Chemistry 102
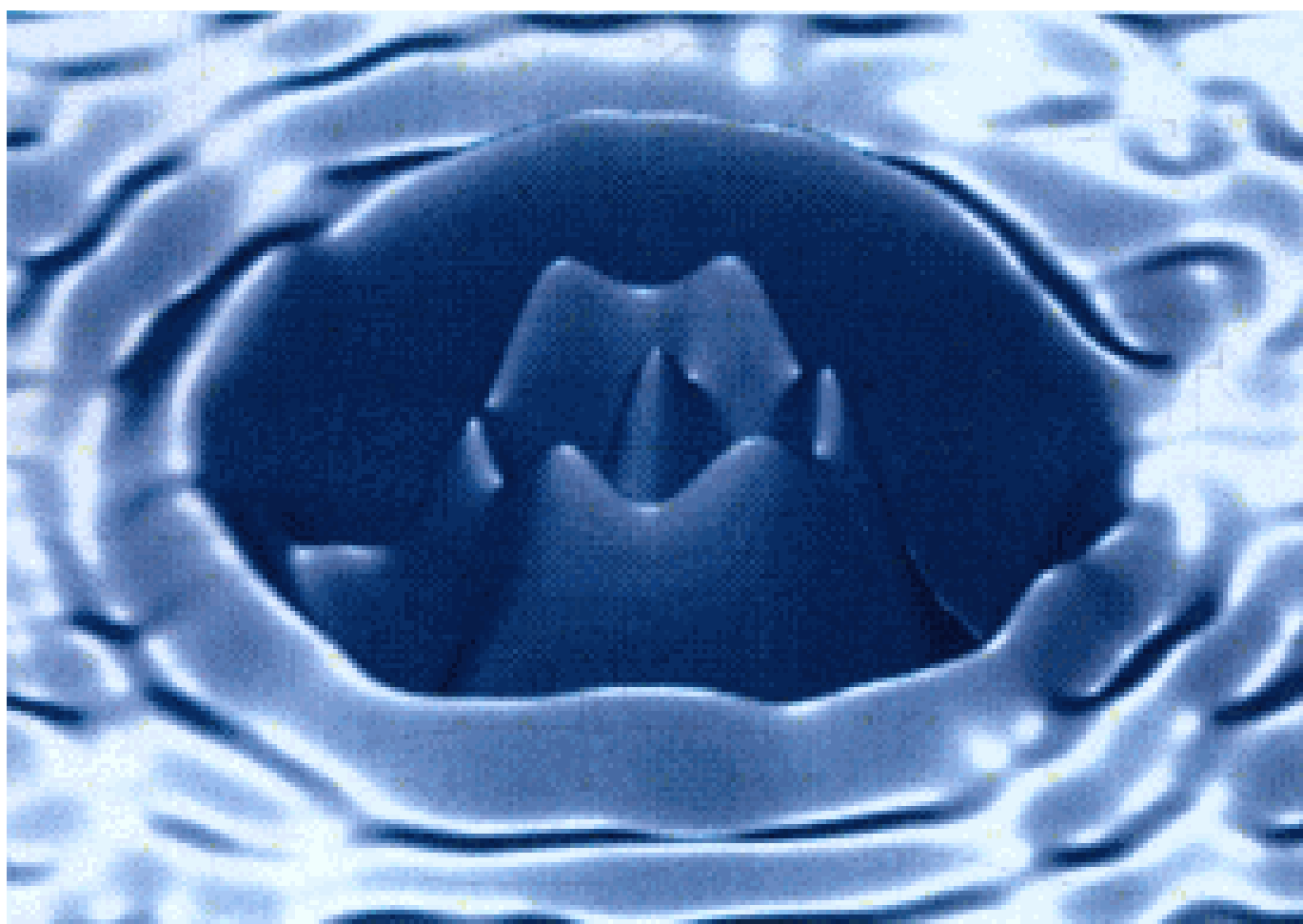
The Complete Notes

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Notes

Contents

See the Course Website (http://ww3.jjc.edu/staff/pmills) for specific test dates and other important information

Legend

You will often find specific icons embedded within the notes. These respective symbols alert the student to the following:

	Represents a *key* fact or other piece of information, such as the definitions of an element and a compound.
	Represents a useful *trick* the student will likely find useful, such as an 'EZ' way to convert between grams and moles for a substance
	Alerts the student to an important relationship between *micro* and *macro* scale properties or phenomena with respect to the material under discussion
✳	**Such material provides a link to interesting (*briefly* discussed) supplemental material, often beyond the scope of the course syllabus**

Cover Art: The 'STM Well' STM image

What is chemistry?

<u>Task</u>: In your own words describe what *you* consider chemistry to be, plus make a list of what *you* think the job of a chemist is:

<u>What is chemistry</u>?

<u>"Official" definition of what chemistry is</u>:

<u>Key words</u>:

<u>Matter</u>: "Stuff" – **anything with mass and volume**. Can you think of anything without mass or volume?

What are the three STATES of matter? Are there any more?

What are the basic building blocks of all matter, be it a diamond, a tree or the air around us? List as many types of matter as you can:

Matter Flow Chart
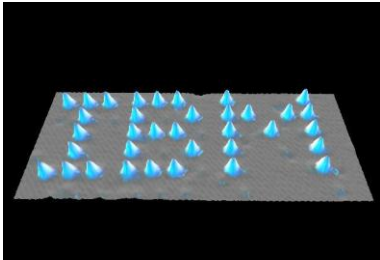
'High Tech' science (STM or AFM, top left) is often based on simple ideas (gramophone, top right). Click logo for 'flyby'.

More recent atomic (STM) images
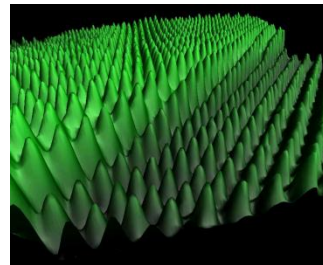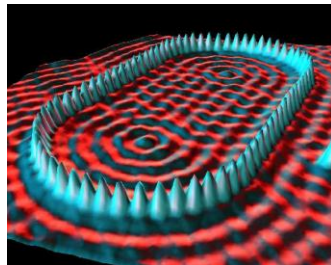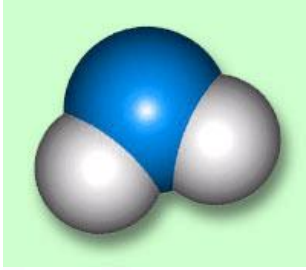
Example: What is water made up from? How do you know?

Summary:

Atoms and molecules are MICROSCOPIC particles (they are very small)

A drop of water is a MACROSCOPIC particle (because you can see it, hold it in your hand etc.)

"Official" definition of what chemists do:

Chemistry in action: Explaining what happens on your BBQ grill.

The burning of a charcoal brick on your backyard grill (MACRO) explained in terms of a *balanced chemical equation* (MICRO)

ANY large (MACRO) scale chemical process can be described using a MICRO scale chemical equation featuring individual atoms and/or molecules

Cartoon representation of the reaction of the pertinent atoms and molecules

The Chemists' description – a balanced chemical equation. This process is repeated many billions of times (MICRO) for the burning of a charcoal briquette (MACRO)

Review Topics

<u>Review</u>: What follows is a recap of the most important topics covered in CHM 101. We will use this material throughout CHM 102, so please ensure that you are familiar with the following questions, as well as the Ch3 & 4 HWK questions, before we move on to the Ch 11 material.

<u>Top Tip:</u> Committing to a rolling review of the ACS / Chem. 101 material is a potentially grade altering decision – *this cannot be over stressed* **(see below)**

1. The Mole

What is a mole (in chemistry terms)?

How is the mole defined?

When is ~~nation nerd~~, sorry, Mole Day?

<u>Question</u>: How many atoms of oxygen in 1.5 moles of O_2?

2. Molar Mass

What is the definition of molar mass ($\mathcal{M}$)?

How can you find the molar mass of any chemical using just the periodic table?

Question: What is the molar mass of carbon dioxide ($\mathcal{M}_{CO2}$)?

What is the relationship between molar mass, #grams and # moles of any chemical?

Question: How many moles of carbon dioxide are there in 27.4 grams of CO_2?

3. Balancing Chemical Equations

Write a balanced chemical equation for the combustion of ethanol (C_2H_6O). <u>Hint</u>: what are the products of combustion for natural (organic) materials?

4. 'Slides and Ladders' (Limiting Reactant Problems)

What mass of CO_2 (g) is formed from the combustion of 4.05 g ethanol? What volume of CO_2 (g) is formed at STP?

5. Concentration / Volume Relationships for Solutions

What is the relationship between the concentration of a solution, the # moles of solute it contains and the volume it occupies?

Question: How many grams of HNO_3 (aq) are there in 100 mL of a 6M nitric acid solution?

Question: What volume of 12 M H_2SO_4 (aq) is needed to completely neutralize 25.0 grams of NaOH(s)? Hint: Use a combined slides and ladders approach.

Recap: <u>The Importance of the mole</u>

Most of the equations we have met in this handout feature # moles as a variable. **Thus, moles can in many ways be considered the chemists' link between macro and micro scale quantities.**

Task: Write down as many equations you can featuring the mole. Use this information to construct a 'spider' (flow) chart illustrating how all these conversions 'go through' moles.

Question 4a (5 points): The products of combustion for *any* carbohydrate in oxygen gas are carbon dioxide and water. Use this information to write a balanced equation for the combustion of sugar ($C_6H_{12}O_6$ (s))

ANS: $C_6H_{12}O_6$ (s) + $6O_2$ (g) → 6 CO_2 (g) + 6 H_2O (g)

Question 4b (10 points): What mass of carbon dioxide gas would be collected from the complete combustion of 5.00 grams of sugar ($C_6H_{12}O_6$ (s))?

ANS: 7.33 g (3 sf)

Question 4c (10 points): What volume of carbon dioxide gas (at STP) would be collected from the complete combustion of 5.00 grams of sugar ($C_6H_{12}O_6$ (s))?

ANS: 3.74 L (3 sf)

Top Tip

Sample Final Exam Questions (CHM 101 syllabus, taken from the 'Final Exam Review' Lecture Notes)

1. In all neutral atoms, there are equal numbers of:

a.   electrons and protons   c.   electrons and neutrons
b.   protons and neutrons   d.   electrons and positrons

2. Which pair of particles has the same number of electrons?

a. F^-, Mg^{2+} c. P^{3-}, Al^{3+}
b.   Ne, Ar   d. Br^-, Se

3. What is the mass percent of oxygen in $Ca(NO_3)_2$?

a.   29.3 %   c.   58.5 %
b.   47.1 %   d.   94.1%

4. A 24.0 g sample of carbon contains how many atoms:

a. 6.02×10^{23} c. 3.01×10^{23}
b. 1.20×10^{24} d. 2.04×10^{24}

5. When 1.187 g of a metallic oxide is reduced with excess hydrogen, 1.054 g of the metal is produced. What is the metallic oxide?

a. Ag_2O c. K_2O
b. Cu_2O d. Tl_2O

6. A single molecule of a certain compound has a mass of 3.4×10^{-22} g. Which value comes closest to the mass of a mole of this compound?

a.   50 g   c.   150 g
b.   100 g   d.   200 g

7. The electronic configuration for the Ca atom is:

a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
b. $1s^2 2s^2 2p^6 3s^2$ d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

8. Two moles of any gas will occupy what volume at STP?

a.   22.4 L   c.   4.48 L
b.   11.2 L   d.   44.8 L

Answers:

1.   a.   5.   b.
2.   a.   6.   d.
3.   c.   7.   c.
4.   b.   8.   d.

Properties of Solutions

Types of Solutions and Solubility

Discussion: What *very* 'general' kinds of solutes can you dissolve in a solvent (say water) to make a solution? Provide examples.

_____ + water	_____ + water	_____ + water

Quick aside: What happens when one solution is mixed with another, or a solution is mixed with more additional solvent?

Spontaneous Mixing

When the barrier is removed, spontaneous mixing occurs, producing a solution of uniform concentration.
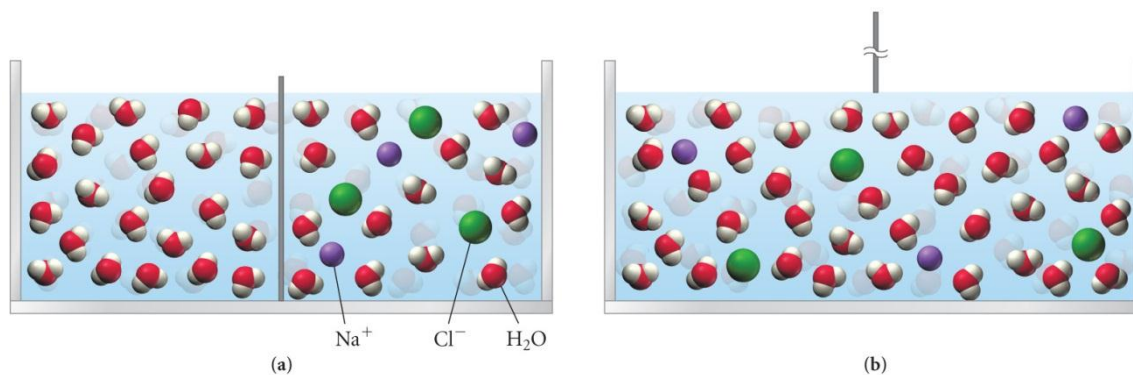
Why do the solutions mix, what's the 'pay off'?

On a *molecular level* the final solution is more 'randomized' (has more ENTROPY*). Chemical systems that possess a higher degree of entropy are more *thermodynamically stable*. 'Nature likes stable'!
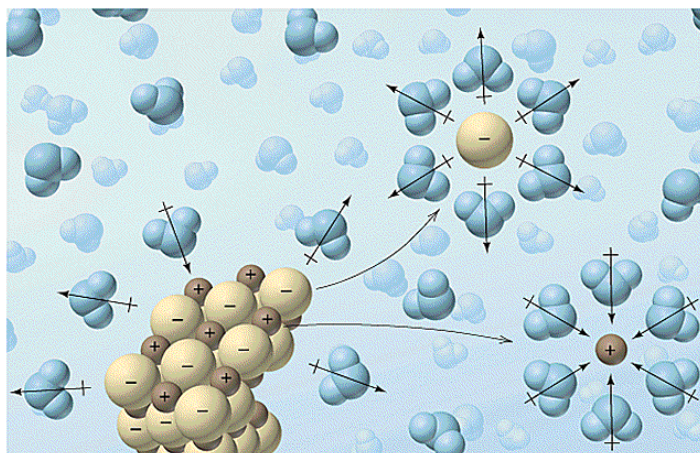
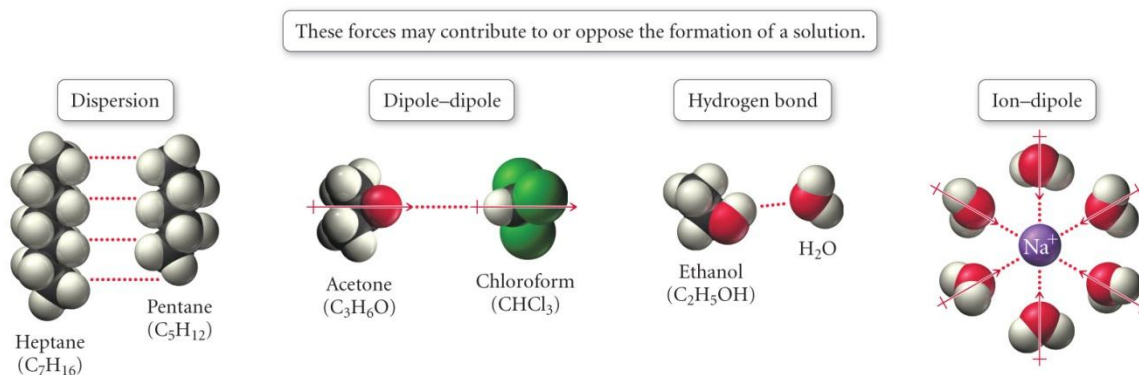*More on Entropy in *Chemical Thermodynamics*

OK, back to it….

