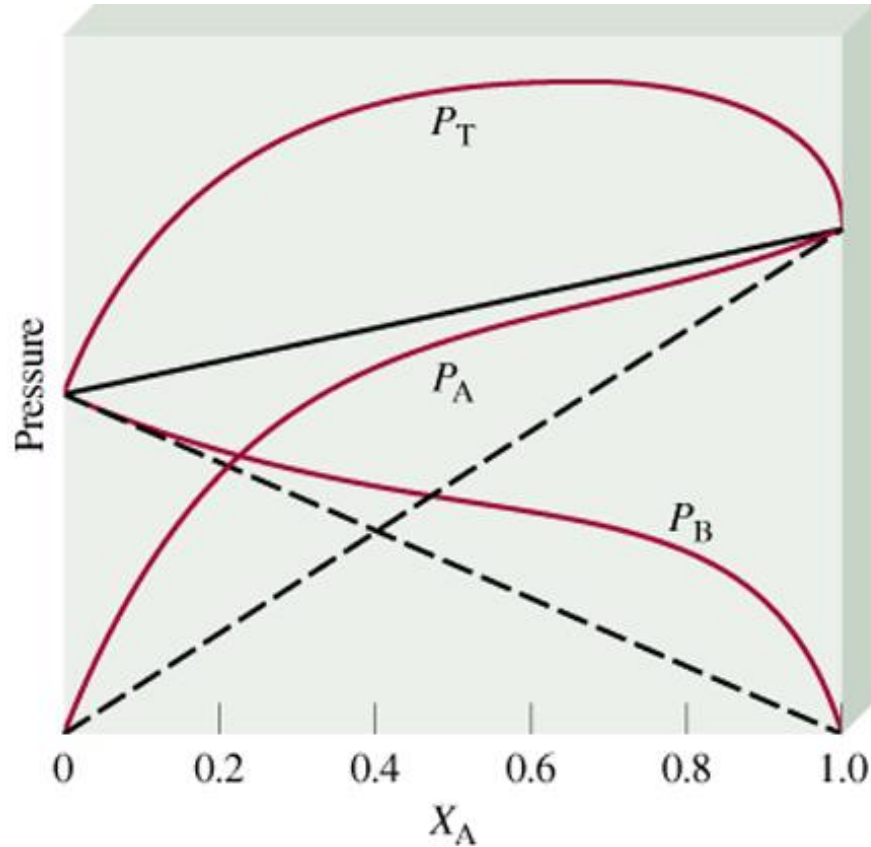
$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

$$P_T = P_A + P_B$$

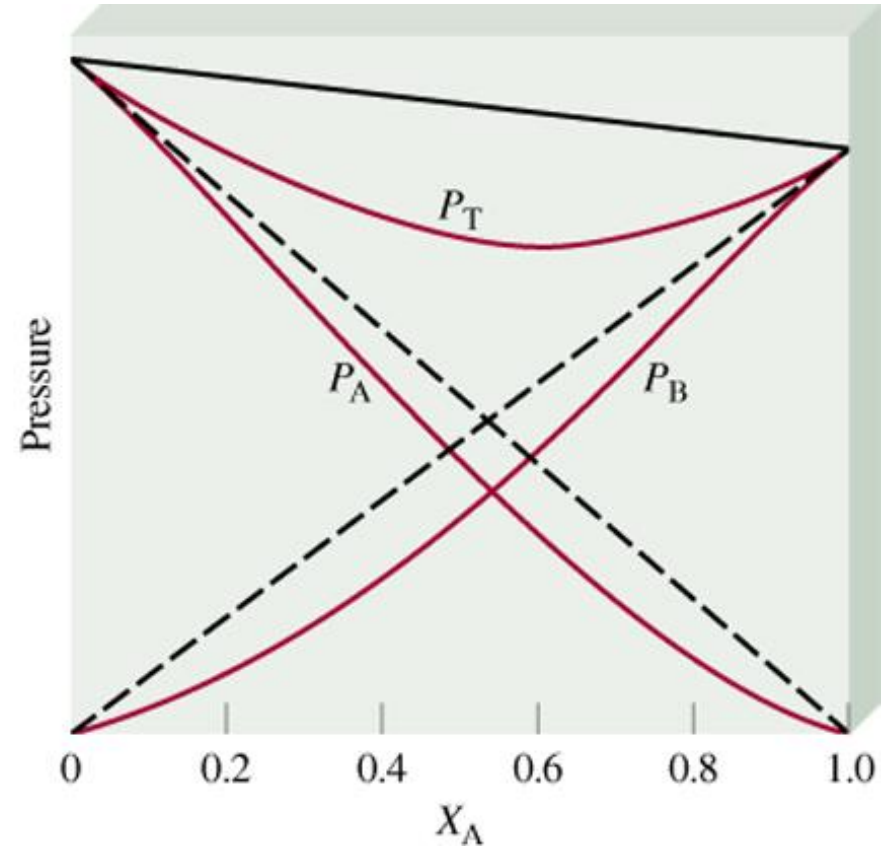
$$P_T = X_A P_A^0 + X_B P_B^0$$

P_T is greater than
predicted by Raoult's law



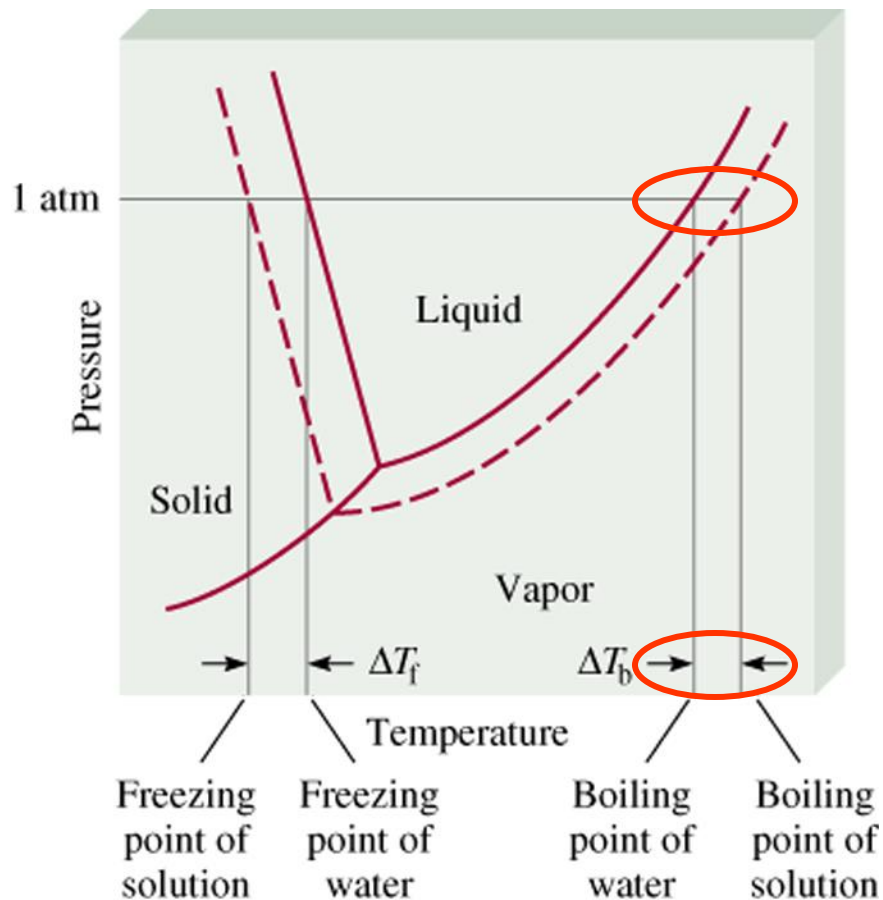
Force
A-B < Force
A-A & Force
B-B

P_T is less than
predicted by Raoult's law



Force
A-B > Force
A-A & Force
B-B

Boiling-Point Elevation



$$\Delta T_b = T_b - T_b^0$$

T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

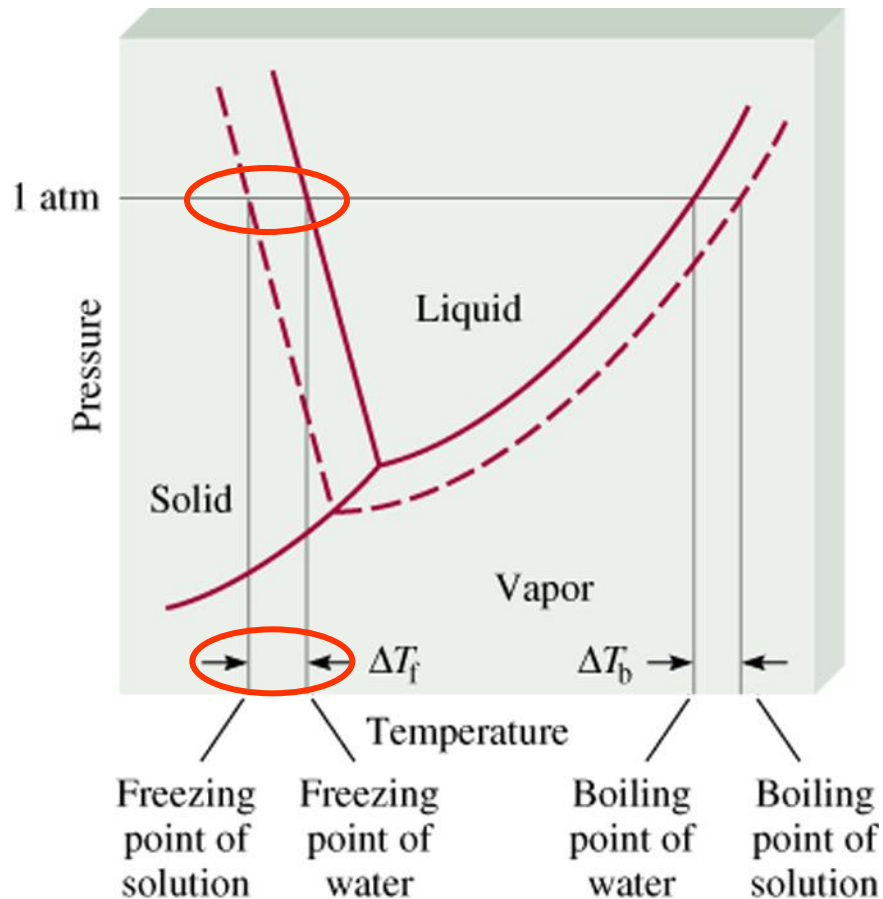
$$T_b > T_b^0 \quad \Delta T_b > 0$$

$$\Delta T_b = K_b m$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant ($^{\circ}\text{C}/m$)

Freezing-Point Depression



$$\Delta T_f = T_f^0 - T_f$$

T_f^0 is the freezing point of the pure solvent

T_f is the freezing point of the solution

$$T_f^0 > T_f \quad \Delta T_f > 0$$

$$\Delta T_f = K_f m$$

m is the molality of the solution

K_f is the molal freezing-point depression constant ($^{\circ}\text{C}/m$)

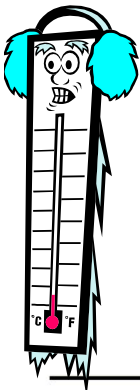
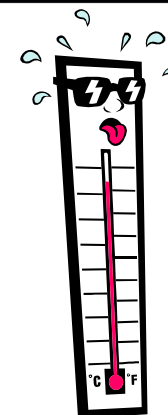
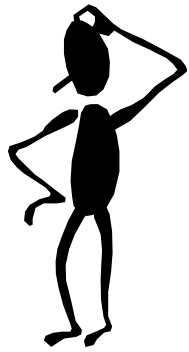


Table 12.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point ($^{\circ}\text{C}$)*	K_f ($^{\circ}\text{C}/m$)	Normal Boiling Point ($^{\circ}\text{C}$)*	K_b ($^{\circ}\text{C}/m$)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	-117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

* Measured at 1 atm.