Based on your current knowledge (recall the intermolecular forces work from CHM 101), *simply* explain why certain classes of compounds will or will not dissolve in water.
<u>*Hint*</u>*: 'like dissolves in like' - old chemistry saying**

*Recall the 'ions' slide, plus basic details on solutions (see Appendix).

These forces may contribute to or oppose the formation of a solution.

Dispersion

Heptane
(C_7H_{16})

Pentane
(C_5H_{12})

Dipole–dipole

Acetone
(C_3H_6O)

Chloroform
($CHCl_3$)

Hydrogen bond

Ethanol
(C_2H_5OH)

H_2O

Ion–dipole

Na^+

Solution Interactions

Solvent–solvent
interactions

Solute–solute
interactions

Solvent–solute
interactions
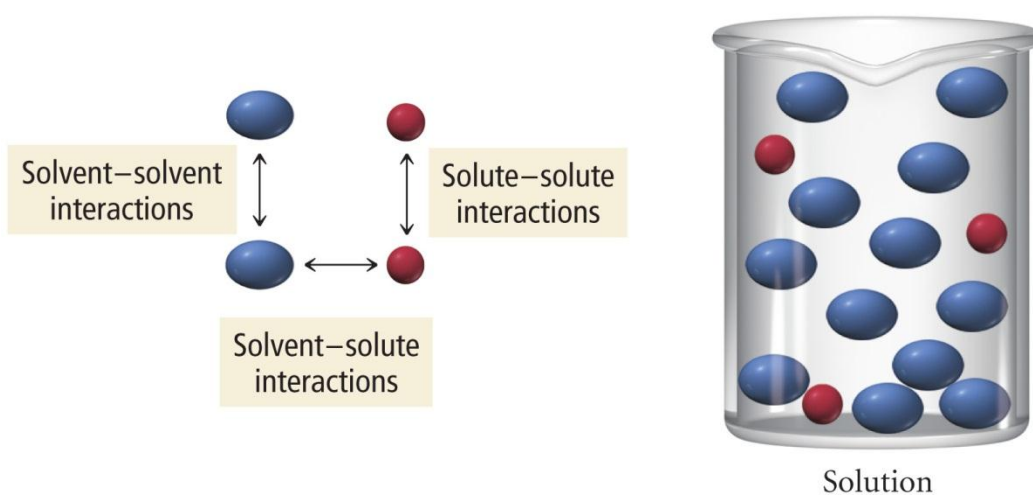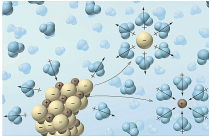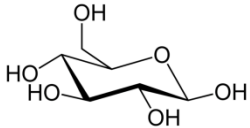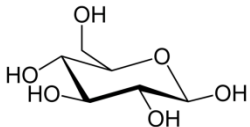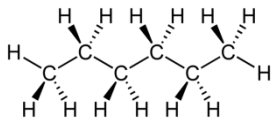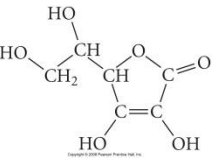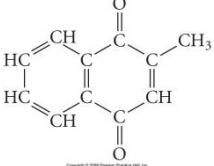
Solution

TABLE 12.2 Relative Interactions and Solution Formation

Solvent–solute interactions	>	Solvent–solvent and solute–solute interactions	Solution forms
Solvent–solute interactions	=	Solvent–solvent and solute–solute interactions	Solution forms
Solvent–solute interactions	<	Solvent–solvent and solute–solute interactions	Solution may or may not form, depending on relative disparity

Task: predict whether the following pairs of compounds are soluble, insoluble, miscible or immiscible. *What's the difference*??

Mixture	Details
Salt (NaCl) with water	
Sugar with water	
Sugar with hexane	
Hexane with water	
Vitamin C with water	
Vitamin K$_3$ with water	

Summary: Recall that '*Nature likes stable*'! Or, in other words, the 'winner' (in terms of the relative strengths of respective intermolecular force combinations) *typically* determines whether the solute /solvent pair are soluble or insoluble.

Solution Energetics

A similar approach can be applied to the formation of solutions, and (similarly) be represented in terms of familiar enthalpy (Hess' Law) relationships and diagrams

Heat of Hydration

Energy

$K^+(g) + F^-(g)$

$\Delta H_{solute} = -\Delta H_{lattice}$
$\Delta H_{solute} = +821 \text{ kJ/mol}$

$\Delta H_{hydration} = -819 \text{ kJ/mol}$

$K^+(aq) + F^-(aq)$

$\Delta H_{soln} = +2 \text{ kJ/mol}$

KF(s)
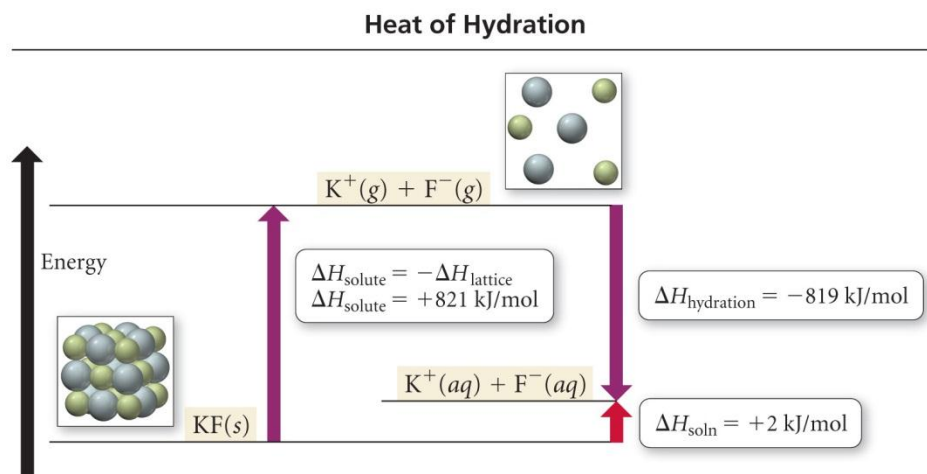
$$\Delta H_{soln} = \Delta H_{solute} + \underbrace{\Delta H_{solvent} + \Delta H_{mix}}$$

$$\Delta H_{soln} = \underset{\substack{\text{endothermic} \\ \text{(positive)}}}{\Delta H_{solute}} + \underset{\substack{\text{exothermic} \\ \text{(negative)}}}{\Delta H_{hydration}}$$

Task: Prove it to yourself; calculate ΔH_{soln} using the ΔH_{solute} and $\Delta H_{hydration}$ values listed above.

Factors Affecting Solubility

Or, in other words, stuff you already know from everyday observation……

Temperature

How are the solubility of solids and gasses *typically* affected by an increase in temperature?
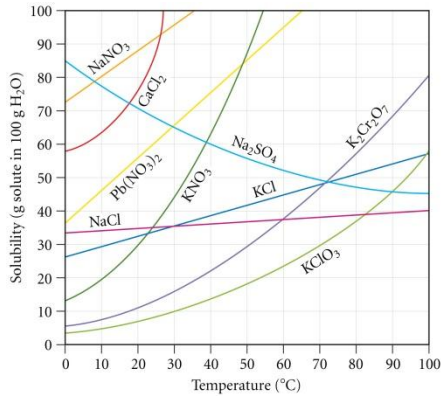
Solids:

Gasses:

Pressure
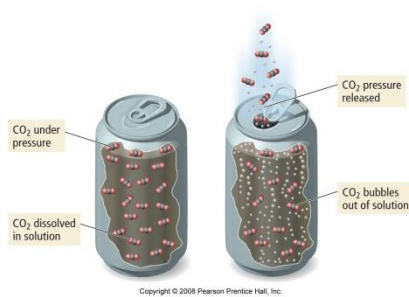
How is the solubility of a gas affected by an increase or decrease in pressure?

Expressing Solution Concentration

Overview: There are four ways of expressing the concentration or 'strength' of a solution – **Mola*rity*** (M, mols/L), **% mass**, **ppm** (parts per million) and **Mola*lity*** (mols/kg). **It is important to know how to determine and convert between these concentration types.**

Familiar Units – Molarity and % mass

1. Molarity**:**

Mola*rity* (M) = number moles of *solute* per Liter of *solution*

* The Molarity (mol/L conc.) is most often printed on lab reagent solution bottles, e.g. 9.0 M H_2SO_4 (aq)

i.e.   **M**olarity = $\dfrac{\text{Moles Solute}}{\text{Liters Solution}}$ Units: mol/L or just **M**

Example: What is the concentration (molarity, M) of a solution made by dissolving 25 g of NaCl in water and making the final volume of the solution equal to 750 mL?

2. % Mass

$$\% \text{ Mass} = \frac{\text{Mass Solute}}{\text{Mass Solution}} \times 100 \% \qquad (\text{units of } \%)$$

Example: What is the % mass concentration of an NaCl in a solution made by dissolving 25 g of NaCl in water and making the final volume of the solution equal to 750 mL? Assume the final solution has a density of 1.15 g/mL

New Units – ppm and Molality

Discussion: Why learn these new unit types? What are they used for?

3. ppm (parts per million)

> **The ppm unit is simply a mass ratio: 'grams per million grams',** i.e. there is a 'difference factor' of 10^6 between mass solute and mass solution. **A better way to express this would be mg solute per kg solution**
>
> **Parts per million = ppm = mg solute per kg of solution**

i.e.   **ppm** = $\dfrac{\text{mg solute}}{\text{kg solution}}$ Units: ppm or mg/kg

> **Regular molarity (mol/L) concs can be easily converted to ppm if the density of the solution is known.** Recall that mass = density x volume

Example: What is the ppm concentration of NaCl in a solution made by dissolving 25 g of NaCl in water and making the final volume of the solution equal to 750 mL? Assume the final solution has a density of 1.15 g/mL

1. Find mass solution

2. Divide mass of solute (in mg) by mass solution (in kg)

4. Molality:

m = Mola*ity* = number moles of *solute* per kg of *solvent*

i.e.   **m**olality = $\dfrac{\text{Moles Solute}}{\text{kg solvent}}$ Units: mol/kg or m

Example: What is the molality of an HCl solution that is 36% by mass?

When presented with a % mass concentration, assume that you have 100 g of this solution. The % mass of solute is than the same numerical value as the mass (in g) of solute in the solution

Mass solute =

Mass SOLVENT =

Molality of solution

Mole fraction

$$\frac{\text{amount solute (moles)}}{\text{amount solution (moles)}}$$

Molality (m)

$$\frac{\text{amount solute (moles)}}{\text{mass solvent (kg)}}$$

Amount in moles — Molar mass — Mass

SOLUTE

Molar volume (gas)

Volume

Density

Mass solution

Density

Parts by mass

$$\frac{\text{mass solute}}{\text{mass solution}}$$

Volume solution

Parts by volume

$$\frac{\text{volume solute}}{\text{volume solution}}$$

Mass — Molar mass — Amount in moles

SOLVENT

Density

Molar volume (gas)

Volume

Molarity (M)

$$\frac{\text{amount solute (moles)}}{\text{volume solution (L)}}$$
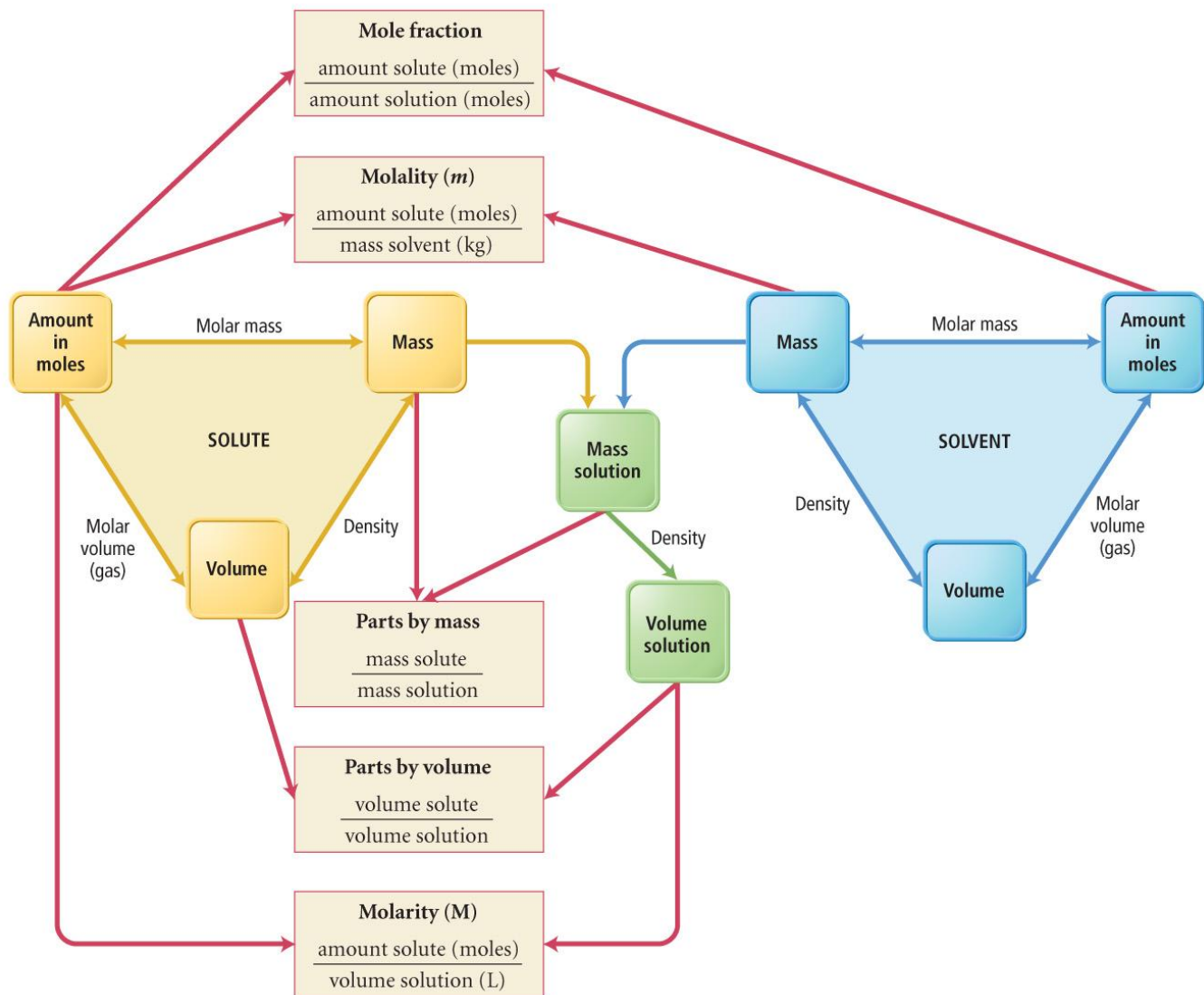
Colligative Properties

Definition: A property of a solution that **_only_** depends on the number of particles dissolved in solution (i.e. concentration), **_not_** the type of particle or their respective chemistries (ions, molecules etc.)

Application 1: Boiling Point Elevation / Freezing Point Depression

Discussion: Why is salt added to pasta water, why is salt spread on the roads in winter?

The change in bpt. or fpt. (ΔT) of a solution is proportional to its mola*lity*. **Bpt. elevation and fpt. depression are colloidal properties – they depend only on the *number* (molality) of solute particles disrupting intermolecular forces between the solvent molecules. It is the solvent's bpt or fpt that is affected.**

Equations

Bpt. Elevation
$\Delta T = K_b\, m$

Fpt. Depression
$\Delta T = K_f\, m$

Where: ΔT = *change* in bpt. or fpt. of the solution compared to the pure solvent
K_b = boiling point elevation constant for the solvent
K_f = freezing point depression constant for the solvent
m = molality of the solution

Water is the most common solvent. Its cryoscopic constants are:

K_b (H_2O) = 0.51 ^{o}C/m   **K_f (H_2O) = 1.86 ^{o}C/m**

Example: Calculate the fpt. of a 30 % by mass ethylene glycol ($C_2H_6O_2$) solution (this is what you probably have in your car, or perhaps in your wine rack)

Ionic Solutes

Unlike molecular solutes (like ethylene glycol), ionic solutes dissociate into *more than one* solvated particle when dissolved.

Eg: $NaCl(s) \rightarrow Na^+ (aq) + Cl^- (aq)$ **(x2 as many ions in solution)**

The higher concentration of solvated particles (ions) in solution *must* be accounted for in elevation / depression problems

Example: What is the boiling point of a solution that has a 2.5 m NaCl conc? What about 2.5 m $CaCl_2$ (sold as 'Quick Melt')

<u>Recall</u>: Phase Diagrams

A Phase Diagram relates the physical state (s, l, g) of a material to pressure and temperature conditions.

Generic Phase Diagram (see appendix)
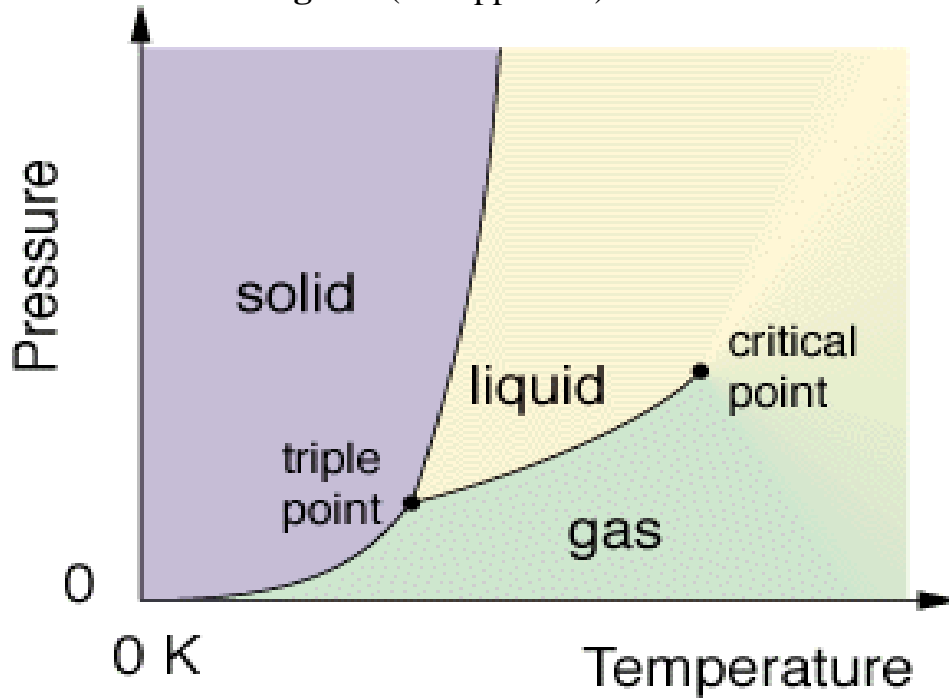
<u>Features of the Graph</u>

<u>Boiling point (l ↔ g)</u>   <u>Triple point</u>

<u>Freezing point (s ↔ l)</u>

                                    <u>Critical point</u>

<u>Sublimation Point (s ↔ g)</u>

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Discussion: How would the phase diagram of water be affected if some NaCl was dissolved in the water being studied? Hint: Think about the effects of bpt. and fpt. changes.

Phase Diagrams for an NaCl (aq) solution (see appendix)
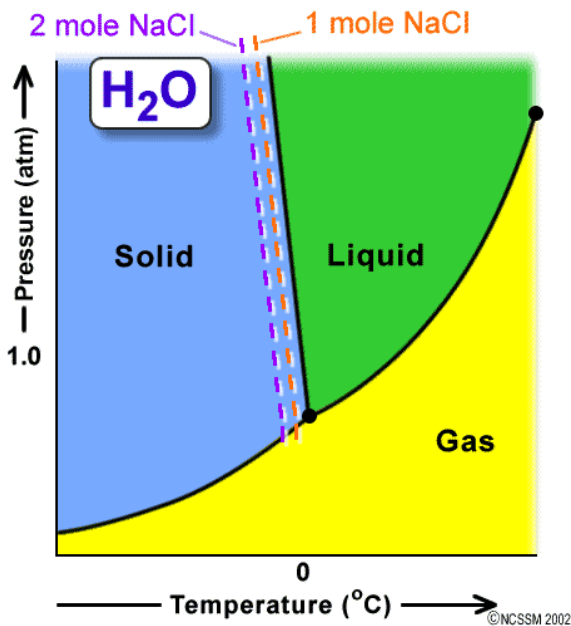
Application 2: Vapor Pressure Lowering

Vapor Pressure = pressure of a gas 'above'
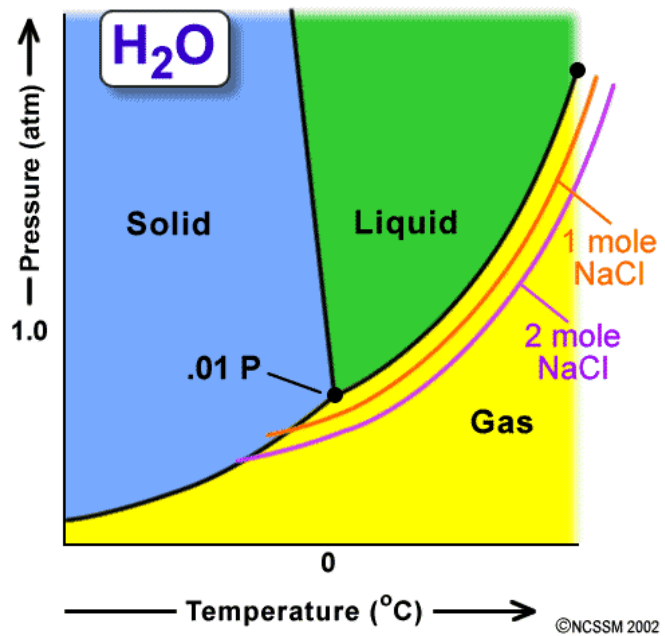a liquid when the two are in dynamic equilibrium*

*more on this in the *Equilibrium* packet, also recall Ch.11.

Dynamic equilibrium:
Rate of evaporation =
rate of condensation

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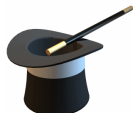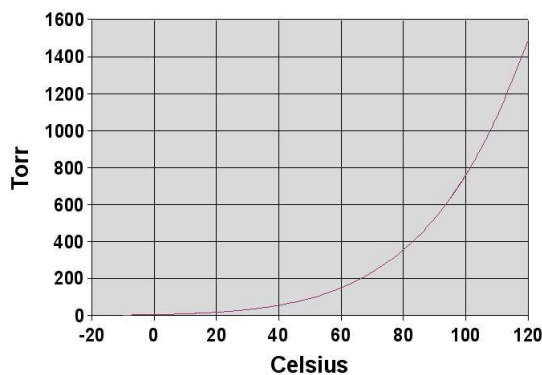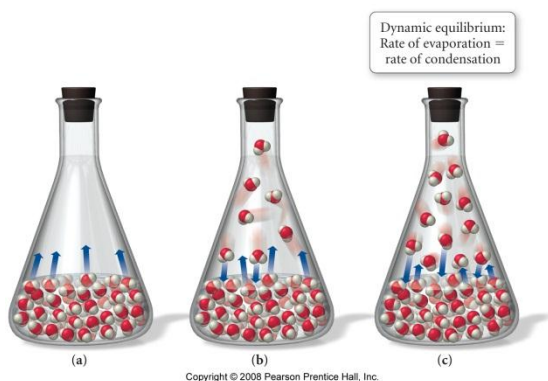
Think of vapor pressure like humidity – there is always a *fixed*
amount (partial pressure) of gaseous material 'above' any liquid
(in a closed container) at a specific temp – recall the CHM 101
'humidity' plot… *What is the vapor pressure of water at 100^oC?*

Think about it. Does the vapor pressure / equilibrium
idea help to explain why clothes on a washing line dry
faster on *warm* and *windy* days??

Raoult's Law Definition: (Recall partial pressure work from CHM 101)

1. <u>Volatile solutes (e.g. ethanol, benzene)</u>

(a) Ideal solution

Vapor pressure
of pure B

Vapor pressure
of pure A

Vapor pressure of solution

Partial pressure
of component B

Partial pressure
of component A

Vapor pressure

X_A

0.0   0.2   0.4   0.6   0.8   1.0
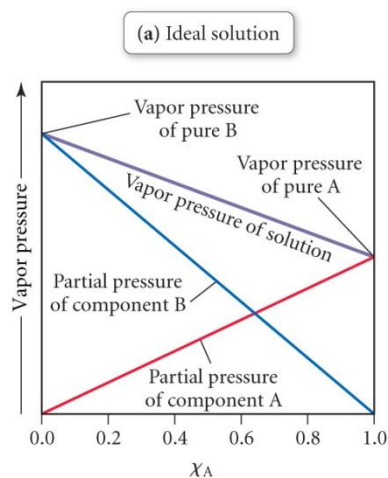
'<u>Using words</u>'

1.

2.

'<u>Using math</u>'

1.   2.

<u>Worked Example (HWK 12.73)</u>: A solution contains 50.0 g heptane (C_7H_{16}) and 50.0 g of octane (C_8H_{18}) at 25°C. The vapor pressures of pure heptane and pure octane at 25°C are 45.8 Torr and 10.9 Torr, respectively. Assuming ideal behavior, calculate:

a. The vapor pressure of each of the solution components in the mixture

b. The total pressure above the solution

c. The composition of the vapor in mass percent
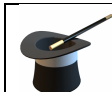
Recall that $p \propto n$, and then let 1 mole. = 1 torr

d. Why is the composition of the vapor different than that of the solution

Deviating from Raoult's Law

> *Solutions* **do not necessarily follow IDEAL (i.e. pure solute or solvent) behavior with regard to their Vapor Pressure v Composition plots – this is called deviating from** Raoult's Law**.**

Discussion: What *microscopic* events would cause a deviation from Raoult's Law, i.e. the vapor pressure for the solution to become greater or less than the partial pressure contributions expected from its pure components?

Positive Deviation   Negative Deviation
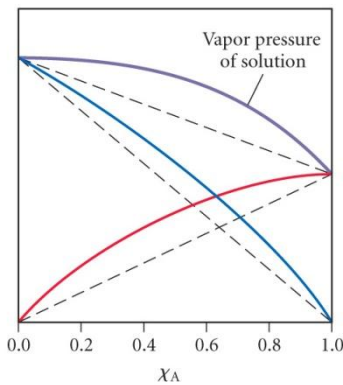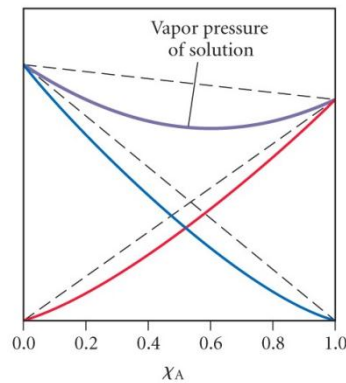
Ans: Ans:

Summary

Deviations from Raoult's Law

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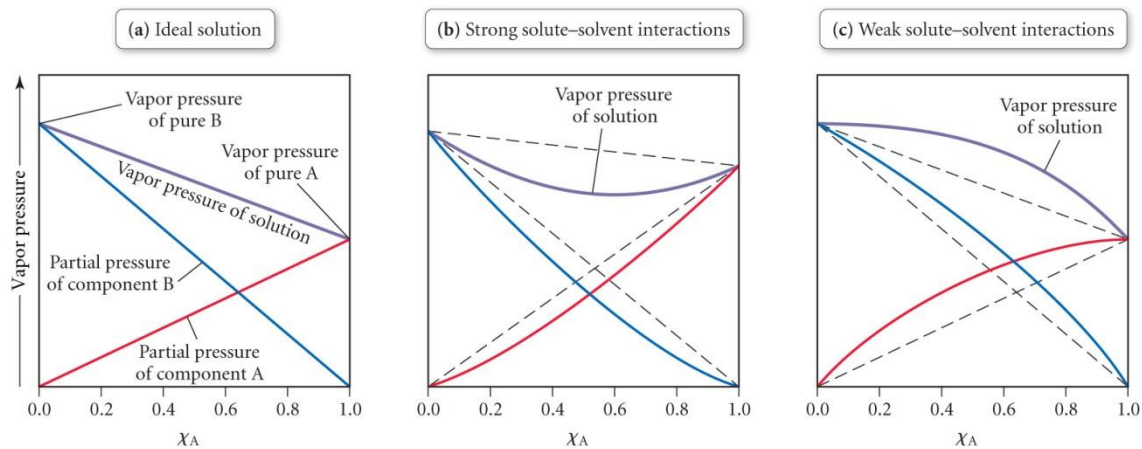
2. <u>Non-Volatile solutes (e.g. sucrose, table salt)</u>
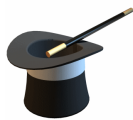
> Since non-volatile solutes will ***not*** generate a respective vapor above the mixture, only the solvent (now with a reduce mole fraction) will generate a slightly reduced, (compared to its pure state) vapor pressure.

<u>Worked Example</u>: Calculate the vapor pressure at 25°C of a solution containing 95.5 g sucrose ($C_{12}H_{22}O_{11}$) and 300.0 mL water. The vapor pressure water at 25°C is 23.8 Torr, assume density H_2O = 1.00 g/mL

<u>Plan</u>:

<u>Execute</u>:

Task: Calculate the vapor pressure at 25°C of a solution containing 55.3 g ethylene glycol ($C_2H_6O_2$) and 285.2 mL water. The vapor pressure water at 25°C is 23.8 Torr, assume density H_2O = 1.00 g/mL.