What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g.

$$\Delta T_f = K_f m \quad K_f \text{ water} = 1.86 ^\circ\text{C}/m$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478 \text{ g} \times \frac{1 \text{ mol}}{62.01 \text{ g}}}{3.202 \text{ kg solvent}} = 2.41 m$$

$$\Delta T_f = K_f m = 1.86 ^\circ\text{C}/m \times 2.41 m = 4.48 ^\circ\text{C}$$

$$\Delta T_f = T_f^0 - T_f$$

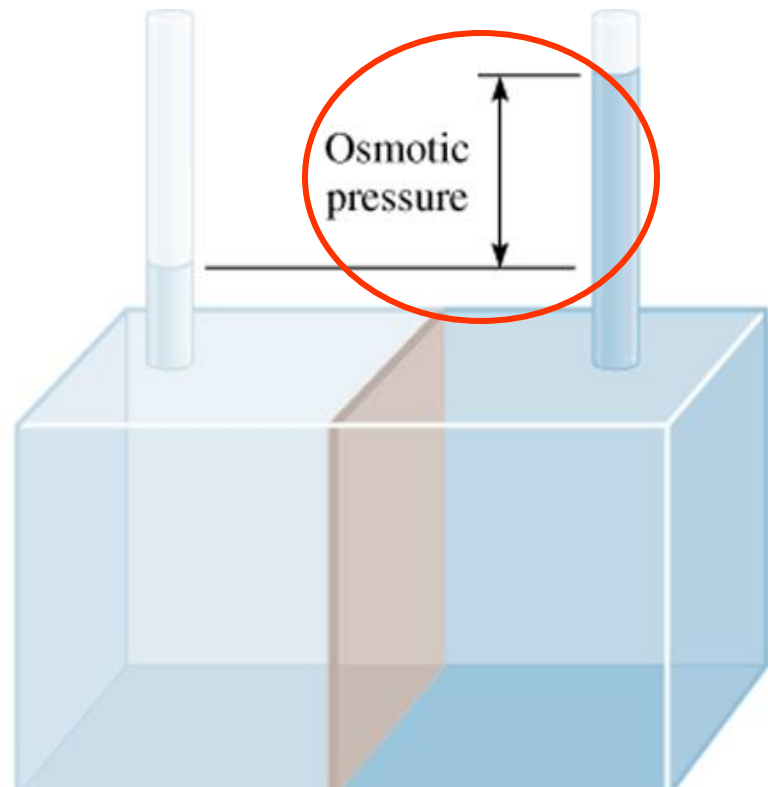
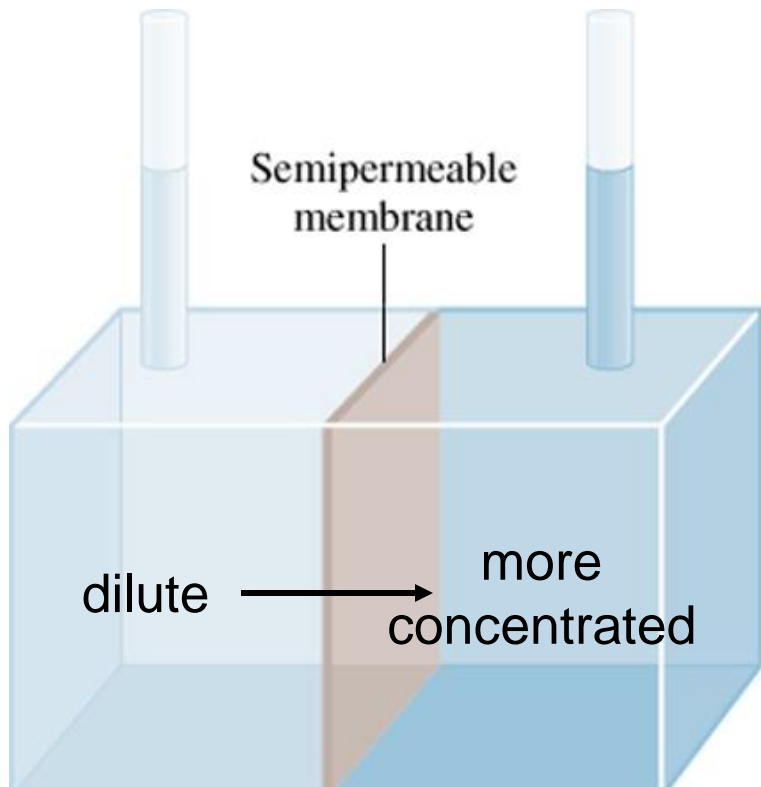
$$T_f = T_f^0 - \Delta T_f = 0.00 ^\circ\text{C} - 4.48 ^\circ\text{C} = -4.48 ^\circ\text{C}$$

Osmotic Pressure (π)

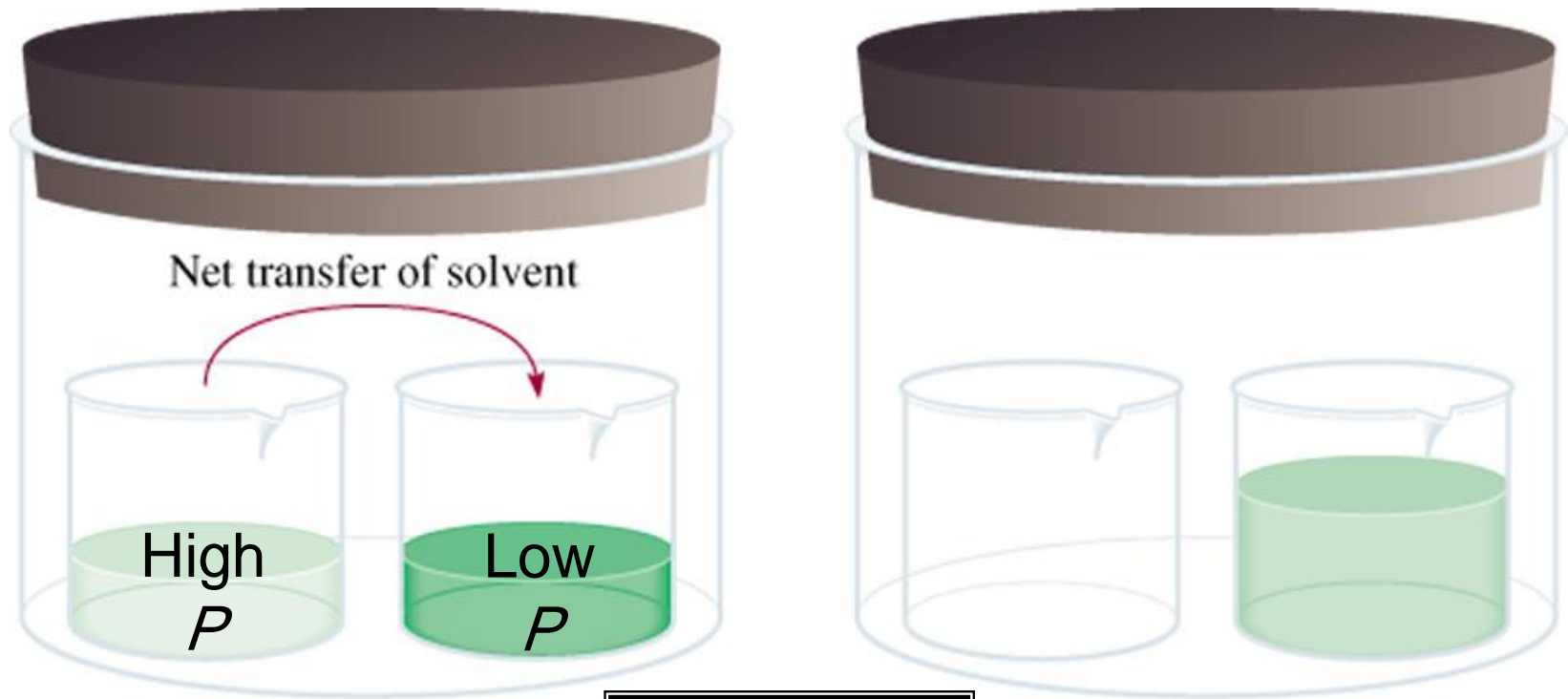
Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

A **semipermeable membrane** allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.



Osmotic Pressure (π)



$$\pi = MRT$$

M is the molarity of the solution

R is the gas constant

T is the temperature (in K)

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering $P_1 = X_1 P_1^0$

Boiling-Point Elevation $\Delta T_b = K_b m$

Freezing-Point Depression $\Delta T_f = K_f m$

Osmotic Pressure (π) $\pi = MRT$

Colligative Properties of Electrolyte Solutions

0.1 *m* NaCl solution \longrightarrow 0.1 *m* Na⁺ ions & 0.1 *m* Cl⁻ ions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

0.1 *m* NaCl solution \longrightarrow 0.2 *m* ions in solution

van't Hoff factor (*i*)

nonelectrolytes	1
NaCl	2
CaCl ₂	3

Colligative Properties of Electrolyte Solutions

Boiling-Point Elevation

$$\Delta T_b = i K_b m$$

Freezing-Point Depression

$$\Delta T_f = i K_f m$$

Osmotic Pressure (π)

$$\pi = iMRT$$

Table 12.3 The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C

Electrolyte	i (Measured)	i (Calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
MgSO ₄	1.3	2.0
MgCl ₂	2.7	3.0
FeCl ₃	3.4	4.0

* Sucrose is a nonelectrolyte. It is listed here for comparison only.

A ***colloid*** is a dispersion of particles of one substance throughout a dispersing medium of another substance.

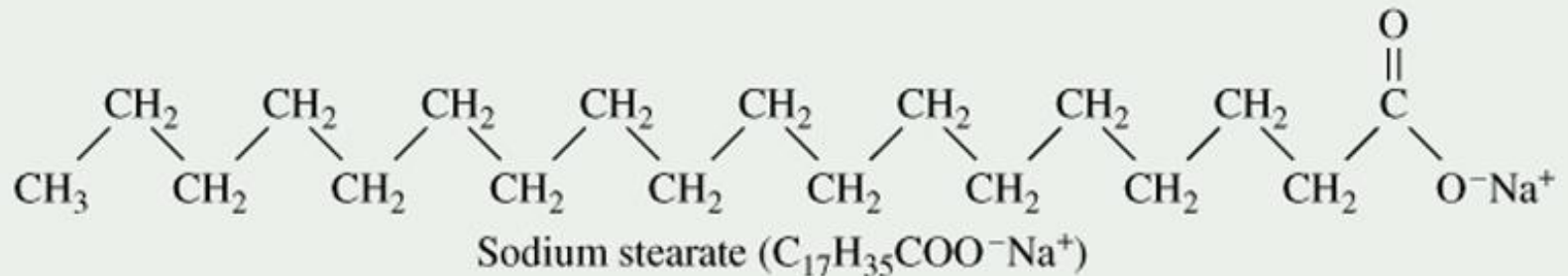
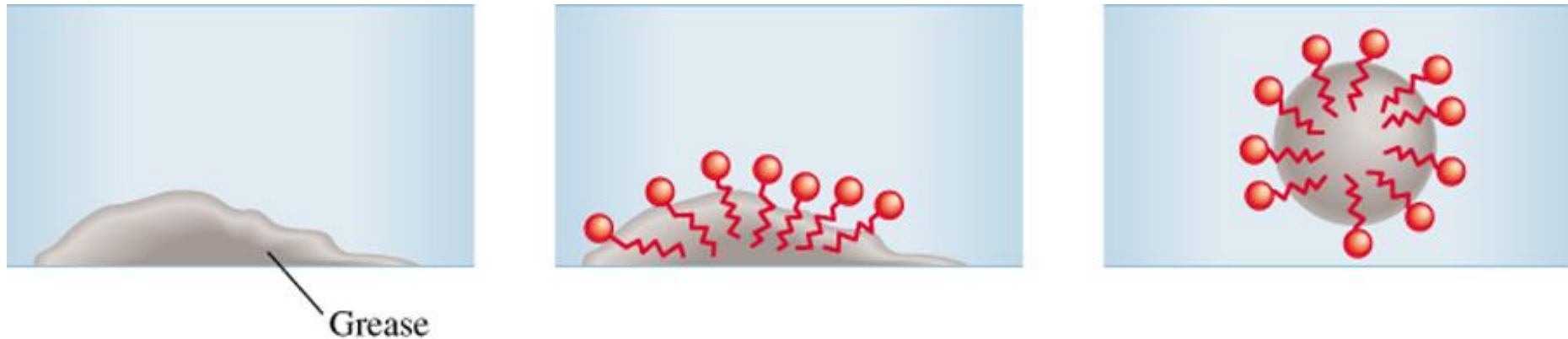
Colloid versus solution

- colloidal particles are much larger than solute molecules
- colloidal suspension is not as homogeneous as a solution

Table 12.4 Types of Colloids

Dispersing Medium	Dispersed Phase	Name	Example
Gas	Liquid	Aerosol	Fog, mist
Gas	Solid	Aerosol	Smoke
Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Emulsion	Mayonnaise
Liquid	Solid	Sol	Milk of magnesia
Solid	Gas	Foam	Plastic foams
Solid	Liquid	Gel	Jelly, butter
Solid	Solid	Solid sol	Certain alloys (steel), gemstones (glass with dispersed metal)

The Cleansing Action of Soap



(a)



Common units of concentration

% by mass – $\text{g solute} / 100 \text{ g solution}$

% by volume – $\text{mL solute} / 100 \text{ mL solution}$

% by mass-volume – $\text{g solute} / 100 \text{ mL solution}$

Molarity – $\text{moles solute} / \text{L solution}$

Molality – $\text{moles solute} / \text{kg solvent}$

Normality – $\text{equivalent moles of solute} / \text{L solution}$

ppt – $\text{grams solute} / \text{thousand grams solution}$

ppm – $\text{g solute} / \text{million g solution}$

ppb – $\text{g solute} / \text{billion g solution}$

lb solute / million gallons solution

Some conversion problems:

136 μg NaCl

? lb NaCl

mL pond water million gallons pond water

What do we need to know?