Recall that for ionic solutions, the concentration of colloidal particles in solution is 'multiplied out' by the number of ions of the formula unit. *Be sure to remember this when answering questions pertaining to ionic solutes.*

e.g. Since NaCl(s) → Na⁺(aq) + Cl⁻(aq) ($i \approx 2$), the effective concentration of particles in 0.20 M NaCl (aq) is…
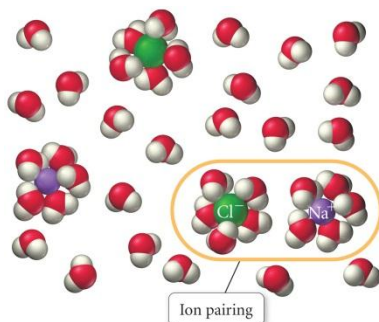
*see appendix for measured i values

Ion pairing

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Application 3: Osmotic Pressure
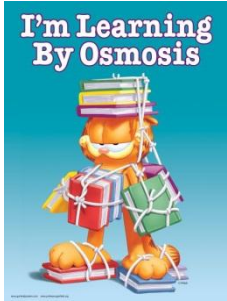
Discussion: Please explain the joke / observation that: "I'm learning through osmosis"
Scientific hint: recall the earlier discussion about mixing solutions

Observation: 'Seawater and Hangovers'

Interior of body cells –dilute solution

Seawater in intestinal tract –concentrated solution

Direction of water flow
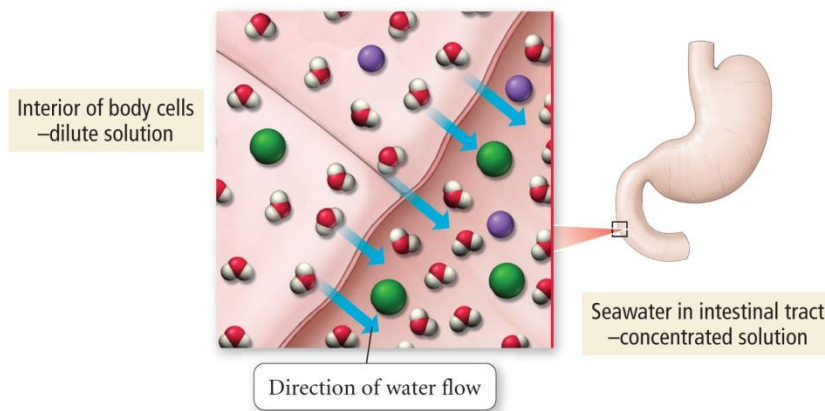
Osmosis and Osmotic Pressure

Initially

At equilibrium

Solvent particle

Water molecules

Water level rises

Pressure of excess fluid = osmotic pressure of solution

Semipermeable membrane
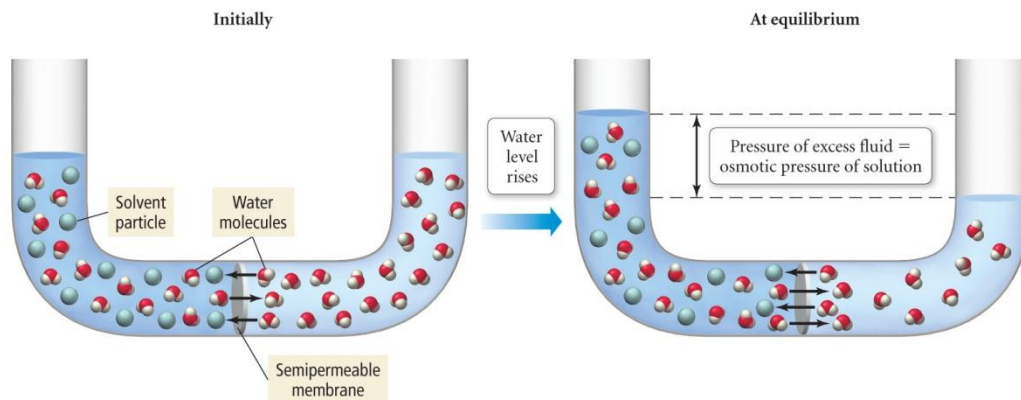
Osmotic Pressure Math

$$\Pi = i\text{MRT}$$

Where: Π = osmotic pressure

i = number of ions per formula unit (ionic solutes only)

M = Molarity (mol/L)

R= gas constant (0.0821 Latm/mol K)

T= temp in K

Worked Example: The osmotic pressure of a solution containing 5.87 mg of an unknown protein (per 10.0 mL of solution) was 2.45 Torr at 25°C. Find the molar mass of the protein.

Extra credit (2 points): Type a brief (less than 100 words) report detailing how *reverse osmosis* works. Include at least one diagram.

The following question was taken from your 1st practice midterm:

Question 5 (30 points): Calculate the osmotic pressure of a solution containing 20.5 mg of hemoglobin in 15.0 mL of solution at 25°C. The molar mass of hemoglobin is 6.5×10^4 g/mol.

Appendix

Chem. 101 Review Material: **Strong, Weak and Non-Electrolytic solutions**

Strong Electrolytes: **Salts**

NaCl (*aq*)
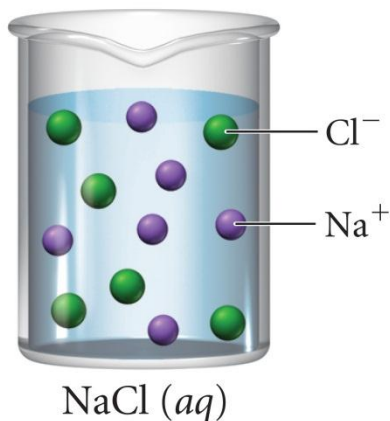
> **Strong electrolytes contain *very* large numbers of dissociated ions when dissolved**

Strong electrolytes are formed from the dissolution of SALTS (e.g. NaCl), which typically <u>undergo complete (100%) dissociation</u>

Weak Electrolytes: **Molecular acids**
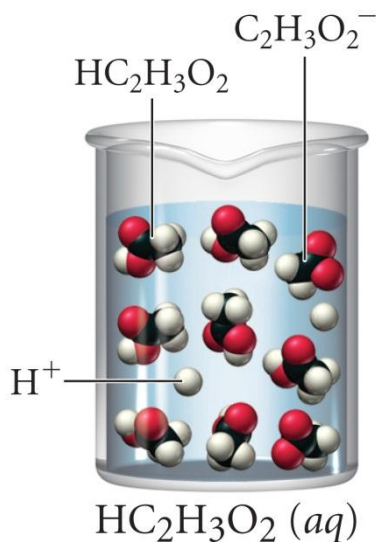
$HC_2H_3O_2$ (*aq*)

> **Weak electrolytes contain 'smaller' numbers of dissociated ions when dissolved**

Weak electrolytes are formed from the dissolution of MOLECULAR ACIDS (generic formula HA, e.g. $H(C_2H_3O_2)$ or HCl), which typically <u>undergo partial (<100%) dissociation</u>

Non Electrolytes: **Molecular Materials**

$C_{12}H_{22}O_{11}$ (aq)
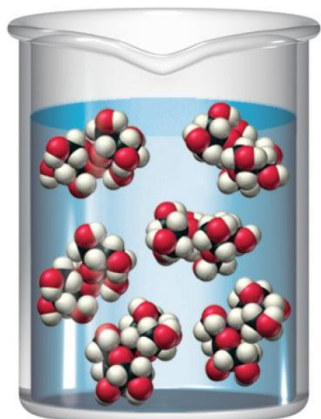
Non-electrolytes contain NO dissociated ions when dissolved, so CANNOT conduct electricity.

$\Rightarrow$ **Since non-electrolytes do NOT contain ions they must be MOLECULAR. As it *cannot* dissociate, molecular material remains INTACT when it dissolves (see below comparison)**

Comparison of (a) ionic and (b) molecular dissolution processes
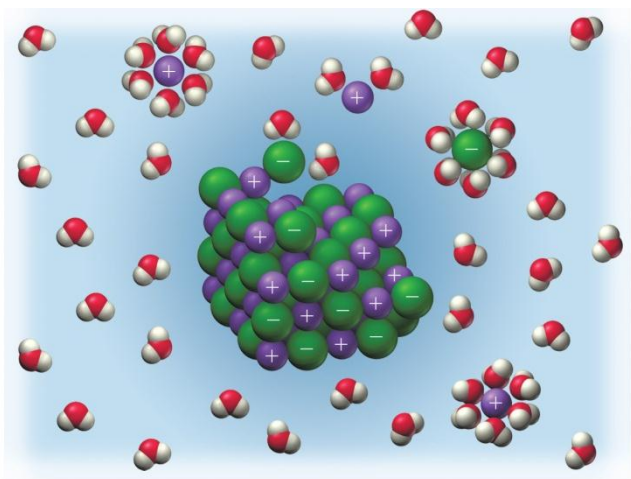
NaCl(aq)   'Sugar' ($C_{12}H_{22}O_{11}$ (aq))

| | | Melting point of solution | Melting point of solvent | | Boiling point of solvent | Boiling point of solution |
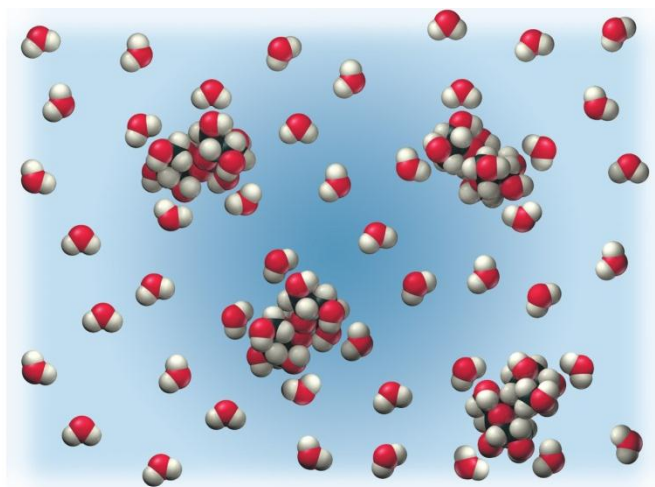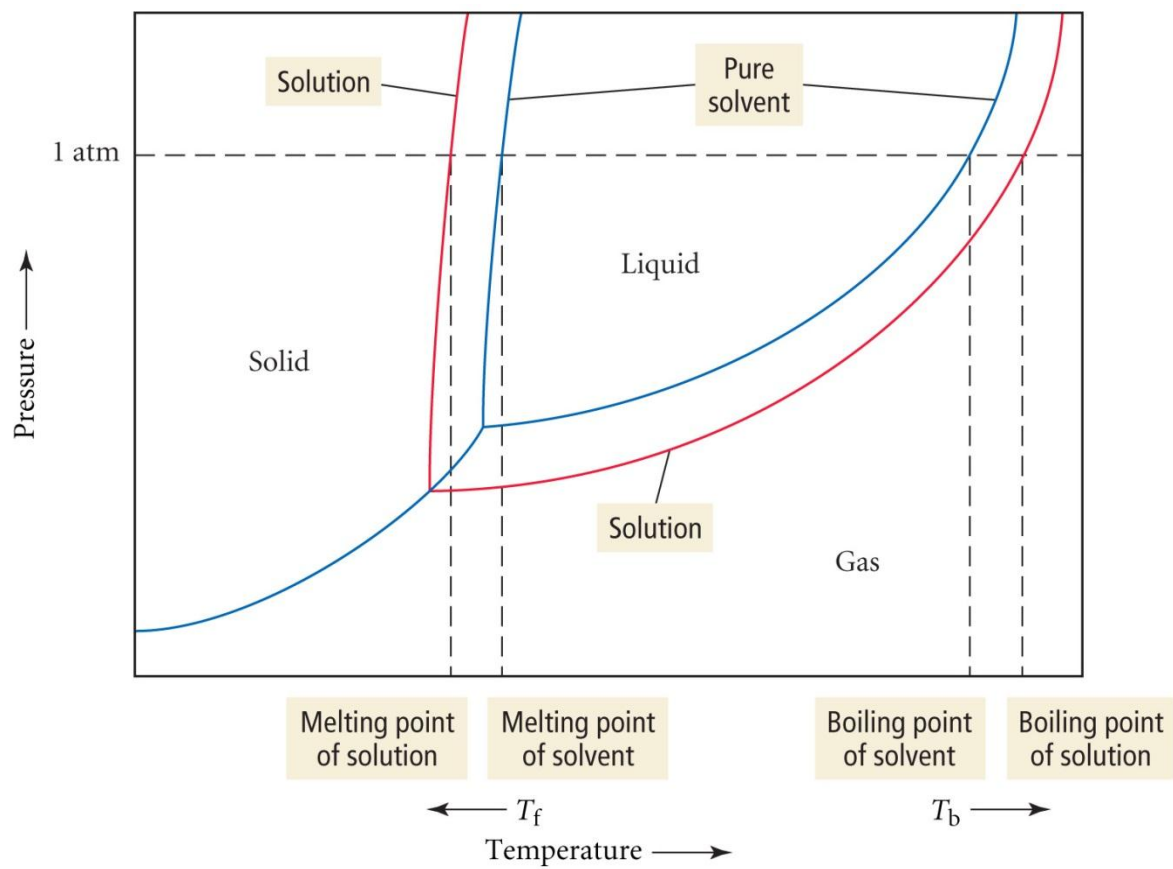
TABLE 12.9 Van't Hoff Factors at 0.05 m Concentration in Aqueous Solution

Solute	i Expected	i Measured
Nonelectrolyte	1	1
NaCl	2	1.9
$MgSO_4$	2	1.3
$MgCl_2$	3	2.7
K_2SO_4	3	2.6
$FeCl_3$	4	3.4
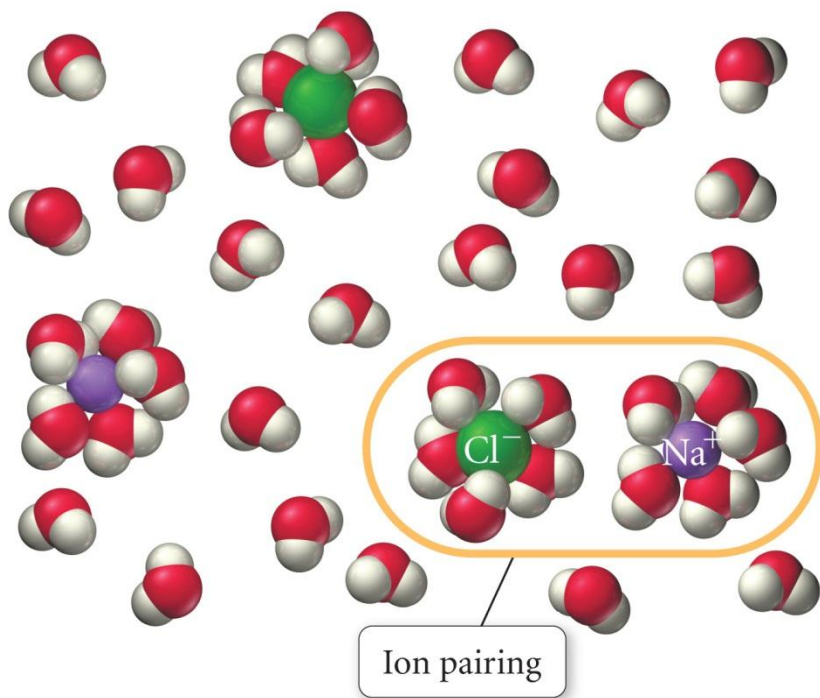
Ion pairing

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Chemical Kinetics 1

Factors that Affect Reaction Rates

General Discussion: Fundamentally speaking, what must happen at the microscopic level during a chemical reaction for 'new' chemical(s) to be formed?

Remember Dr. Mills favorite saying……

"Chemistry is a bit like Scottish soccer – it's basically a bunch of round things bumping into one another"

One time British soccer icon 'Gazza' with a gyro

Gazza playing out his career with Glasgow Rangers

A **fixed** fraction of all molecular collisions are fruitful.

These *fruitful collisions* result in the formation of 'new' product species

Question: What would happen to the **rate of reaction** (i.e. the speed of the reaction) if the number of molecular scale collisions among the reactants were:

a. Increased?   b. Decreased?

Always remember that the speed (or rate) of a chemical reaction is directly proportional to the number of molecular* collisions per second occurring among the reactants – some fixed fraction of which will be fruitful

Discussion: Which *macro* scale variables (i.e. in lab) can chemists alter to ultimately **increase the number of molecular collisions** among chemical reactants per second; thereby increasing the reaction rate? List them:

1.   2.

3.   4.

1. Concentration of Reactants
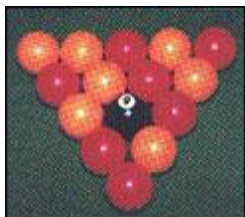
Observation: Which would result in a greater number of ball-on-ball collisions – your break in 9-ball or 'regular' 15-ball pool? Why?

2. Presence of a catalyst

Discussion: What is a catalyst / what does a catalyst do?

<u>Example</u>: the Pt/Pd catalyst in your car's muffler, a two-way catalyst

<u>Questions</u>: Which *two* 'unpleasant' gasses are produced through the incomplete combustion of gasoline? How are these gases converted to more benign products?

Step 1: Adsorption and bond weakening   Step 2: Migration

Step 3: Bond reorganization   Step 4: Desorption
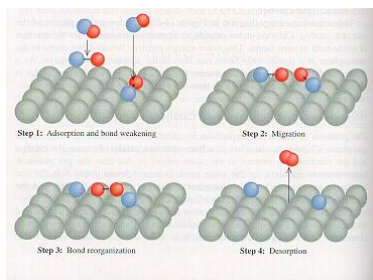
3. Temperature at which the reaction occurs

<u>Discussion</u>: What happens to the rate of molecular collisions (therefore the rate of reaction) when the temperature of the reaction vessel is increased? Why?

The kinetic energy (K.E.) of a molecular* species is proportional to the ambient temperature.

Molecular KE $= \frac{1}{2} mv^2 = kT$ (k is the Boltzmann constant)

$$\boxed{\text{i.e. Temp} \propto v^2 \propto (\textbf{reaction rate})^2}$$

4. Surface Area of a Solid Reactant

Why does powdered sugar dissolve much more quickly than 'trendy' crystalline sugar swizzles? What's happening on the micro scale?

Definition of Reaction Rate

Discussion Questions

1. How do you know that a reaction is occurring or has finished?

2. How then, would you measure the speed (or rate) of reaction? <u>Hint</u>: How is rate of distance traveled (speed) measured by your car's 'speedo'?

Definition of Reaction Rate

3. How would you define 'reaction rate' or 'rate of reaction' mathematically? <u>Hint</u>: Think about expressing rate of change in calculus.

<u>Example</u>: The decomposition of dinitrogen pentoxide

$$2\ N_2O_5\ (g)\ \rightarrow\ 4\ NO_2\ (g)\ +\ O_2\ (g)$$

The rate of reaction can be expressed in terms or *either* the decrease in $[N_2O_5]$ with time *or* the increase of $[NO_2]$ or $[O_2]$ with time.

<u>Task</u>: write calculus style relationships illustrating the above

Rate of formation wrt. O_2 =

Rate of formation wrt. NO_2 =

Rate of loss wrt. N_2O_5 =

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Application: AVERAGE reaction rates
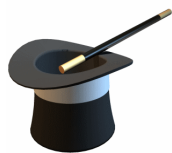
> **Average reaction rates are 'as advertised' - the average speed (rate) of a reaction over an extended (measurable) period of time**

Worked Example: If it takes 32 seconds to see the appearance of 2 moles O_2 (g) (within a 1.0 L container) from the above reaction, what is the average rate of reaction over this time period?

> *Difference* **is always found by subtracting the initial condition from the final condition in chemistry problems**
>
> **i.e: Δ(variable) = final value variable – initial value variable**

Calculations

$\Delta [O_2] =$

$\Delta t =$

$\Rightarrow$ Average rate of reaction = $\dfrac{\Delta [O_2]}{\Delta t}$ =

Note: The unit for rate of reaction is always mols L^{-1}/s (mols L^{-1} s^{-1})

Instantaneous Rates of Reaction

Analogy: The difference between *average* and *instantaneous* rates

Average rate analogy: It takes ~60 minutes to travel the 60 miles from JJC to downtown Chicago. What is the average speed during the journey?

Instantaneous rate analogy: Is it likely that you will travel at exactly 60 miles/hr for the entire duration of the journey?

Open road speed ≈

Congested expressway speed ≈

Discussion: How would you expect the instantaneous rate of reaction to vary through the course of any reaction? What molecular level events are responsible for this trend?

Generic Graph of Concentration *Reactant* v Time for a chemical reaction
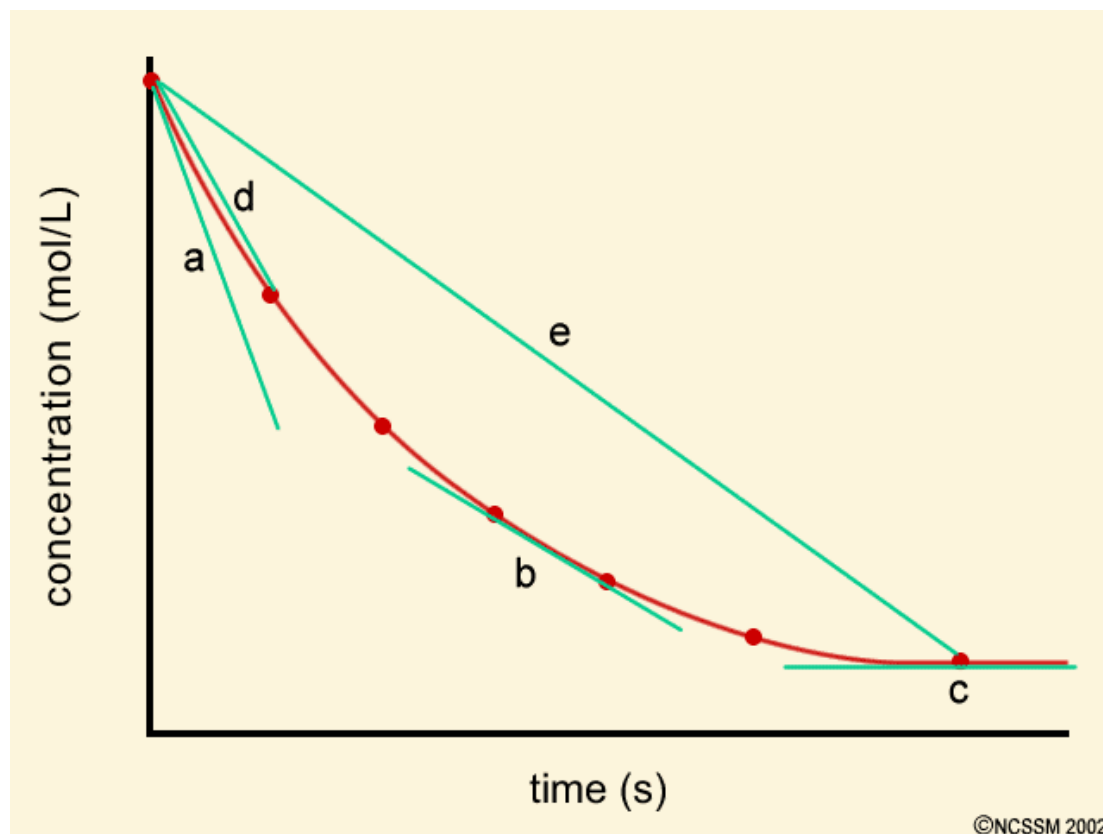
Features of the graph

Discussion: If the [reactants] *decreases* with time for any reaction (above), then: 1) How does [products] vary with time? 2) How does the *rate of formation* of products vary with time?

(a) rate of reaction decreases with time

(b) concentration of reactant decreases with time

(c) concentration of product increases with time
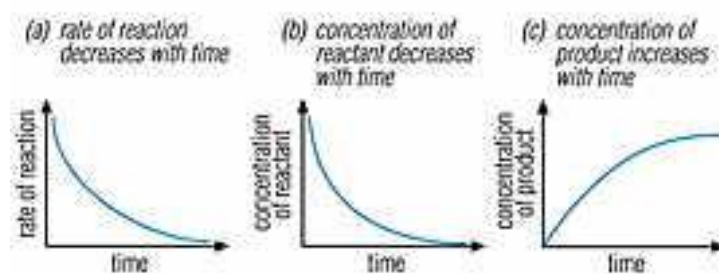
Overview Example: Graph of product conc. v time – measuring the rate of HI (g) formation and the rate of H_2 (g) disappearance for the reaction:

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightarrow 2 \text{ HI(g)}$$
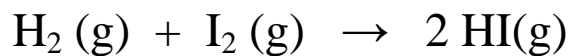
i.e.
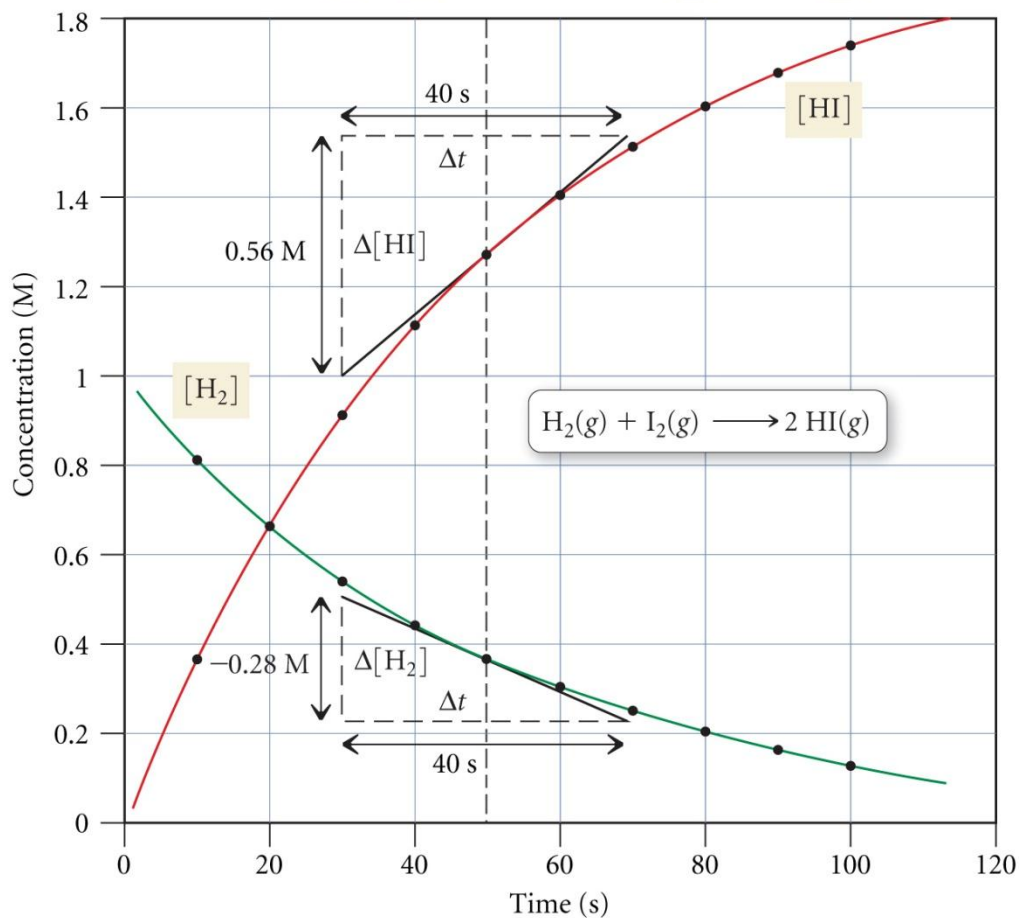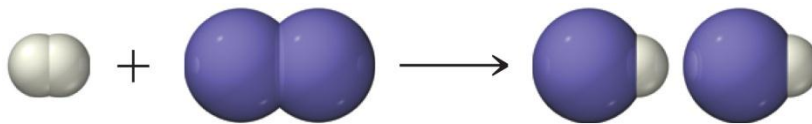
General Features of the graphs

Calculating the *instantaneous* rates of reaction

Recap: While a 'true' instantaneous rate can only be found by determining the *exact* gradient (slope) of the rate of reaction ([conc] v time) graph at a specified time (how?), a good approximation can be found through

either:

Graphical Method: Draw a tangent line to the experimental rate of reaction graph at the time of interest, and then find its gradient (by hand, or modern computer programs and/or graphical calculators can also do this)

Task: Use the 'graphical' method to find the instantaneous rate of reaction at t= 50 seconds in terms of change in [HI] with time

or

Equation of a Line Method: Use the equation of a line equation, i.e. $y_2 - y_1 = m(x_2 - x_1)$, to solve for the gradient of the curve (m) given a pair of adjacent experimental data points
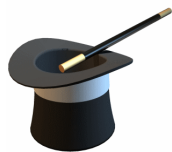
Determine Δ[conc] and Δt values using 'equidistant' data points either side of the required time. Divide these determined values to find the instantaneous rate at the desired time

Task: Use the 'equation' method to find the instantaneous rate of reaction at t= 50 seconds in terms of change in [H_2] with time (see p 566 or appendix for data table). Discussion: why are your two answers different (more later)?

<u>Wrap Up Example</u>: Consider our previous example (see p 566 and appendix for graph and data table).

$$H_2 \text{ (g)} + I_2 \text{ (g)} \quad \rightarrow \quad 2 \text{ HI(g)}$$
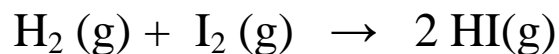
<u>Experimental</u>: As you will discover in lab, for most kinetic studies the concentration of a reactant, *or* product, is monitored with time; i.e. [conc] values are recorded at for a series of regular time intervals during the experiment. This raw data is then either used directly or plotted as a standard 'reaction rate' or [conc] v time graph shown here – see HWK for examples.

<u>Wrap up</u>: Using the tabulated experimental data and/or graph from p 566 of *Tro* (see appendix too), determine the instantaneous rate of the reaction, with respect to the disappearance of H_2(g), at t = 80 s.

Summary:

The instantaneous rate of reaction is a measure of either the *rate of change* of [reactant] or [product] at a fixed point in time (some fixed time after the reactants are mixed)

The instantaneous rate is found by determining the slope (gradient) of the [conc] v time reaction rate graph at a specified time after the reaction has commenced.

Reaction Rates and Stoichiometry

<u>Discussion</u>: For the reaction:

$$C_4H_9Cl \text{ (aq)} + H_2O \text{ (l)} \rightarrow C_4H_9OH \text{ (aq)} + HCl \text{ (aq)}$$
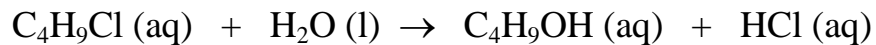
Is the rate of appearance C_4H_9OH (aq) = rate of appearance HCl (aq)? How do you know? Write a rate expression illustrating this relationship

Is the rate of disappearance C_4H_9Cl (aq) = rate of disappearance H_2O (l)? Write a rate expression illustrating this relationship

Write a rate expression illustrating the relationship between the rate of disappearance C_4H_9Cl (aq) and the rate of appearance HCl (aq)

Example: For the reaction:

$$2\ N_2O_5\ (g)\ \rightarrow\ 4\ NO_2\ (g)\ +\ O_2\ (g)$$

The rate of reaction can be expressed in terms of either $[N_2O_5]$, $[NO_2]$ or $[O_2]$

Does $[NO_2]$ increase at a faster, slower, or at the same rate as $[O_2]$? Express this relationship as a rate expression

Does $[N_2O_5]$ decrease at a faster, slower, or at the same rate as $[O_2]$? Express this relationship as a rate expression

The reaction between hydrogen and nitrogen to form ammonia is known as the Haber process:

$$N_2 \text{ (g)} \ + \ 3H_2 \text{ (g)} \ \rightarrow \ 2NH_3 \text{ (g)}$$
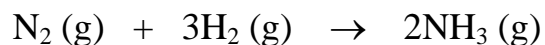
<u>Question 1a</u> (3 points each): Express the rate of the above reaction in terms of changes in $[N_2]$ with time, $[H_2]$ with time, and $[NH_3]$ with time.

<u>Question 1b</u> (16 points): When $[H_2]$ is decreasing at 0.175 $molL^{-1}s^{-1}$, at what rate is $[NH_3]$ increasing?