Some conversion problems:

136 μg NaCl

? lb NaCl

mL pond water million gallons pond water

What do we need to know?

- How many μg in a lb?
- How many mL in a million gallons?

Some conversion problems:

136 μg NaCl

? lb NaCl

ml pond water million gallons pond water

453.6 g = 1 pound

1 μg = 10^{-6} g

1 mL = 10^{-3} L

1.057 L = 1 quart

4 quarts = 1 gallon

Some conversion problems:

$$\frac{136 \mu\text{g NaCl}}{\text{mL pond water}} * \frac{10^{-6} \text{ g}}{1 \mu\text{g}} * \frac{1 \text{ lb}}{453.6 \text{ g}} = \frac{2.998 \times 10^{-7} \text{ lb}}{\text{mL pond water}}$$

$$\frac{2.998 \times 10^{-7} \text{ lb}}{\text{mL pond water}} * \frac{1 \text{ mL}}{10^{-3} \text{ L}} * \frac{1.057 \text{ L}}{1 \text{ qt}} = \frac{3.17 \times 10^{-4} \text{ lb}}{\text{qt}}$$

$$\frac{3.17 \times 10^{-4} \text{ lb}}{\text{qt}} * \frac{4 \text{ qt}}{1 \text{ gal}} * \frac{10^6 \text{ gal}}{\text{million gal}} = \frac{1.26 \times 10^3 \text{ lb}}{\text{million gal}}$$

Some conversion problems:

Convert 36% by mass of HCl to Molarity.

How do we start?

Some conversion problems:

Convert 36% by mass of HCl to Molarity.

How do we start?

Units! Units! Units!

Some conversion problems:

Convert 36% by mass of HCl solution to Molarity.

36 g HCl

100 g solution

Moles HCl

1 L solution

What do we need to know?

Some conversion problems:

Convert 36% by mass of HCl solution to Molarity.

36 g HCl

100 g solution

Moles HCl

1 L solution

What do we need to know?

- Molar mass of HCl
- Density of HCl solution

Some conversion problems:

Convert 36% by mass of HCl solution to Molarity.

36 g HCl

100 g solution

Moles HCl

1 L solution

What do we need to know?

- Molar mass of HCl (36.46 g/mol – from Periodic table)
- Density of HCl solution (from where???)

Density – your critical judgment

For a solution, sometimes you know the density, sometimes you don't.

There are tables, but they are not all inclusive.

You might, for example, find in a table that:

Density (30% HCl) = 1.12 g/mL

Density (40% HCl) = 1.23 g/mL

Density (36% HCl) = ???

Interpolate or Assume

Density (30% HCl) = 1.12 g/mL

Density (40% HCl) = 1.23 g/mL

Density (36% HCl) = ???

You could assume that 36% is closest to 40% and use 1.23 g/mL. This is legitimate, although not 100% accurate. Results may vary, depending on how good the assumption is.

Interpolate or Assume

Density (30% HCl) = 1.12 g/mL Density (40% HCl) = 1.23 g/mL
Density (36% HCl) = ???

You could assume that density changes linearly with concentration (it doesn't, but it is pseudo-linear for small changes). In that case, you would "linearly interpolate" the density.

$$\frac{1.23 \text{ g/mL} - 1.12 \text{ g/mL}}{40\% \text{ HCl} - 30\% \text{ HCl}} = 0.011 \frac{\text{g/mL}}{\%} = 0.011 \frac{\text{g}}{\text{mL}\%}$$

$$1.12 \text{ g/mL} + 0.011 \text{ g/mL}\% * 6\% = 1.186 \text{ g/mL} = 1.19 \text{ g/mL}$$

This is legitimate, although still not 100% accurate, but probably better than the previous assumption.

If I don't have Density tables...

For dilute solutions, you can get pretty close by assuming the density of the solution is the same as the density of pure water.

For concentrated solutions (like 36%), this is probably not a good assumption, but it is better than nothing!

Solving the problem (finally)

Convert 36% by mass of HCl solution to Molarity.

36 g HCl
100 g solution

Moles HCl
1 L solution

What do we need to know?

- Molar mass of HCl (36.46 g/mol – from Periodic table)
- Density of HCl solution (1.19 g/mL – by assuming linear change)

Solving the problem (finally)

$$\frac{36 \text{ g HCl}}{100 \text{ g sol}} * \frac{1 \text{ mol}}{36.46 \text{ g}} * \frac{1.19 \text{ g}}{1 \text{ mL}} * \frac{1000 \text{ mL}}{1 \text{ L solution}}$$

$$= 11.7 \frac{\text{mol HCl}}{\text{L solution}} = 11.7 \text{ M HCl}$$

(if you don't specify solvent, usually assumed to be water)

Common units of concentration

% by mass – $\text{g solute} / 100 \text{ g solution}$

% by volume – $\text{mL solute} / 100 \text{ mL solution}$

% by mass-volume – $\text{g solute} / 100 \text{ mL solution}$

Molarity – $\text{moles solute} / \text{L solution}$

Molality – $\text{moles solute} / \text{kg solvent}$

Normality – $\text{equivalent moles of solute} / \text{L solution}$

ppt – $\text{grams solute} / \text{thousand grams solution}$

ppm – $\text{g solute} / \text{million g solution}$

ppb – $\text{g solute} / \text{billion g solution}$

lb solute / million gallons solution

All are important, but...

Moles! Moles! Moles!

Molarity – moles solute/L solution (most common)

Molality – moles solute/kg solvent (not very common)

Normality – equivalent moles of solute/L solution
(specialized usage)

What's “equivalent moles”?

Normality vs. Molarity

Molarity = moles solute/L solution

- generic, just the moles folks

Normality = equivalent moles of solute/L solution

- specific, it takes into account the actual chemistry of the solute.

Acids

What's an acid?

Within the Bronsted-Lowry theory of acids/bases, an acid is a proton (H^+) donor and a base is a proton acceptor.

Can you think of examples of acids or bases?

Some acids and bases

NaOH – base

$\text{Mg}(\text{OH})_2$ – base

HCl – acid (hydrochloric acid)

HF – acid (hydrofluoric acid)

H_2SO_4 – acid (sulfuric acid)

Acid – what's it good for?

Protons

If we define an acid as a proton donor, the proton is what makes it what it is.

Consider two solutions:

1 M HCl

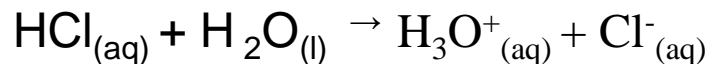
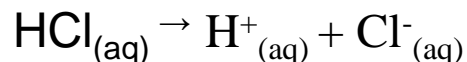
1 M H₂SO₄

How are they the same? How are they different?

Consider two solutions:

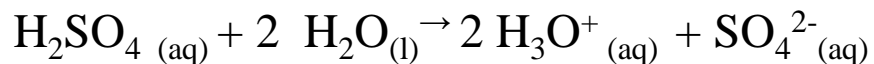
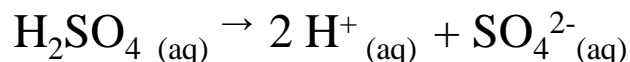
1 M HCl

1 mole molecules/L
H⁺ Cl⁻ in solution



1 M H₂SO₄

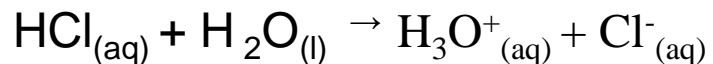
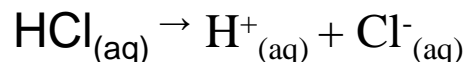
1 mole molecules/L
H⁺ and SO₄²⁻ in solution



Consider two solutions:

1 M HCl

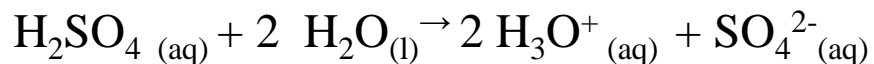
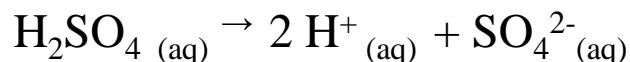
1 mole molecules/L
H⁺ Cl⁻ in solution



1 mol H⁺/L solution

1 M H₂SO₄

1 mole molecules/L
H⁺ and SO₄²⁻ in solution

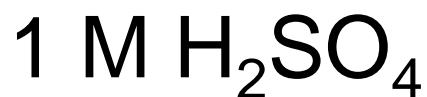


2 mol H⁺/L solution

Consider two solutions:

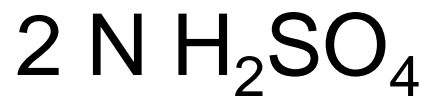


1 mole molecules/L
1 mole H⁺/L solution



1 mole molecules/L
2 mol H⁺/ L solution

They are both acids, they are defined by their ability to donate protons. The protons are the “equivalents” for an acid.



Solution Concentration

- **Molarity** is the moles of solute per liter of solution.

$$\text{Molarity (M)} = \frac{\text{moles of solute (mol)}}{\text{volume of solution (L)}}$$

- **Molarity** is the most frequently used concentration in chemical situations. Needed in many calculations to determine how many moles are present in a certain volume of solution:

$$\text{moles of solute} = \text{volume of solution} \times \text{molarity}$$

More Concentration Units

$$\text{Percent by mass} = \frac{\text{amount of solute (g)}}{\text{amount of solution (g)}} \times 100\%$$

$$\text{Percent by volume} = \frac{\text{volume of solute (L)}}{\text{volume of solution (L)}} \times 100\%$$

$$\text{Mass/volume percent} = \frac{\text{amount of solute (g)}}{\text{volume of solution (L)}} \times 100\%$$

Solutions By “Parts”

- **Parts per million** is the number of particles of solute per one-million particles of solution. Fluoridated drinking water contains ~ 1 ppm of fluoride ion.

$$1 \text{ ppm} = 1 \text{ mg/L} \quad (10^{-3})$$

- **Parts per billion** is the number of particles of solute per one-billion particles of solution.

$$1 \text{ ppb} = 1 \text{ } \mu\text{g/L} \quad (10^{-6})$$

- **Parts per trillion** is the number of particles of solute per one-trillion particles of solution.

$$1 \text{ ppt} = 1 \text{ ng/L} \quad (10^{-9})$$

Molality

- *Molarity* varies with temperature due to the expansion or contraction in the volume of the solution.
- To be independent of temperature, a concentration unit must be based on mass only, not volume.
- **Molality (m)** is the number of moles of solute per one kilogram of *solvent* (not solution!). **Molality does not vary with temperature.**

$$M = \frac{\text{moles of solute (mol)}}{\text{volume of solution (L)}}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

An Example

Example: ()

How many milliliters of water ($d = 0.998 \text{ g/mL}$) are required to dissolve 25.0 g of urea and thereby produce a 1.65 m solution of urea, $\text{CO}(\text{NH}_2)_2$?