A reaction with a fast rate

A + B ⟶ C
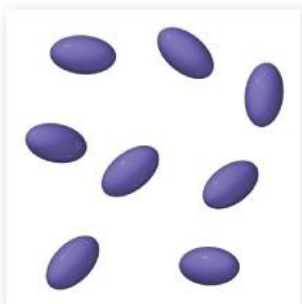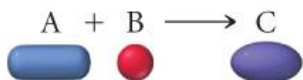
Time

A reaction with a slow rate

X + Y ⟶ Z
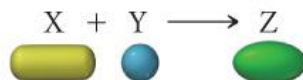
Time (s)	$[H_2]$ (M)	$\Delta[H_2]$	Δt
0.000	1.000		
10.000	0.819	−0.181	10.000
20.000	0.670	−0.149	10.000
30.000	0.549	−0.121	10.000
40.000	0.449	−0.100	10.000
50.000	0.368	−0.081	10.000
60.000	0.301	−0.067	10.000
70.000	0.247	−0.054	10.000
80.000	0.202	−0.045	10.000
90.000	0.165	−0.037	10.000
100.000	0.135	−0.030	10.000
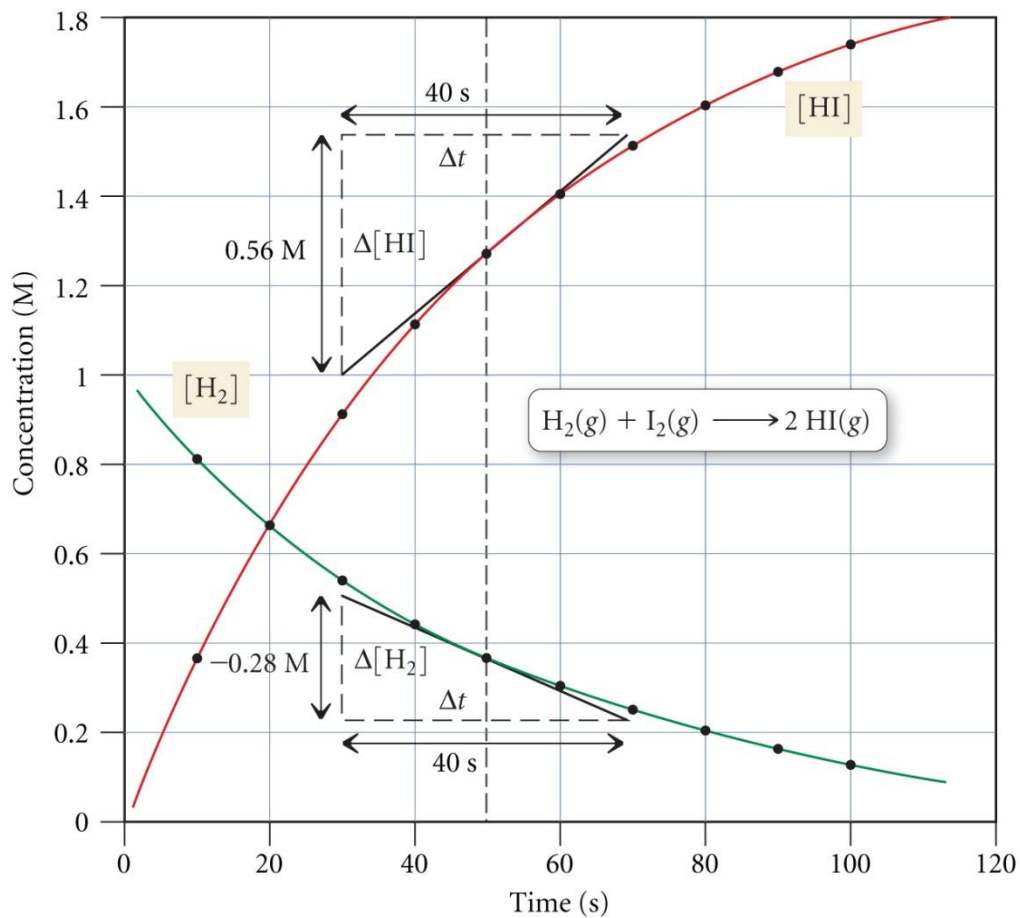
Chemical Kinetics 2

Either the concentration of reactants **or** the temperature at which a reaction occurs is typically varied when performing kinetic studies.

Concentration (the rate equation / initial rate method) and *temperature* effects (the Arrhenius equation) will be covered separately in 'Chemical Kinetics 2' & 'Chemical Kinetics 3', respectively.

Concentration and Rate – The *Initial* Rate Method

Recap: What happens to the rate of any reaction when [reactants] is increased? What fundamental *microscopic* events lead to this *macroscopic* observation?

Overview: The initial rate method involves measuring the *initial* rate of reaction (gradient of the [conc] v time plot at t=0) of *either* the disappearance of reactant(s) *or* the initial rate of appearance of product(s) *for a set of experiments featuring reactants of various starting concentrations*.

This data allows for the determination of the Rate Law Equation (discussed below). **Determining the Rate Law Equation is the primary objective of most kinetic studies**.

Recall: Generic Graph of Concentration *Reactant* v Time for a chemical reaction:
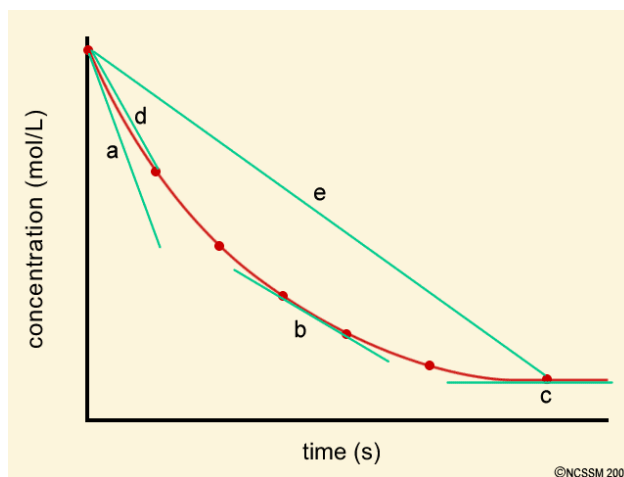
The *initial rate* of reaction ((a), gradient of the curve at t=0) is typically extrapolated. In contrast, *instantaneous rates* (b), (c) and (d) are calculated via the graphical and/or tabular methods discussed in 'Chemical Kinetics 1'. Therefore:

> The **INITIAL** RATE $\approx$ the INSTANTANEOUS RATE at t= 0

Determining the Rate Law

Discussion:

How would you expect the initial rate of reaction of any chemical process to vary with the concentration of the reactants? Express this with an equation.

Would you expect all of the reactants to be equally important with regard to the overall rate of reaction? Express this with an equation.

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A chemical equation and its respective rate law equation are related via the following generic expression:

For: $aA + bB \rightarrow cC + dD$

$$Rate = k[A]^m[B]^n$$

Graphical Examples (details later)

Rate versus Reactant Concentration

Zero order
Rate $= k[A]^0$

First order
Rate $= k[A]^1$

Second order
Rate $= k[A]^2$

Rate (M/s) vs [A]
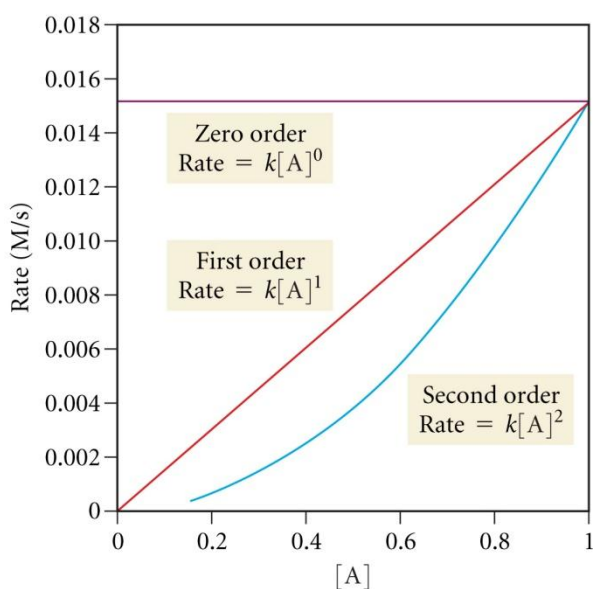
Reactant Concentration versus Time

Second order
$n = 2$

First order
$n = 1$

Zero order
$n = 0$

[A] vs Time (s)
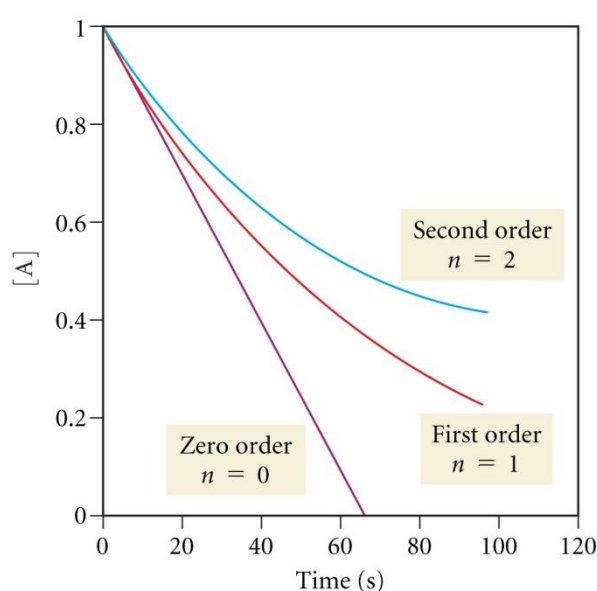
Where:

(initial) **rate** of reaction $= \dfrac{\Delta [\text{Chemical}]}{\Delta t}$

$k =$ Rate constant – determined from initial rate data

$[A], [B] =$ Reactant concentrations

m, n $=$ *Experimentally determined* (from initial rate data) reactant 'orders'. The stoichiometic constants (a, b etc) are **not** the same as the order determined for their respective concentrations (e.g. $[A]^m$, $[B]^n$) although they may *coincidently* have the same numerical value (0, 1 or 2)

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Worked Example:

For the reaction: A + B → C, the following data was obtained experimentally:

Experiment#	[A]	[B]	Initial rate (M/s)
1	0.100	0.100	4 x 10^{-5}
2	0.100	0.200	4 x 10^{-5}
3	0.200	0.100	16 x 10^{-5}

Find: a.   The rate law expression for this process
        b.   The numerical value and units of the rate constant, k
        c.   The rate of reaction when [A] = 0.05M and [B] = 0.10M
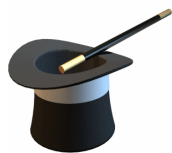
'Right off the bat' - by looking at the table, which reactant has the biggest affect on the initial rate of reaction?

Which reactant has no affect on the initial rate of reaction?

What does this mean in terms of what's happening on the microscopic level?

<u>Game Plan</u>: Assume Rate $= k[A]^m[B]^n$, then:

1.	Determine the values of m and n through 'observation' (easy problems) or by manipulating rate law expressions for specific experimental sets – 'math' method
2.	Find k via 'insert and evaluate' for an experimental data set
3.	Use the completed rate law expression to find reaction rate when $[A] = 0.05$ M and $[B] = 0.10$ M

<u>1. Finding the order of reaction with respect to each reactant</u>

To find the order of reaction for a reactant, two experimental data sets must be compared. This can be done in either of two ways - via 'Math' or though simple 'Observation'

A. 'Mathematical' Method for Determination of Reaction Orders

	Substitute values of [reactant] and initial rate directly into the respective rate expressions for a pair of experimental data sets (Note: the first data set is usually the 'denominator' – see below example)
	Divide these two equations by one another to find the value of the order of reaction for a reactant.
	Repeat the process for remaining data sets in order to determine each order of reaction for each reactant

<u>Walk through</u> Recall that: Rate $= k\ [A]^m[B]^n$ (*just substitute the numbers*)

 (2)

(1)

Now, for the missing order, divide a pair of data sets where the required reactant's conc. is altered:

$$\frac{(3)}{(1)}$$

B. 'Observation' Method for Determination of Reaction Orders

For easy numbers (like those in the example) simply use the following relationship for a pair of experimental data sets:

(Factor [reactant] is multiplied) $^{\text{order wrt that reactant}}$ = Factor rate is multiplied

Note: This method ONLY works if one [reactant] is varied (by an integer multiple) with all other [reactant(s)] remaining fixed.

e.g: For experiments (1) and (3)

[A] is doubled, while [B] remains constant. The rate increases by a factor of x4 between the two data sets (4 x 10^{-5} M/s compared to 16 x 10^{-5} M/s)

Therefore:

$$2^m = 4$$

Question: What is the value of m, i.e. the order wrt [A]?

Answer:

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<u>Task</u>: Analyze data sets 1 and 2, determine the order of reaction wrt [B]

<u>The 'orders' can now be included in the rate law expression</u>:

$$\textbf{i.e. Rate} = \textbf{\textit{k}}\textbf{[A]}^2\textbf{[B]}^0$$

The reaction is said to be 'second order wrt **A**' and 'zero order wrt **B**'

<u>Discussion</u>: What does this statement mean in terms of how each reactant affects the overall rate of reaction? Recall previous graphs.

The reaction is said to be 'second order overall'.

<u>Discussion</u>: How is the overall rate of reaction related to the individual orders of reaction for each reactant?

2. Finding the numerical value and units of k (the rate constant)
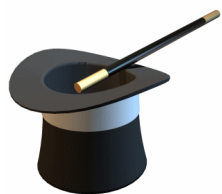
A. Substitute values of initial rate, [reactant(s)] and respective order(s) from any experimental data set into the rate expression.

B. Rearrange the equation obtained to make k the subject. Solve for k. Keep the units of each quantity in the equation – these will be determine the units of k

Note: Since the order of reaction wrt **B** is zero it can now be excluded from the rate expression. Why?

$$\text{rate} = k\,[A]^2$$

$$k = \frac{\text{rate}}{[A]^2}$$

Substituting values from Experiment #1(line 1):

$$k = \frac{4.0 \times 10^{-5}\ \text{M/s}}{[0.100\text{M}]^2}$$

$$= 4.0 \times 10^{-3}\ \text{M}^{-1}/\text{s}$$

UNITS:

The units of k depend on those of the other variables – be sure to derive the units of k work them out each time you find its numerical value

3. Use the completed rate law expression to find reaction rate for defined values of [A] and [B]

> The complete *quantitative* form of the rate equation can now be written out – simply substitute values for k and the orders wrt each reactant into the equation's generic form:

$$Rate = k[A]^m \cancel{[B]^n}$$

$$Rate = 4.0 \times 10^{-3} \ M^{-1}/s \ [A]^2$$

Task: Determine the rate of reaction when [A] = 0.05 M and [B] = 0.10 M
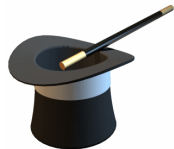
> The rate of reaction for any condition of [reactant(s)] can be determined from the quantitative form of the rate equation - simply 'insert and evaluate'.
>
> Note: Recall that the units of reaction rate are always M/s

ANS = 1.0×10^{-5} M/s

Task: Determine the quantitative rate law expression, including the numerical value of k, for the following process:

$$H_2O_2 \text{ (aq)} + 3I^- \text{ (aq)} + 2H^+ \text{ (aq)} \rightarrow I_3^- \text{ (aq)} \ H_2O \text{ (l)}$$

Initial rate data:

Experiment	$[H_2O_2]$	$[I^-]$	$[H^+]$	Initial rate (M/s)
1	0.01	0.01	0.0005	1.15×10^{-6}
2	0.02	0.01	0.0005	2.30×10^{-6}
3	0.01	0.02	0.0005	2.30×10^{-6}
4	0.01	0.01	0.0010	1.15×10^{-6}

Recall: rate $= k \ [H_2O_2]^m[I^-]^n[H^+]^p$, so values for each order (n, m and p) must be determined.