Mole Fraction And Mole Percent

- The **mole fraction** (x_i) of a solution component i is the fraction of all the molecules in the solution that are molecules of i .

$$x_i = \frac{\text{amount of component } i \text{ (mol)}}{\text{total amount of solution components (mol)}} = n_i / n_{total}$$

$$x_i < 1; \quad x_1 + x_2 + x_3 + \dots = 1$$

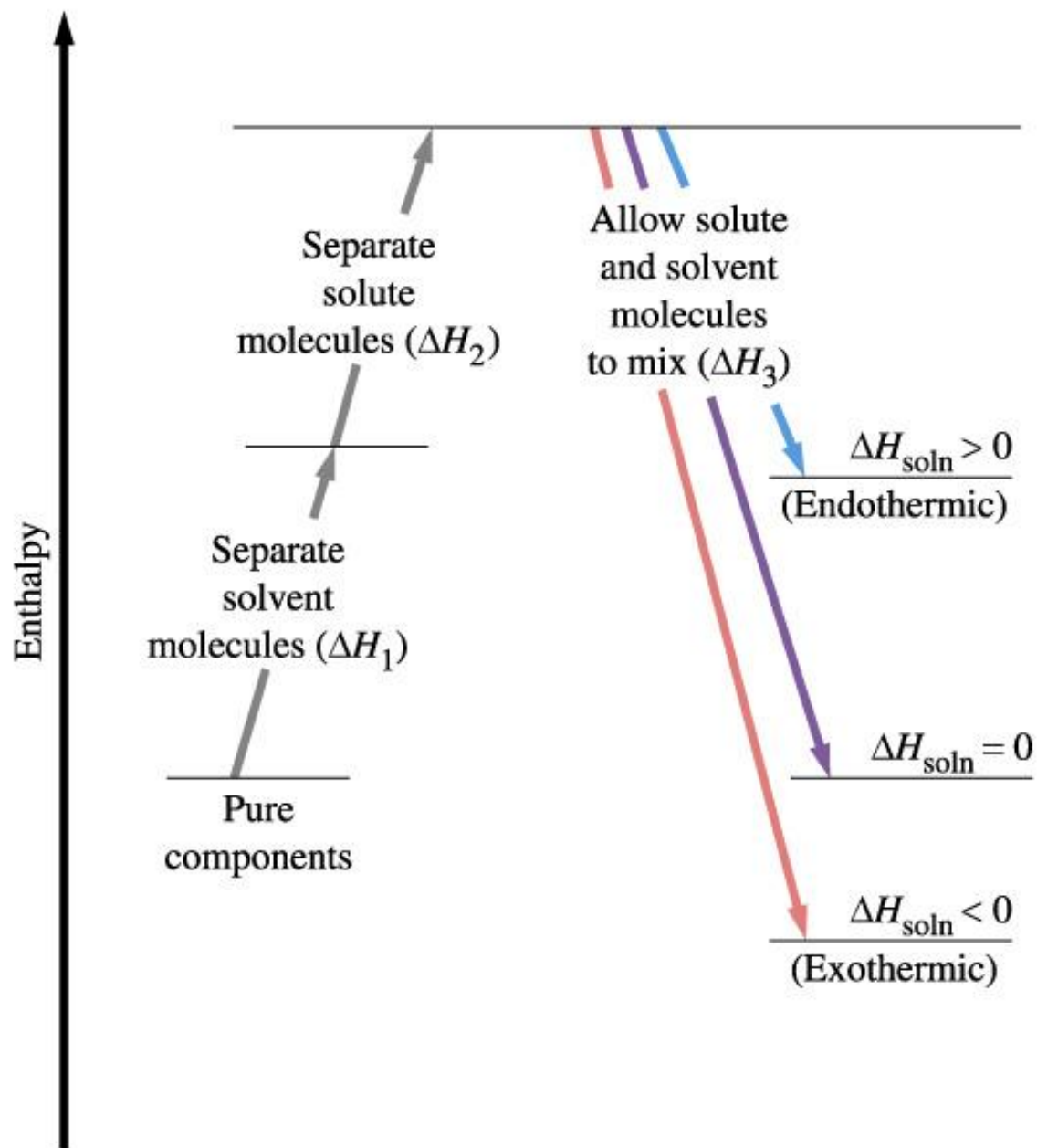
- The **mole percent** of a solution component is its mole fraction multiplied by 100%.

An Example

Example 12.6 (p.516)

An aqueous solution of ethylene glycol used as an automobile engine coolant is 40.0% $\text{HOCH}_2\text{CH}_2\text{OH}$ by mass and has a density of 1.05 g/mL. What are the (a) molarity, (b) molality, and mole fraction of $\text{HOCH}_2\text{CH}_2\text{OH}$.

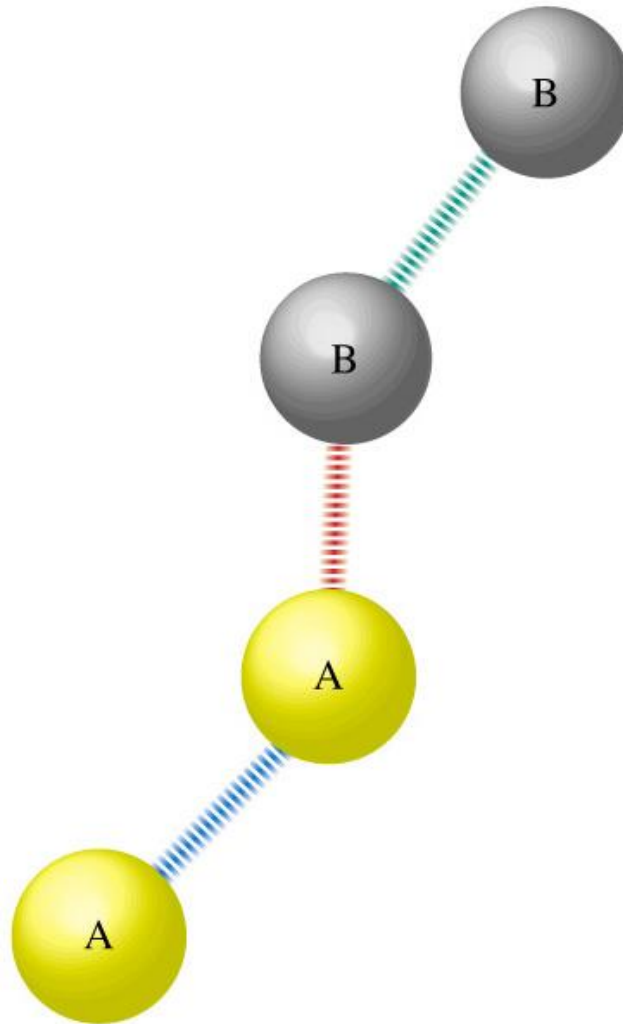
Illustrating enthalpy terms when solute dissolves in solvent



Intermolecular Forces In Solution Formation

- If all **intermolecular forces are of comparable strength**, this type of solution is called an **ideal solution** and $\Delta H_{\text{soln}} = 0$.
- If the intermolecular forces between solute and solvent molecules are *stronger* than other intermolecular forces,
 $\Delta H_3 > \Delta H_1 + \Delta H_2$, $\Delta H_{\text{soln}} < 0$ - **exothermic**.
- If the intermolecular forces between solute and solvent molecules are *weaker* than other intermolecular forces,
 $\Delta H_3 < \Delta H_1 + \Delta H_2$, $\Delta H_{\text{soln}} > 0$ – **endothermic**.
- If the intermolecular forces between solute and solvent are *much weaker* than other intermolecular forces, the solute does not dissolve in the solvent. The compound is described as relatively **insoluble** in the solvent.

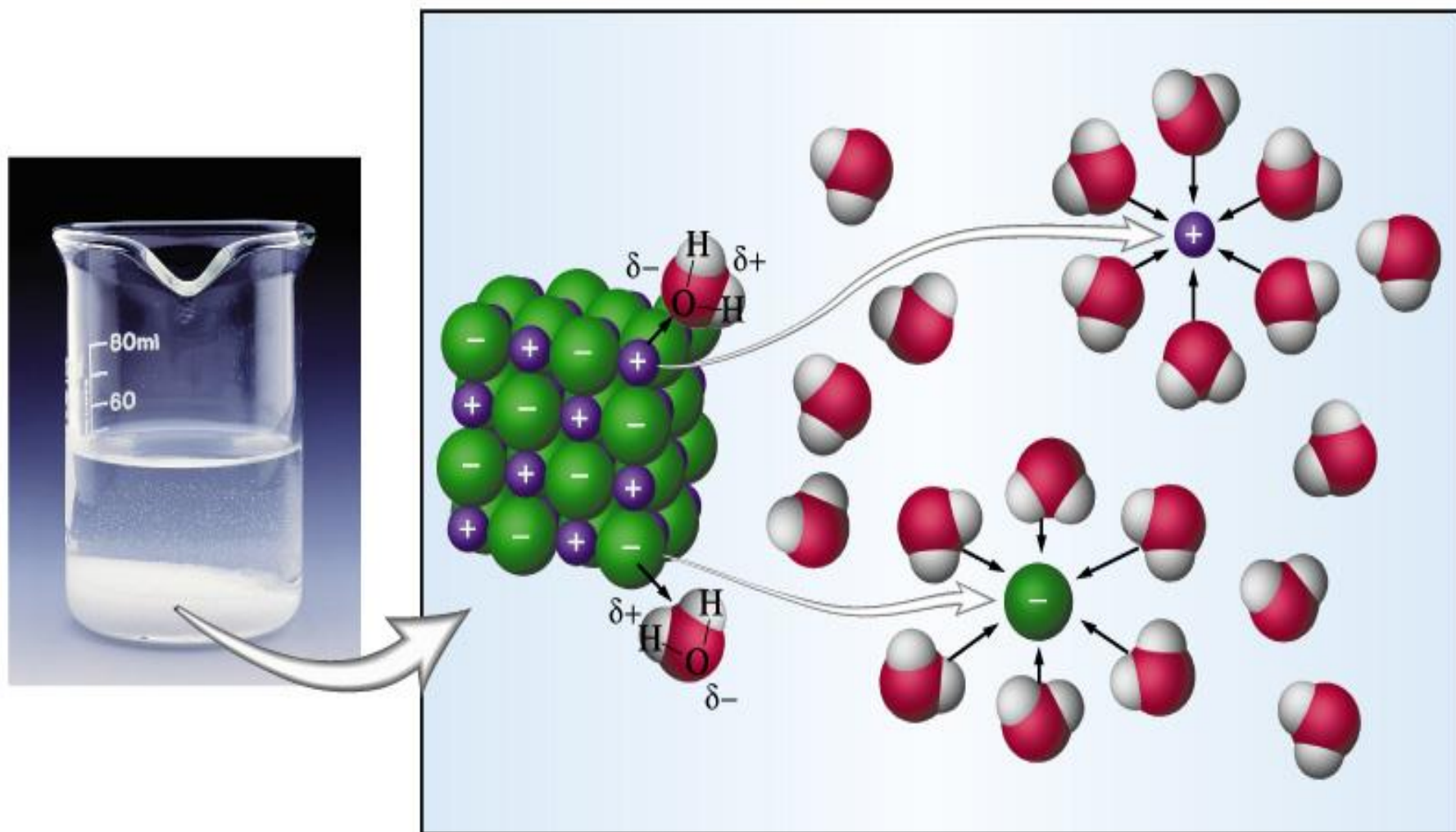
Intermolecular Forces In Solution



Aqueous Solutions Of Ionic Compounds

- Two forces
 - **inter-ionic attractions** that hold ions together in crystal
 - ***ion-dipole forces***, the attraction of water dipoles for cations and anions, that cause an ionic solid to dissolve in water
- The extent to which an ionic solid dissolves in water is determined largely by the competition between inter-ionic attractions and the ion-dipole attractions.

Ion-Dipole Forces in Dissolution



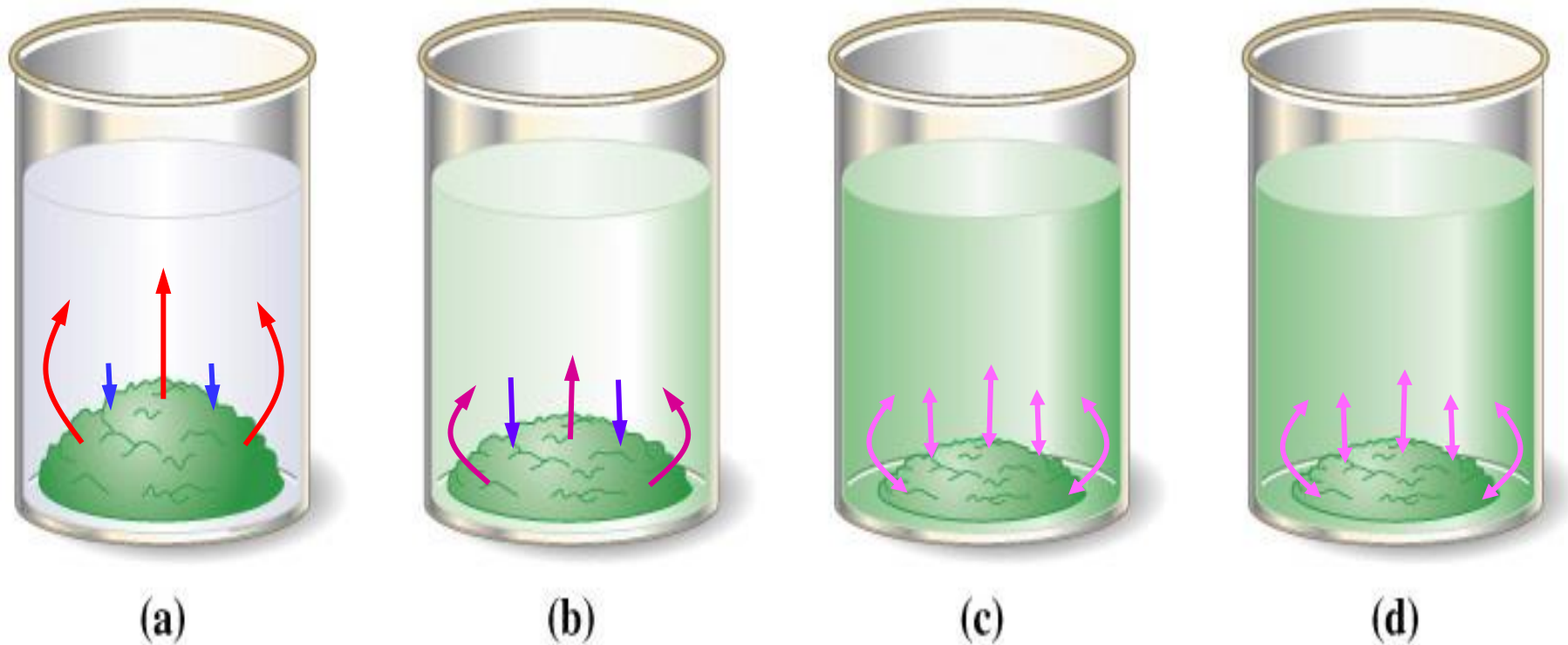
An Example

Example 12.8

Predict whether each of the following is likely to be a solution or a heterogeneous mixture.

- a. ethanol, CH_3OH , and water, HOH
- b. Pentane, $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, and octane, $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
- c. Sodium chloride, NaCl , and carbon tetrachloride, CCl_4
- d. 1-decanol, $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$, and water, HOH

Formation of a Saturated Solution



Dynamic equilibrium: rate of crystallization = rate of dissolving

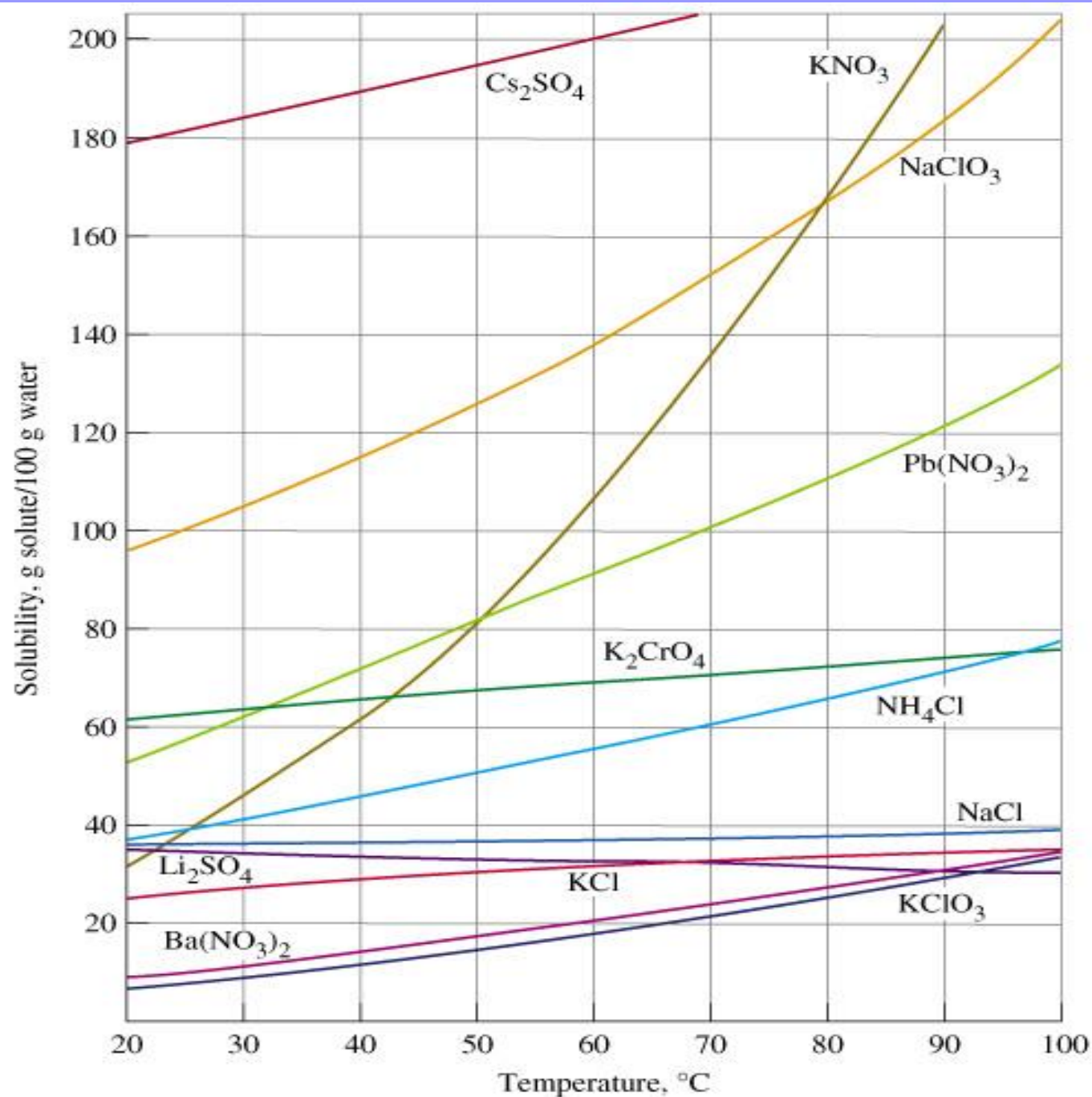
Some Solubility Terms

- Liquids that mix in all proportions are called **miscible**.
- When there is a **dynamic equilibrium** between an undissolved solute and a solution, the solution is **saturated**.
- The concentration of the solute in a saturated solution is the **solubility** of the solute.
- A solution which contains less solute than can be held at equilibrium is **unsaturated**.

Solubility As A Function of Temperature

- About 95% of all ionic compounds have aqueous **solubilities that increase significantly with increasing temperature.**
- Most of the remainder have solubilities that change little with temperature.
- A very few have solubilities that decrease with increasing temperature.
- A **supersaturated** solution is created when a warm, saturated solution is allowed to cool without the precipitation of the excess solute.

Some Solubility Curves



Selective Crystallization



When $\text{KNO}_{3(s)}$ is crystallized from an aqueous solution of KNO_3 containing CuSO_4 as an impurity, CuSO_4 remains in the solution.

The Solubilities Of Gases

The solubilities of gases depend on temperature and pressure.

- Most gases become **less soluble** in liquids **as the temperature increases**.
- At a constant temperature, the solubility (S) of a gas is directly proportional to the pressure of the gas (P_{gas}) in equilibrium with the solution.

$$S = k P_{\text{gas}} \quad (k > 1)$$

The value of k depends on the particular gas and the solvent.

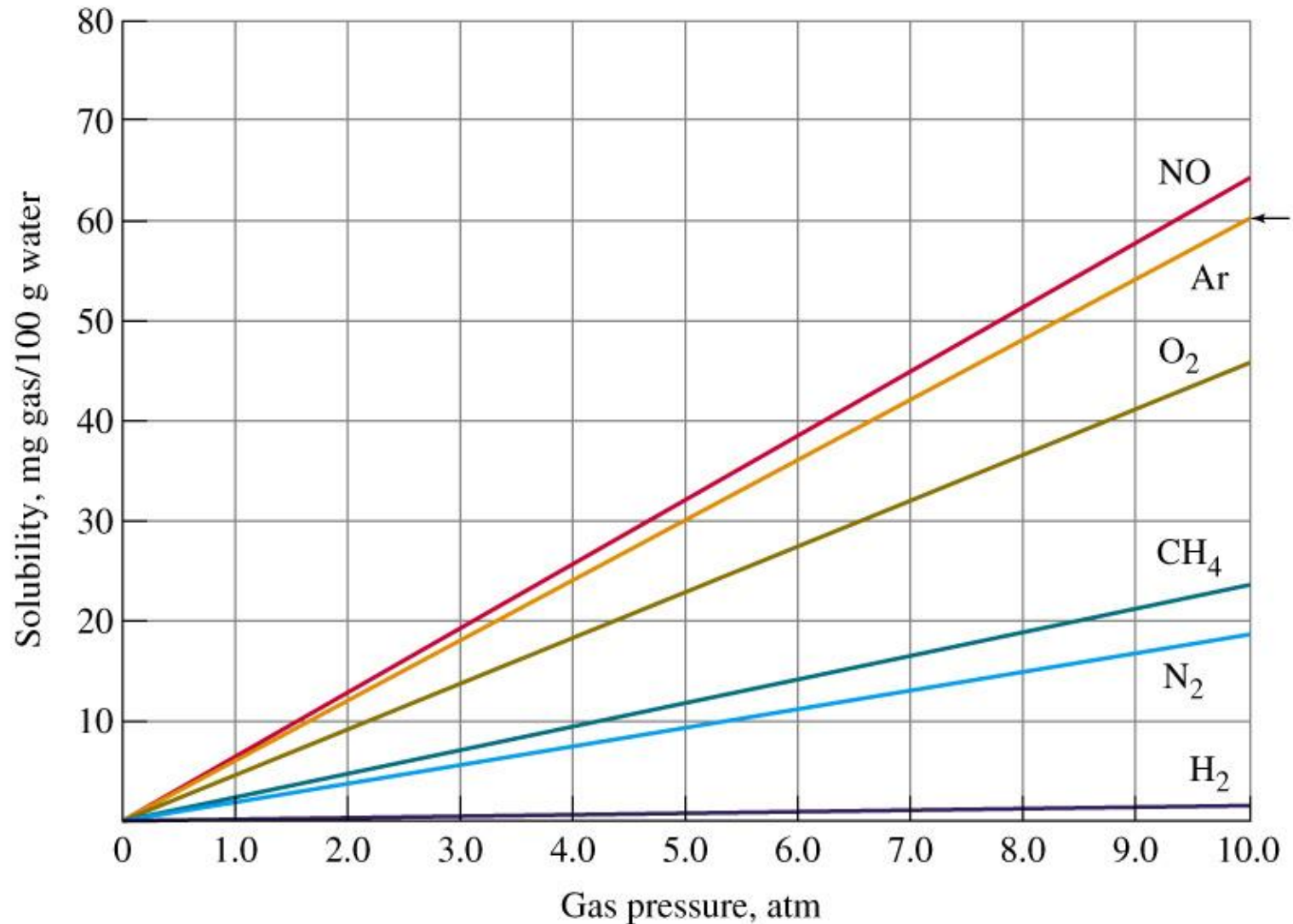
- The effect of pressure on the solubility of a gas is known as **Henry's Law**.

Effect of Pressure on Solubility of Gases



As a gas is compressed into a smaller volume, increasing the number of molecules per unit volume, the number of dissolved molecules per unit volume – the concentration of the solution – also increases.