Concentration and Rate – Integrated Rate Law Expressions

Recap: The *initial*, *average* and/or '*instantaneous*' rate(s) of reaction are calculated by finding the gradient of the experimentally determined [conc.] v time plot by either:

1. Finding the gradient of a tangent line applied to the data at the point of interest *or*

2. Finding the gradient between a pair of data points straddling the point of interest
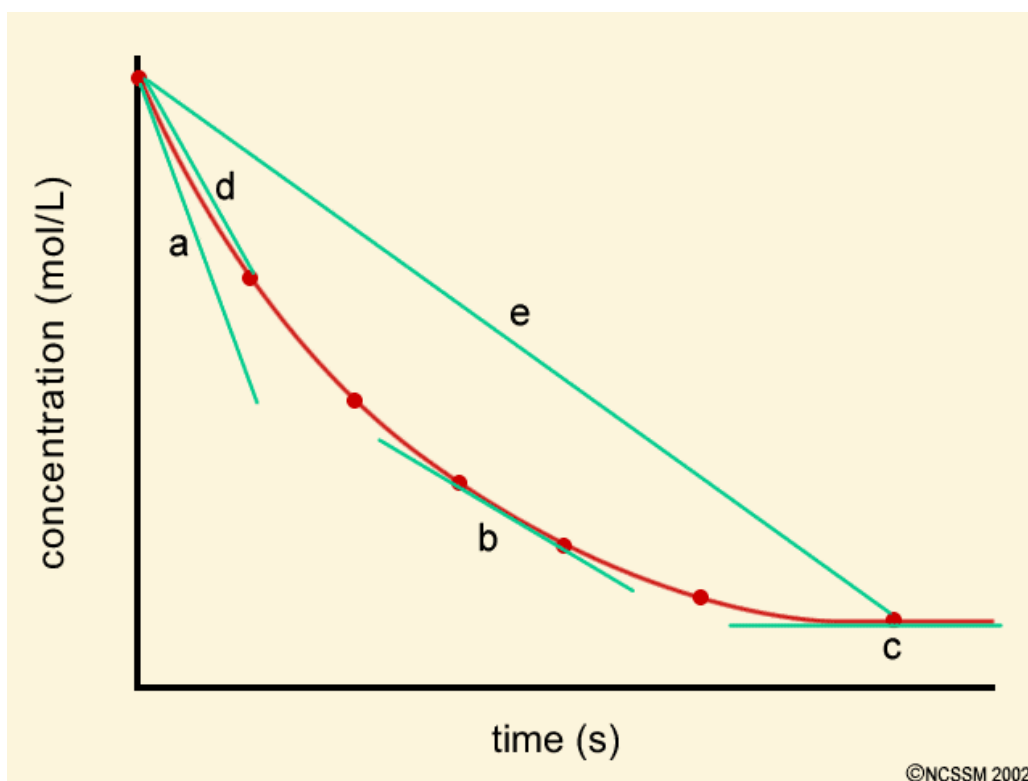
Recall: initial rate and [reactant] data acquired for a series of experimentally determined [conc.] v time plots are utilized in the determination of the reaction's respective rate law expression:

Generically:	$aA + bB \rightarrow cC + dD$	Rate $= k[A]^m[B]^n$

Discussion: Consider the following simple, generic decomposition reaction:

$$A \rightarrow B$$
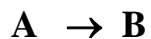
For such a reaction, which is typically either first or second order, the following respective rate expressions would apply:

1st order rxn: **Rate** $= k[A]^1$ 2nd order rxn: **Rate** $= k[A]^2$

Which reaction would proceed at a faster rate (assuming k was similar in each case) – the 1st or 2nd order process? Why?

In the boxes below, sketch simple [reactant] v time plots for chemical processes that are 1st and 2nd order *overall*, respectively. Recall previous slides.
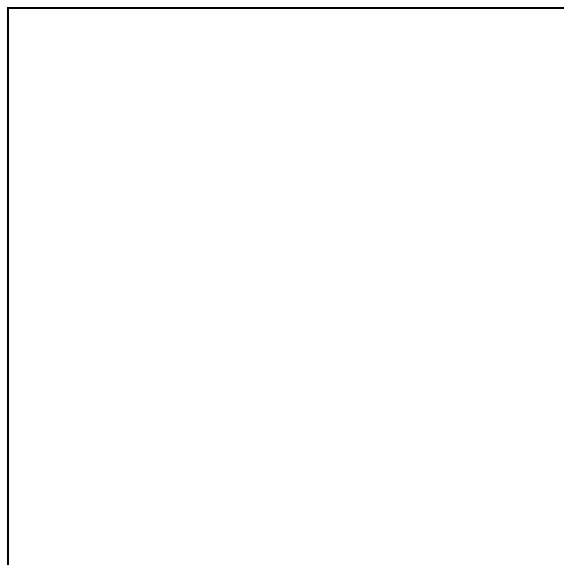
First order overall   **Second order overall**

First order processes have *'shallow'* rate of reaction curves

Second order processes have *'steep'* rate of reaction curves

Discussion: Which mathematical functions (when graphed) have similar features to the first and second order rate of reaction curves?

First and second order reaction processes may be described by $y = e^{-x}$ and $y = \frac{1}{x}$ functions, respectively

Linear ($y = mx + b$) versions of either the first or second order rate plots may be obtained through integration of their respective line-shapes.

These important results yield equations that allow k and [reactant] to be found at *any* time during the reaction

Integrated Rate Equation for 1st Order Reactions

Process: A $\rightarrow$ B   Rate $= \dfrac{-\Delta [A]}{\Delta t} = k[A]^1$

Derivation:

<u>Result:</u> $\ln [A]_t - \ln [A]_0 = -kt$ <u>or</u> $\ln [A]_t = -kt_t + \ln [A]_0$

<u>Interpretation:</u>

$$\ln [A]_t = -kt + \ln [A]_0$$
$$y = mx + b$$

> **A plot of ln (or $\log_{10}$) [reactant] v time will yield a LINEAR plot for a 1st order process.**
>
> **The plot will have a slope of $-k$ and an intercept of $\ln[A]_0$ (natural log of [reactant] at t=0)**

<u>Generic Graph</u>
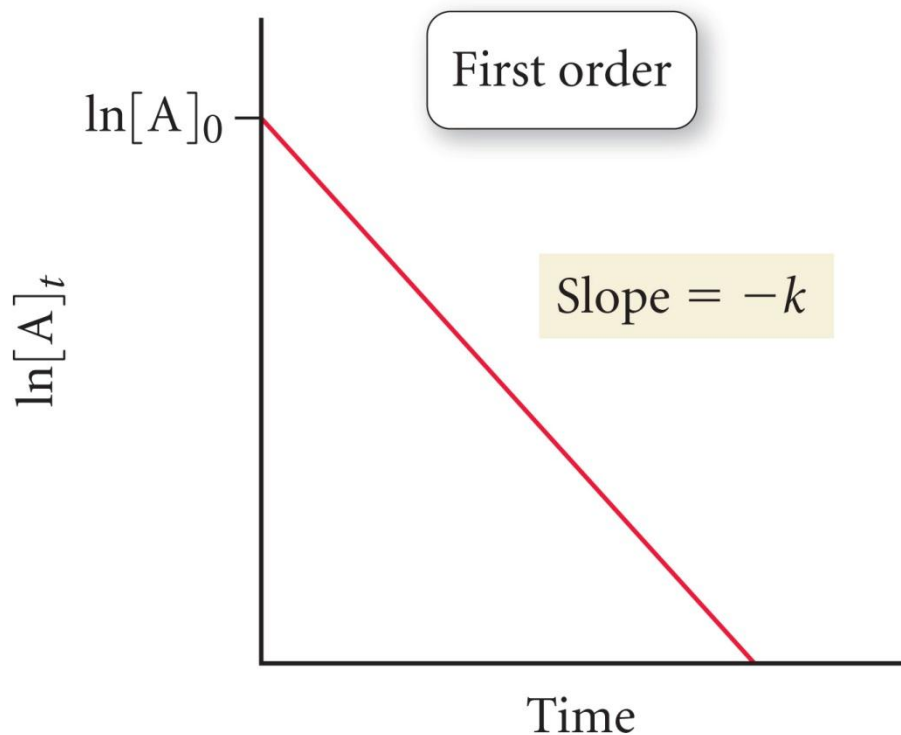
Example (p581 & appendix): the decomposition of SO_2Cl_2

$$SO_2Cl_2 \text{ (g)} \rightarrow SO_2 \text{ (g)} + Cl_2 \text{ (g)}$$

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Integrated Rate Equation for 2nd Order Reactions

Process: A → B

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k[A]^2$$

Derivation:
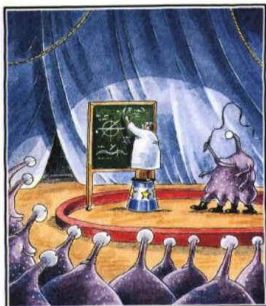
Abducted by an alien circus company,
Professor Doyle is forced to write calculus
equations in center ring.

Result: $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

Interpretation: $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

$$y = mx + b$$

> A plot of 1/[reactant] v time will yield a LINEAR plot for a 2nd order process.
>
> The plot will have a slope of k and an intercept of 1/[A]$_0$ (reciprocal of [reactant] at t=0)

Generic Graph

Second order

$$\text{Slope} = k$$

y-axis: $\dfrac{1}{[A]_t}$

$\dfrac{1}{[A]_0}$

Time
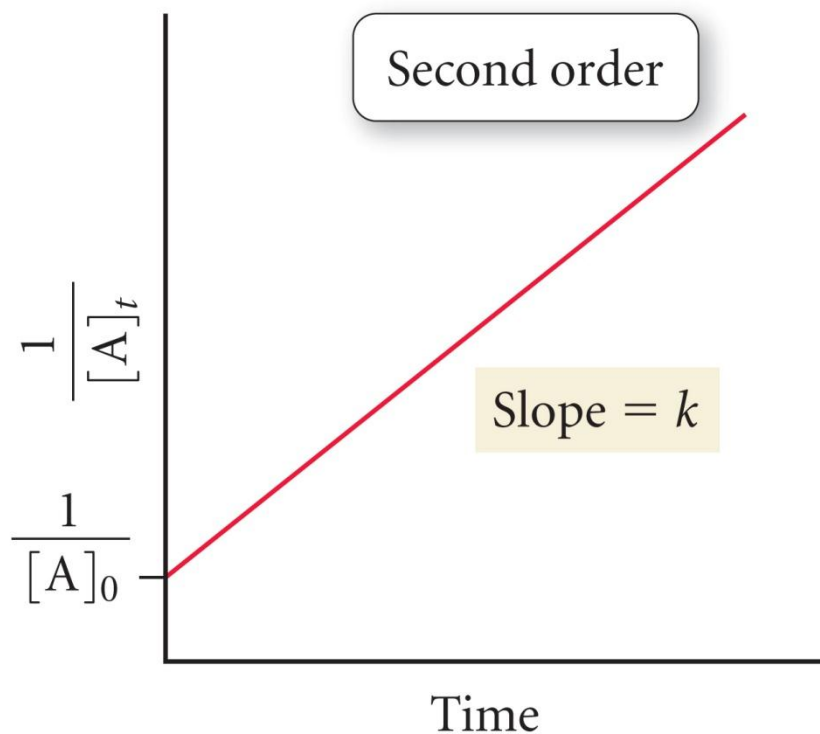
Example (p 583 & appendix): experimental data for the decomposition of nitrogen dioxide

$$2\ NO_2\ (g)\ \rightarrow\ 2\ NO\ (g)\ +\ O_2\ (g)$$
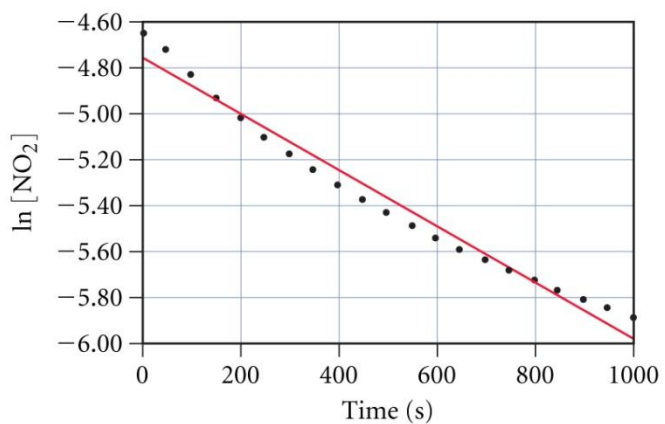
1st order plot is non liner – **reject**

$y = 0.255x + 100$
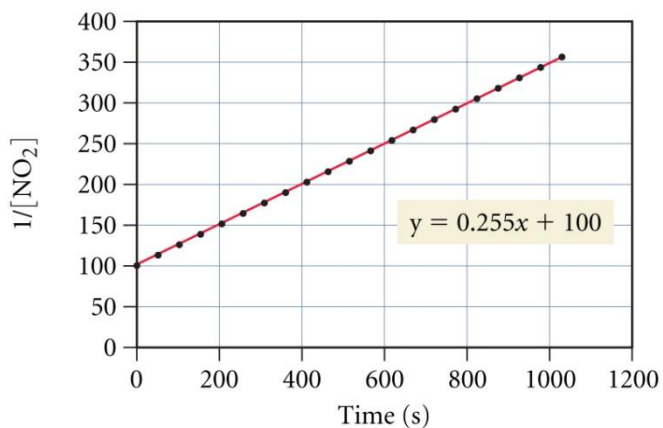
2nd order plot is liner – '**good to go**'!

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<u>Worked Example</u>: For the reaction:

$$2 \ N_2O_5 \ (g) \ \rightarrow \ 4 \ NO_2 \ (g) \ + \ O_2 \ (g)$$

The following data was acquired via an initial rates experimental analysis:

$$Rate = k \ [N_2O_5]^1, \ \ where \ k = 4.8 \ x \ 10^{-4} \ s^{-1}$$

<u>Task</u>: If the initial concentration of dinitrogen pentoxide is $5.0 \ x \ 10^{-3}$ M, what is this reactant's concentration after 625 seconds?

<u>Discussion</u>: How would you solve this problem (there are two methods)?

<u>Plan and execution</u>:

<u>ANS</u>: $3.7 \ x \ 10^{-3}$ M

Reaction Half-Life

Discussion: What do you understand by the phrase 'half-life'
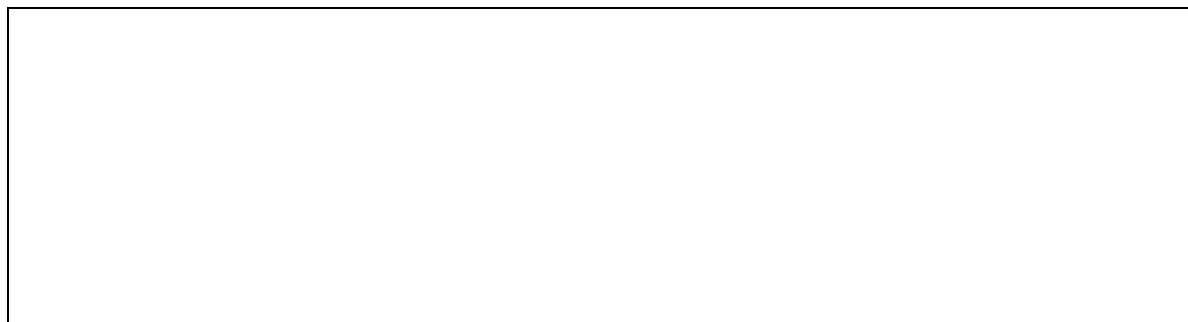
Relationship between [reactant] and time for 1, 2 and 3 half-lives

At t_0

For a first-order reaction, the half-life is constant and independent of concentration