Aqueous Solubility As A Function Of Gas Pressure



Vapor Pressures of Solutions

- **Raoult's law** states that the vapor pressure of the solvent above a solution (P_{solv}) is the product of the vapor pressure of the pure solvent (P°_{solv}) and the mole fraction of the solvent in the solution (x_{solv}):

$$P_{\text{solv}} = x_{\text{solv}} \cdot P^{\circ}_{\text{solv}}$$

- The vapor in equilibrium with an ideal solution of two volatile components has a higher mole fraction of the more volatile component than is found in the liquid.

Colligative Properties

Colligative Properties – physical properties of solutions that depend on the number of solute particles present but not on the identity of the solute.

- Freezing point depression
- Boiling point elevation

Freezing Point Depression and Boiling Point Elevation

- Consider solutions with
 - a volatile solvent
 - a solute: nonvolatile, nonelectrolytic, and soluble in liquid solvent but not frozen solvent
- The vapor pressure of the solution is that of the solvent in the solution, and at all temperatures this vapor pressure is *lower* than that of the pure solvent.
- The presence of the solute lowers (*depresses*) the freezing point of the solvent (ΔT_f) and increases (*elevates*) the boiling point of the solvent (ΔT_b).



Δ

$-X$

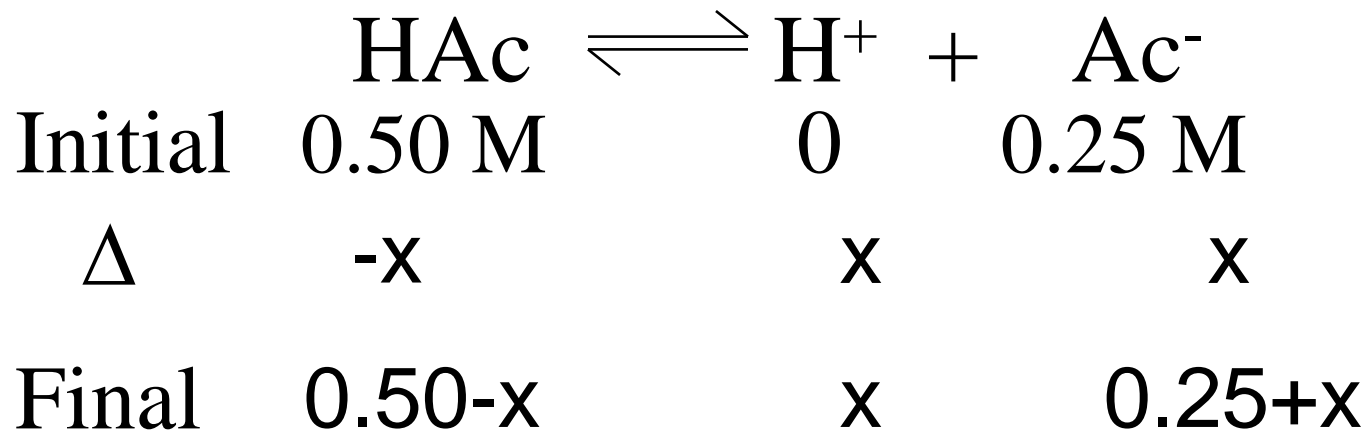
X

X

X

- Choose x to be small





- Do the math
- $K_a = 1.8 \times 10^{-5}$

$$1.8 \times 10^{-5} = \frac{x(0.25+x)}{(0.50-x)} = \frac{x(0.25)}{(0.50)}$$

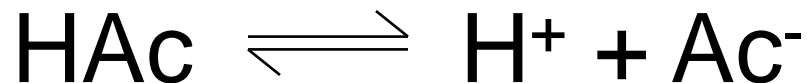
- Assume x is small
- Assumption is valid

$$x = 3.6 \times 10^{-5}$$

- $\text{pH} = -\log (3.6 \times 10^{-5}) = 4.44$

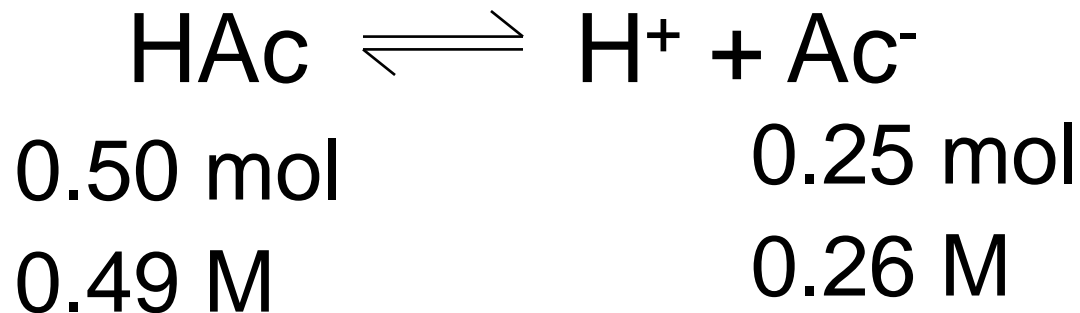
Adding a strong acid or base

- Do the stoichiometry first.
 - Use moles not molar
- A strong base will grab protons from the weak acid reducing $[HA]_0$
- A strong acid will add its proton to the anion of the salt reducing $[A^-]_0$
- Then do the equilibrium problem.
- What is the pH of 1.0 L of the previous solution when 0.010 mol of solid NaOH is added?

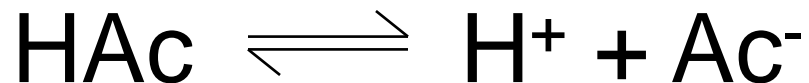


	0.25 mol
0.49 mol	0.26 mol

- In the initial mixture $M \times L = \text{mol}$
- $0.50 \text{ M HAc} \times 1.0 \text{ L} = 0.50 \text{ mol HAc}$
-
- Adding 0.010 mol OH^- will reduce the HAc and increase the Ac^- by 0.010 mole
- Because it is in 1.0 L , we can convert it to molarity



- In the initial mixture $M \times L = \text{mol}$
- $0.50 \text{ M HAc} \times 1.0 \text{ L} = 0.50 \text{ mol HAc}$
- $0.25 \text{ M Ac}^- \times 1.0 \text{ L} = 0.25 \text{ mol Ac}^-$
- Adding 0.010 mol OH^- will reduce the HAc and increase the Ac^- by 0.010 mole
- Because it is in 1.0 L , we can convert it to molarity



0.50 mol

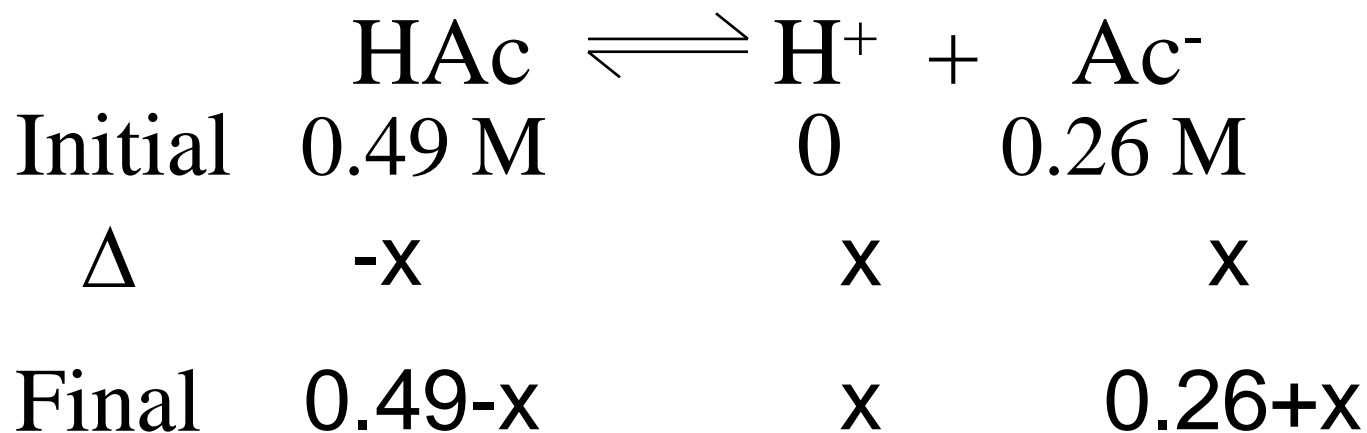
0.25 mol

0.49 M

0.26 M

- Fill in the table

	$\text{HAc} \rightleftharpoons \text{H}^+ + \text{Ac}^-$		
Initial	0.49 M	0	0.26 M
Δ	-x	x	x
Final	0.49-x	x	0.26+x



- Do the math
- $K_a = 1.8 \times 10^{-5}$

$$1.8 \times 10^{-5} = \frac{x(0.26+x)}{(0.49-x)} \quad \frac{x(0.26)}{(0.49)}$$

- Assume x is small
- Assumption is valid

$$x = 3.4 \times 10^{-5}$$

- $\text{pH} = -\log (3.4 \times 10^{-5}) = 4.47$

Notice

- If we had added 0.010 mol of NaOH to 1 L of water, the pH would have been.
- 0.010 M OH⁻
- pOH = 2
- pH = 12
- But with a mixture of an acid and its conjugate base the pH doesn't change much
- Called a buffer.

- $K_a = \frac{[H^+][A^-]}{[HA]}$
- so $[H^+] = \frac{K_a [HA]}{[A^-]}$
- The $[H^+]$ depends on the ratio $[HA]/[A^-]$
- taking the negative log of both sides
- $pH = -\log(K_a [HA]/[A^-])$
- $pH = -\log(K_a) - \log([HA]/[A^-])$
- $pH = pK_a + \log([A^-]/[HA])$

This is called the Henderson-Hasselbach equation

- $\text{pH} = \text{pK}_a + \log([A^-]/[HA])$
- $\text{pH} = \text{pK}_a + \log(\text{base/acid})$
- Works for an acid and its salt
- Like HNO_2 and NaNO_2
- Or a base and its salt
- Like NH_3 and NH_4Cl
- But remember to change K_b to K_a

- Calculate the pH of the following
 - 0.75 M lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) and 0.25 M sodium lactate ($K_a = 1.4 \times 10^{-4}$)
-
- pH = 3.38

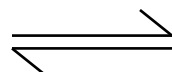
- Calculate the pH of the following
- 0.25 M NH_3 and 0.40 M NH_4Cl
($K_b = 1.8 \times 10^{-5}$)
- $K_a = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$
- $K_a = 5.6 \times 10^{-10}$
- remember its the ratio base over acid

● pH = 9.05

- What would the pH be if .020 mol of HCl is added to 1.0 L of both of the preceding solutions.
- What would the pH be if 0.050 mol of solid NaOH is added to 1.0 L of each of the proceeding.
- Remember adding acids increases the acid side,
- Adding base increases the base side.

Prove they're buffers

- What would the pH be if .020 mol of HCl is added to 1.0 L of preceding solutions.
- 0.75 M lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) and 0.25 M sodium lactate ($K_a = 1.4 \times 10^{-4}$)

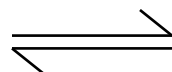


Initially	0.75 mol	0	0.25 mol
After acid	0.77 mol		0.23 mol

Compared to 3.38 before acid was added

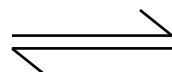
Prove they're buffers

- What would the pH be if 0.050 mol of solid NaOH is added to 1.0 L of the solutions.
- 0.75 M lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) and 0.25 M sodium lactate ($K_a = 1.4 \times 10^{-4}$)



Prove they're buffers

- What would the pH be if .020 mol of HCl is added to 1.0 L of preceding solutions.
- 0.25 M NH_3 and 0.40 M NH_4Cl
 $K_b = 1.8 \times 10^{-5}$ so $K_a = 5.6 \times 10^{-10}$

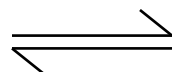


Initially	0.40 mol	0	0.25 mol
After acid	0.42 mol		0.23 mol

Compared to 9.05 before acid was added

Prove they're buffers

- What would the pH be if 0.050 mol of solid NaOH is added to 1.0 L each solutions.
- 0.25 M NH_3 and 0.40 M NH_4Cl
 $K_b = 1.8 \times 10^{-5}$ so $K_a = 5.6 \times 10^{-10}$



Initially	0.40 mol	0	0.25 mol
After acid	0.35 mol		0.30 mol

Compared to 9.05 before acid was added

Buffer capacity

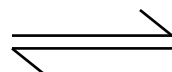
- The pH of a buffered solution is determined by the ratio $[A^-]/[HA]$.
- As long as this doesn't change much the pH won't change much.
- The more concentrated these two are the more H^+ and OH^- the solution will be able to absorb.
- Larger concentrations = bigger buffer capacity.

Buffer Capacity

- Calculate the change in pH that occurs when 0.020 mol of HCl(g) is added to 1.0 L of each of the following:
- 5.00 M HAc and 5.00 M NaAc
- 0.050 M HAc and 0.050 M NaAc
- $K_a = 1.8 \times 10^{-5}$
- $\text{pH} = \text{pK}_a$

Buffer Capacity

- Calculate the change in pH that occurs when 0.040 mol of HCl(g) is added to 1.0 L of 5.00 M HAc and 5.00 M NaAc
- $K_a = 1.8 \times 10^{-5}$

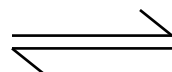


Initially	5.00 mol	0	5.00 mol
After acid	5.04 mol		4.96 mol

Compared to 4.74 before acid was added

Buffer Capacity

- Calculate the change in pH that occurs when 0.040 mol of HCl(g) is added to 1.0 L of 0.050 M HAc and 0.050 M NaAc
- $K_a = 1.8 \times 10^{-5}$



Initially	0.050 mol	0	0.050 mol
After acid	0.090 mol	0	0.010 mol

Buffer capacity

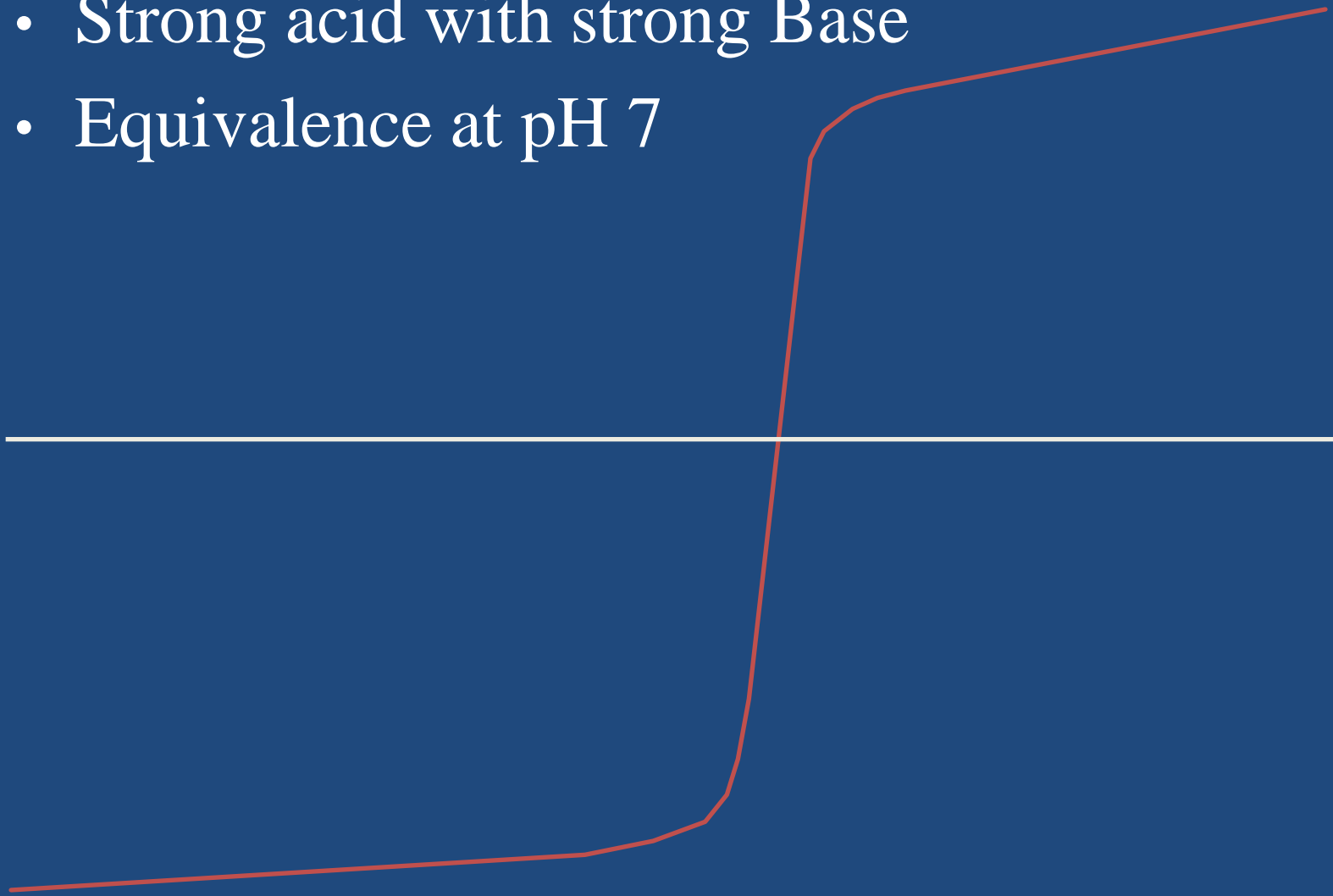
- The best buffers have a ratio
- $[A^-]/[HA] = 1$
- This is most resistant to change
- True when $[A^-] = [HA]$
- Makes $pH = pK_a$ (since $\log 1 = 0$)

Titration

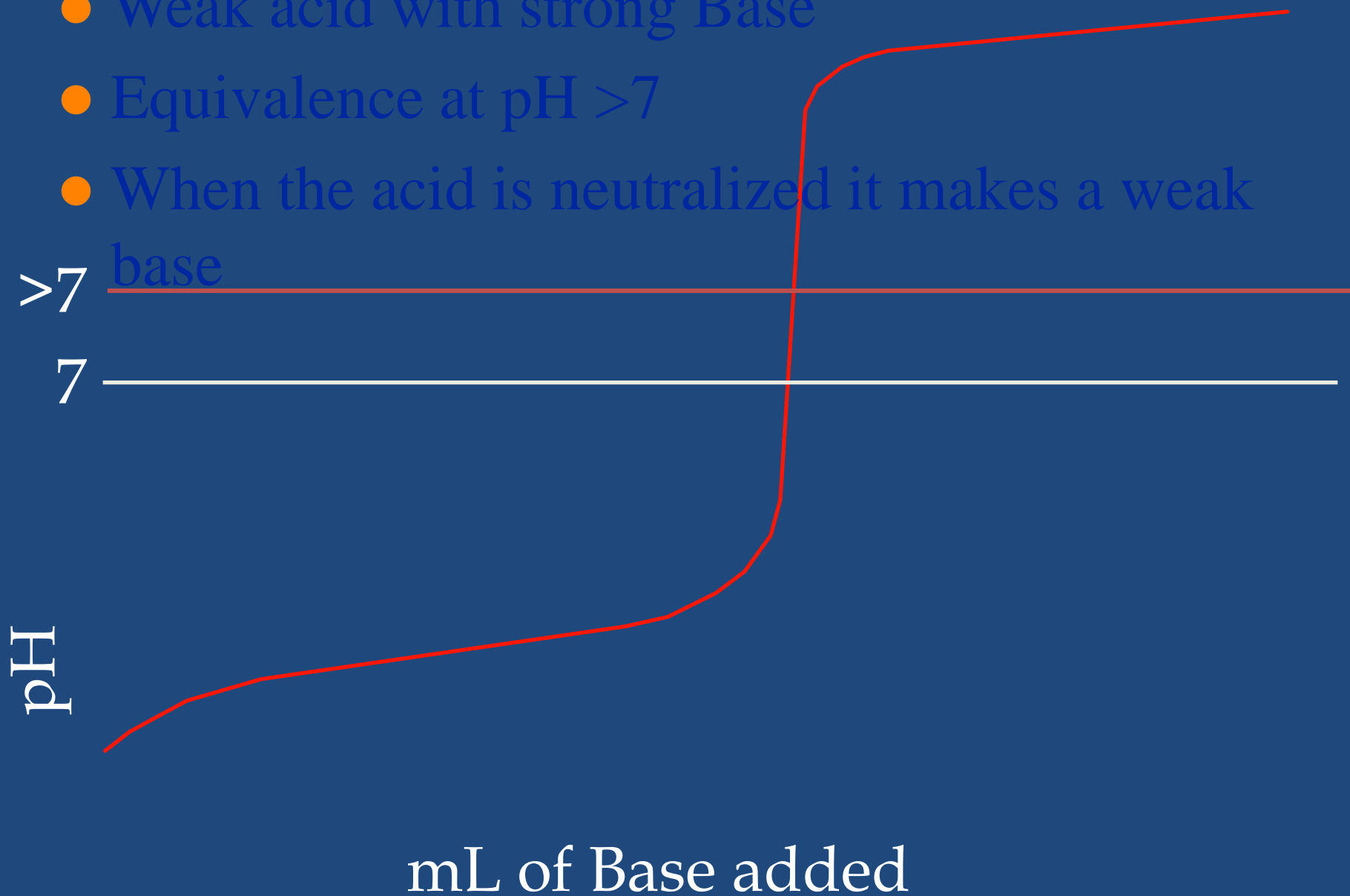
- Millimole (mmol) = $1/1000$ mol
- Molarity = $\text{mmol/mL} = \text{mol/L}$
- Makes calculations easier because we will rarely add liters of solution.
- Adding a solution of known concentration until the substance being tested is consumed.
- This is called the equivalence point.
- Graph of pH vs. mL is a titration curve.

Titration Curves

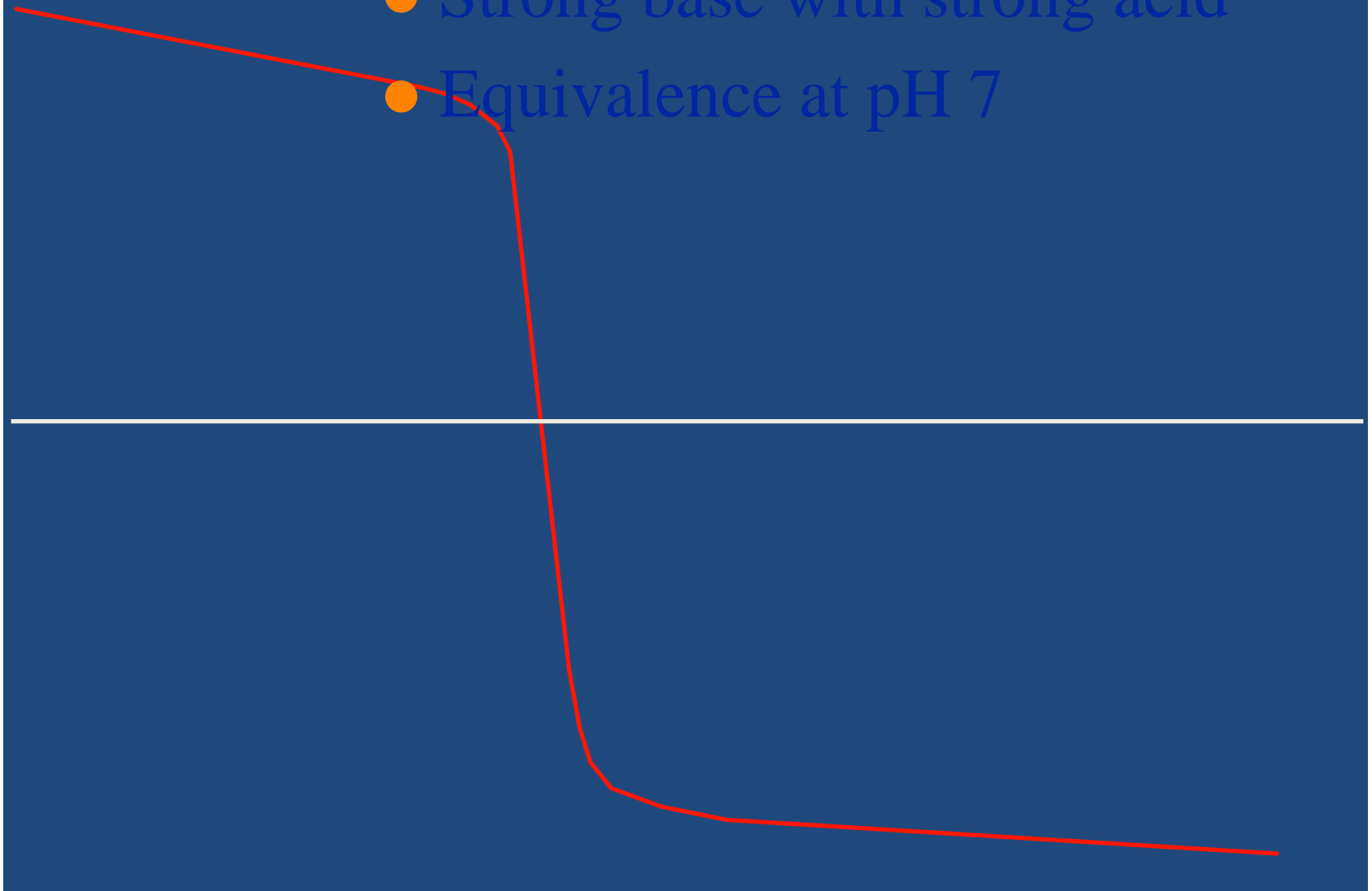
- Strong acid with strong Base
- Equivalence at pH 7



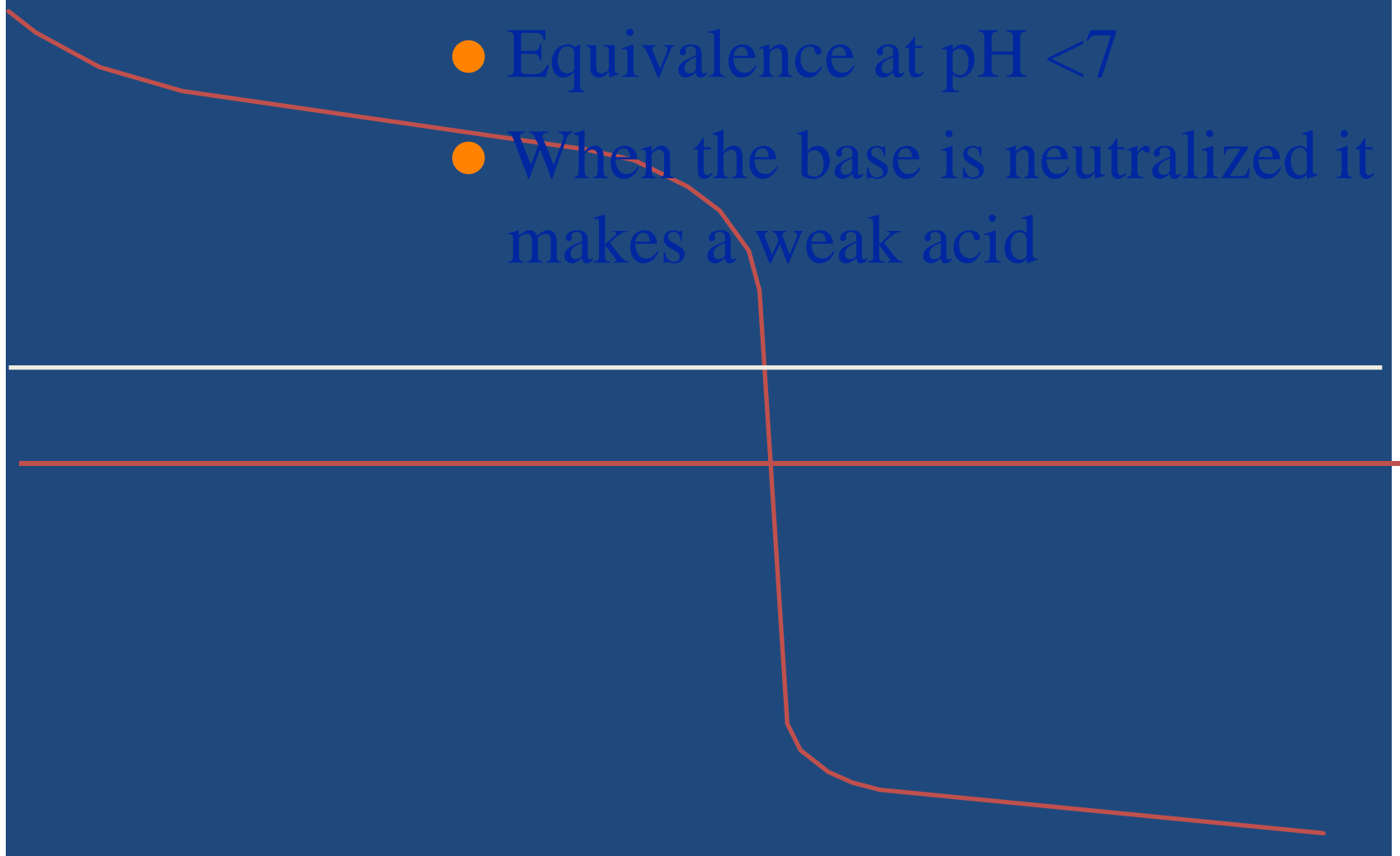
- Weak acid with strong Base
- Equivalence at $\text{pH} > 7$
- When the acid is neutralized it makes a weak base



- Strong base with strong acid
- Equivalence at pH 7



- Weak base with strong acid
- Equivalence at $\text{pH} < 7$
- When the base is neutralized it makes a weak acid



Strong acid with Strong Base

- Do the stoichiometry.
- $\text{mL} \times \text{M} = \text{mmol}$
- There is no equilibrium .
- They both dissociate completely.
- The reaction is $\text{H}^+ + \text{OH}^- \rightarrow \text{HOH}$
- Use $[\text{H}^+]$ or $[\text{OH}^-]$ to figure pH or pOH
- The titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH

Weak acid with Strong base

- There is an equilibrium.
- Do stoichiometry.
 - Use moles
- Determine major species
- Then do equilibrium.
- Titrate 50.0 mL of 0.10 M HF (K_a = 7.2×10^{-4}) with 0.10 M NaOH

Summary

- Strong acid and base just stoichiometry.
- Weak acid with 0 ml of base - K_a
- Weak acid before equivalence point
 - Stoichiometry first
 - Then Henderson-Hasselbach
- Weak acid at equivalence point- K_b
 - Calculate concentration
- Weak acid after equivalence - leftover strong base.
 - Calculate concentration

Summary

- Weak base before equivalence point.
 - Stoichiometry first
 - Then Henderson-Hasselbach
- Weak base at equivalence point K_a .
 - Calculate concentration
- Weak base after equivalence – left over strong acid.
 - Calculate concentration

Indicators

- Weak acids that change color when they become bases.
- weak acid written HIn
- Weak base
- $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$
clear red
- Equilibrium is controlled by pH
- End point - when the indicator changes color.
- Try to match the equivalence point

Indicators

- Since it is an equilibrium the color change is gradual.
- It is noticeable when the ratio of $[\text{In}^-]/[\text{HI}]$ or $[\text{HI}]/[\text{In}^-]$ is 1/10
- Since the Indicator is a weak acid, it has a K_a .
- pH the indicator changes at is.
- $\text{pH} = \text{pK}_a + \log([\text{In}^-]/[\text{HI}]) = \text{pK}_a + \log(1/10)$
- $\text{pH} = \text{pK}_a - 1$ on the way up

Indicators

- $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{HI}]}{[\text{In}^-]}\right) = \text{pK}_a + \log(10)$
- $\text{pH} = \text{pK}_a + 1$ on the way down
- Choose the indicator with a pK_a 1 more than the pH at equivalence point if you are titrating with base.
- Choose the indicator with a pK_a 1 less than the pH at equivalence point if you are titrating with acid.

Solubility Equilibria

Will it all dissolve, and if not, how much?

- All dissolving is an equilibrium.
- If there is not much solid it will all dissolve.
- As more solid is added the solution will become saturated.
- Solid \rightleftharpoons dissolved
- The solid will precipitate as fast as it dissolves .
- Equilibrium

General equation

- M^+ stands for the cation (usually metal).
- Nm^- stands for the anion (a nonmetal).
- $M_aNm_b(s) \rightleftharpoons aM^+(aq) + bNm^-(aq)$
- $K = [M^+]^a[Nm^-]^b/[M_aNm_b]$
- But the concentration of a solid doesn't change.
- $K_{sp} = [M^+]^a[Nm^-]^b$
- Called the **solubility product** for each compound.

Watch out

- Solubility is not the same as solubility product.
- Solubility product is an equilibrium constant.
- it doesn't change except with temperature.
- Solubility is an equilibrium position for how much can dissolve.
- A common ion can change this.

Calculating K_{sp}

- The solubility of iron(II) oxalate FeC_2O_4 is 65.9 mg/L
- The solubility of Li_2CO_3 is 5.48 g/L

Calculating Solubility

- The solubility is determined by equilibrium.
- Its an equilibrium problem.
- Watch the coefficients
- Calculate the solubility of SrSO_4 , with a K_{sp} of 3.2×10^{-7} in M and g/L.
- Calculate the solubility of Ag_2CrO_4 , with a K_{sp} of 9.0×10^{-12} in M and g/L.

Relative solubilities

- K_{sp} will only allow us to compare the solubility of solids that fall apart into the same number of ions.
- The bigger the K_{sp} of those the more soluble.
- If they fall apart into different number of pieces you have to do the math.

Common Ion Effect

- If we try to dissolve the solid in a solution with either the cation or anion already present less will dissolve.
- Calculate the solubility of SrSO_4 , with a K_{sp} of 3.2×10^{-7} in M and g/L in a solution of 0.010 M Na_2SO_4 .
- Calculate the solubility of SrSO_4 , with a K_{sp} of 3.2×10^{-7} in M and g/L in a solution of 0.010 M SrNO_3 .

pH and solubility

- OH^- can be a common ion.
- More soluble in acid.
- For other anions if they come from a weak acid they are more soluble in a acidic solution than in water.



- Reduces $[\text{C}_2\text{O}_4^{-2}]$ in acidic solution.

Precipitation

- Ion Product, $Q = [M^+]^a[Nm^-]^b$
- If $Q > K_{sp}$ a precipitate forms.
- If $Q < K_{sp}$ No precipitate.
- If $Q = K_{sp}$ equilibrium.
- A solution of 750.0 mL of $4.00 \times 10^{-3}M$ $Ce(NO_3)_3$ is added to 300.0 mL of $2.00 \times 10^{-2}M$ KIO_3 . Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}M$) precipitate and if so, what is the concentration of the ions?

Selective Precipitations

- Used to separate mixtures of metal ions in solutions.
- Add anions that will only precipitate certain metals at a time.
- Used to purify mixtures.
- Often use H_2S because in acidic solution Hg^{+2} , Cd^{+2} , Bi^{+3} , Cu^{+2} , Sn^{+4} will precipitate.

Selective Precipitation

- Then add OH^- -solution $[\text{S}^{-2}]$ will increase so more soluble sulfides will precipitate.
- Co^{+2} , Zn^{+2} , Mn^{+2} , Ni^{+2} , Fe^{+2} , $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$

Selective precipitation

- Follow the steps
- First with insoluble chlorides (Ag, Pb, Ba)
- Then sulfides in Acid.
- Then sulfides in base.
- Then insoluble carbonate (Ca, Ba, Mg)
- Alkali metals and NH_4^+ remain in solution.

Complex ion Equilibria

- A charged ion surrounded by ligands.
- Ligands are Lewis bases using their lone pair to stabilize the charged metal ions.
- Common ligands are NH_3 , H_2O , Cl^- , CN^-
- Coordination number is the number of attached ligands.
- $\text{Cu}(\text{NH}_3)_4^{2+}$ has a coordination # of 4

The addition of each ligand has its own equilibrium

- Usually the ligand is in large excess.
- And the individual K 's will be large so we can treat them as if they go to completion.
- The complex ion will be the biggest ion in solution.

- Calculate the concentrations of Ag^+ , $\text{Ag}(\text{S}_2\text{O}_3)^-$, and $\text{Ag}(\text{S}_2\text{O}_3)_2^-$ in a solution made by mixing 150.0 mL of 0.010 M AgNO_3 with 200.0 mL of 5.00 M $\text{Na}_2\text{S}_2\text{O}_3$
- $\text{Ag}^+ + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)^- \quad K_1 = 7.4 \times 10^8$
- $\text{Ag}(\text{S}_2\text{O}_3)^- + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^- \quad K_2 = 3.9 \times 10^4$