After 1 half-life

After 2 half-lives

After 3 half-lives
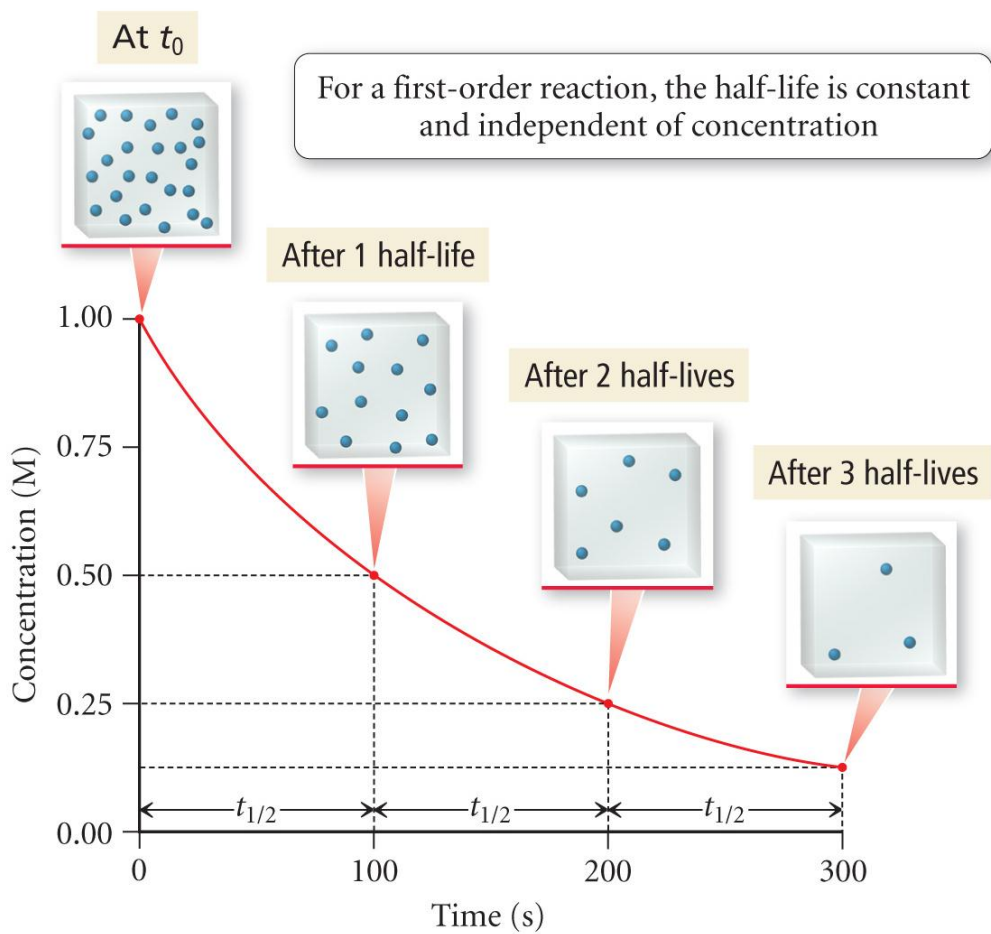
<u>Half–life expressions</u>
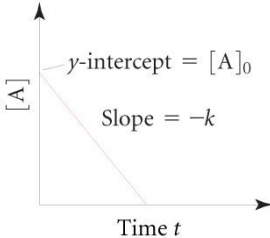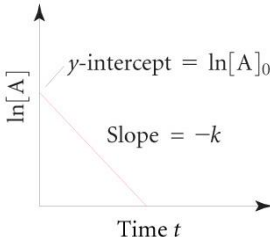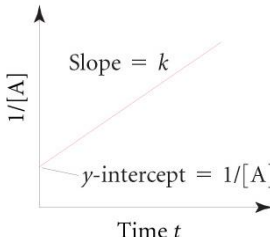
> **By definition, the [reactant] ([A]$_t$) is exactly half it's initial value ([A]$_0$) after one half-life for any reaction.**
>
> This fact allows for relationships between half-life (t$_{1/2}$), k and (for second order processes) [A]$_0$ to be determined

<u>Derivation</u>: 1st order reactions

<u>Task</u>: Derive an expression for the half-life of a 2nd order process in terms of k and [A]$_0$

<u>Summary</u>: (p 587 & appendix)

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	$\text{Rate} = k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$	$y\text{-intercept} = [A]_0$ $\text{Slope} = -k$	$t_{1/2} = \dfrac{[A]_0}{2k} = \dfrac{1}{k}\dfrac{[A]_0}{2}$
1	$\text{Rate} = k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln\dfrac{[A]_t}{[A]_0} = -kt$	$y\text{-intercept} = \ln[A]_0$ $\text{Slope} = -k$	$t_{1/2} = \dfrac{0.693}{k} = \dfrac{1}{k}(0.693)$
2	$\text{Rate} = k[A]^2$	$M^{-1}s^{-1}$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\text{Slope} = k$ $y\text{-intercept} = 1/[A]_0$	$t_{1/2} = \dfrac{1}{k[A]_0} = \dfrac{1}{k}\dfrac{1}{[A]_0}$

<u>Example</u>: For the reaction:

$$SO_2Cl_2\ (g)\ \rightarrow\ SO_2\ (g)\ +\ Cl_2\ (g)$$

Assuming the reaction is first order overall and $k = 2.20 \times 10^{-5}\ s^{-1}$, then:

1. What is the half-life of SO_2Cl_2 (g)?

2. How long would it take for 50% of the sample to decompose?

3. How long would it take for 75% of the sample to decompose? Trick??

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Question (14.19)

For the reaction: A + B → C

The rate equation has the form: rate $= k\,[A]^x$. What is the value of x if:

   a. The rate triples when [A] triples?

   b. The rate increases eightfold when [A] is doubled?

   c. There is no change in rate when [A] is tripled?

Discussion: What is the 'trick' (i.e. what underlying theory is being tested?)

The following question was taken from your 1st practice midterm:

Consider the generic reaction:

$$A + B + C \rightarrow D$$

Assuming the above reaction was analyzed using the initial rate method at 25°C, use the data below to determine:

1. The order of reaction with respect to each reactant and the overall order of the reaction. **Summarize your findings in the form of a complete rate equation**.
2. The value of k at this temperature.
3. What is the rate of reaction when the concentrations of *each* reactant is 0.50 M,

Experiment	Initial concentrations (molL^{-1})			Initial rate (molL^{-1}s^{-1})
	A	B	C	
1	0.10	0.10	0.50	1.5 x 10^{-6}
2	0.20	0.10	0.50	3.0 x 10^{-6}
3	0.10	0.20	0.50	6.0 x 10^{-6}
4	0.10	0.10	1.00	1.5 x 10^{-6}

Question 3a (10 points): The decomposition of N_2O_5 (g) is a first order process:

$$2N_2O_5 \text{ (g)} \quad \rightarrow \quad 4NO_2 \text{ (g)} + O_2 \text{ (g)}$$

The concentration of N_2O_5 (g) may be monitored with time using a simple diode colorimeter. If, during such an experiment, k is determined to be 5.2 x 10^{-4} s^{-1}, then what is the half-life of the reaction measured in minutes?

Question 3b (15 points): If, in the above experiment, an absorbance of 0.84 is recorded immediately prior to the commencement of N_2O_5 (g) decomposition (i.e. at t = 0), then what absorbance value will be recorded record after exactly one half-life has passed? Recall that Abs $\propto$ [N_2O_5]

For the above reaction, what Abs value would be detected by the colorimeter after exactly three half-lives had passed?

Zero order

Slope $= -k$

Time

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First order

Slope = $-k$

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Slope y intercept

$y = -0.000290t - 2.30$

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Second order

$$\frac{1}{[A]_t}$$

$$\frac{1}{[A]_0}$$

Slope $= k$

Time

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$y = 0.255x + 100$

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Half-Life for a First-Order Reaction

At t_0

For a first-order reaction, the half-life is constant and independent of concentration

After 1 half-life

After 2 half-lives

After 3 half-lives

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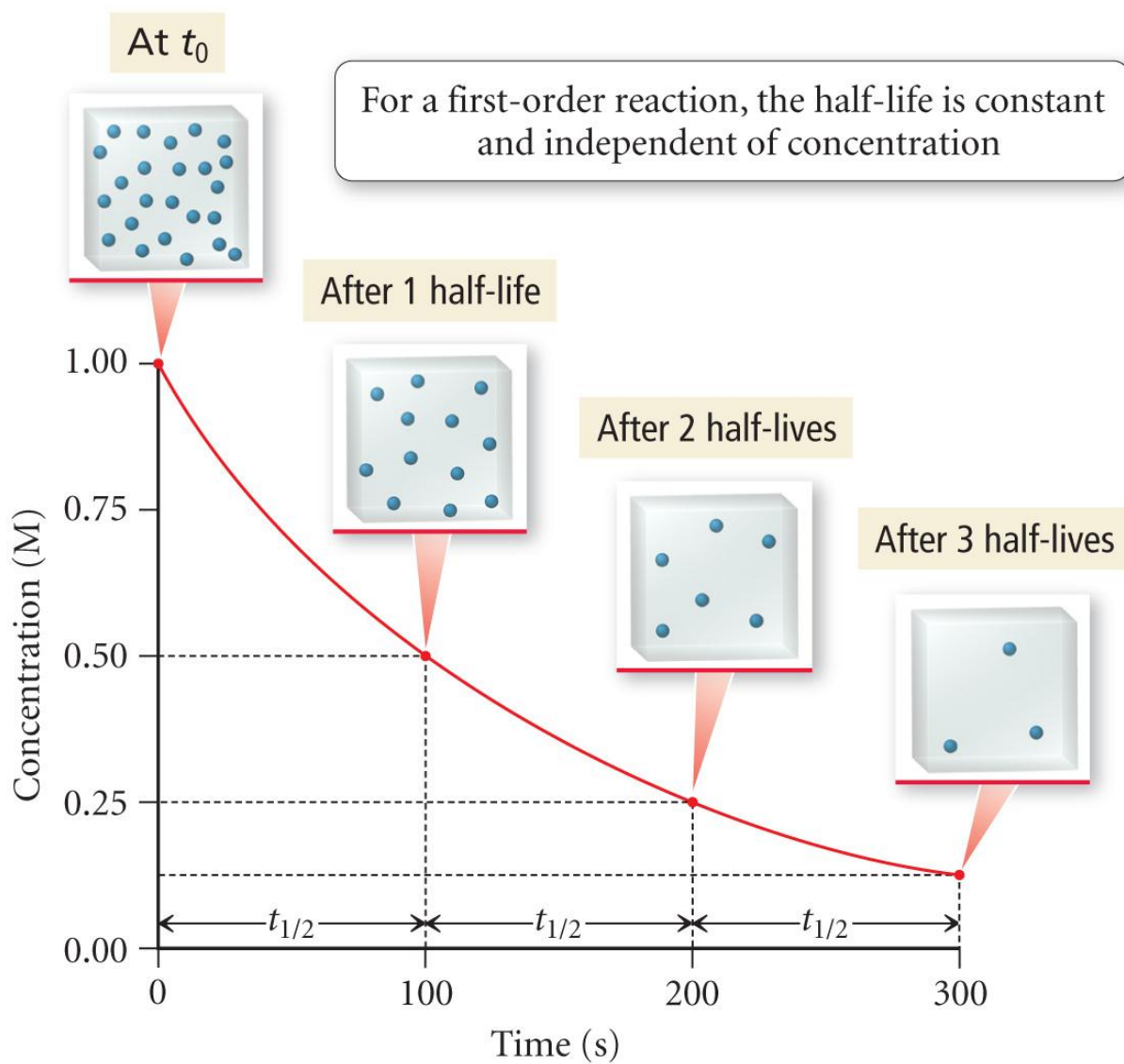
TABLE 13.2 Rate Law Summary Table

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate $= k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$	y-intercept $= [A]_0$; Slope $= -k$ (plot of $[A]$ vs. Time t)	$t_{1/2} = \dfrac{[A]_0}{2k} = \dfrac{1}{k}\dfrac{[A]_0}{2}$
1	Rate $= k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\quad$ $\ln\dfrac{[A]_t}{[A]_0} = -kt$	y-intercept $= \ln[A]_0$; Slope $= -k$ (plot of $\ln[A]$ vs. Time t)	$t_{1/2} = \dfrac{0.693}{k} = \dfrac{1}{k}(0.693)$
2	Rate $= k[A]^2$	$M^{-1}s^{-1}$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	Slope $= k$; y-intercept $= 1/[A]_0$ (plot of $1/[A]$ vs. Time t)	$t_{1/2} = \dfrac{1}{k[A]_0} = \dfrac{1}{k}\dfrac{1}{[A]_0}$

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Chemical Kinetics 3

| Reading: | Ch 13 sections 5-7 | Homework: | Chapter 13: 57*, 59*, 61*, 63*, 65*, 69, 73, 75 Excel assignment* (see assignments for link) |

* = 'important' homework question

Temperature and Rate – Transition State Theory and the Arrhenius Equation

Background: Recall that the number of 'fruitful' collisions per unit time among the reactant(s) determine the overall rate of reaction.

Discussion: What factors determine if a *single* collision will be fruitful?

1.	
2.	
3.	

| 🔑 | **The above are the three basic assumptions of *collision theory*** |

Collision Theory

For a reaction to occur, the reactant molecules must collide with energy greater than some minimum value (E_a) and have the correct spatial orientation. E_a is the activation energy.

Recap: At a defined temperature, a reaction rate is described by the rate equation:

Generically: $aA + bB \rightarrow cC + dD$ $Rate = k[A]^m[B]^n$

Observation: Rates of reaction typically increase *substantially* for a relatively small elevation of temperature.

Discussion: How does increasing temperature effect the rate equation?

(see slide of k v temp)

The makeup of k

The three collision theory variables (*energy of reactants*, *frequency of collisions* and *orientation of reactants*), when combined, give rise to the rate constant k. Clearly, the value of k varies with temperature(!)

Mathematically:

$$k = Zpf$$

where: k = rate constant

Z = frequency of collisions

p = fraction of molecules with correct orientation

f = fraction of molecules with E_a or greater

Discussion: To what extent are Z, p and f affected by temperature?

Collision Frequency (Z) – recall *Chemical Kinetics 1*

$$KE = \tfrac{1}{2}\,mv^2 = kT \text{ (k is the Boltzmann constant). } \textbf{i.e. Temp} \propto \textbf{v}^2$$

Reactant Orientation (p)

Random (see slide) – temp has NO effect, some *fixed* fraction of reactant(s) will have the correct orientation

(a) Proper orientation — Reaction products: N_2O ... $+$ ... $O\,C\,O$

(b) Wrong orientation — No reaction

(c) Wrong orientation — No reaction

(d) Wrong orientation — No reaction
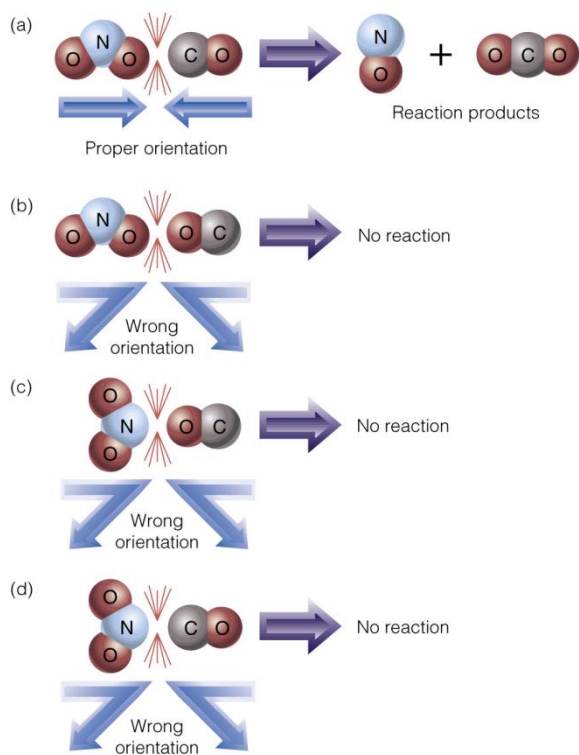
Transition State Theory

Only reactants colliding with the correct orientation (a) may give rise to an *activated complex*, or *transition state* species

The reactants must also have greater than a minimum amount of 'collision energy' (E_a, see next) in order to form an activated complex (see additional slide).

We will return to this topic later in the handout

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Fraction of molecules with E$_a$ or greater (f)

Q: Do all molecules of a compound have the same speed at, say, room temperature?

A:

The distribution of molecular speeds - the Boltzmann distribution

Features

As temperature increases, the fraction
of molecules with enough energy to surmount
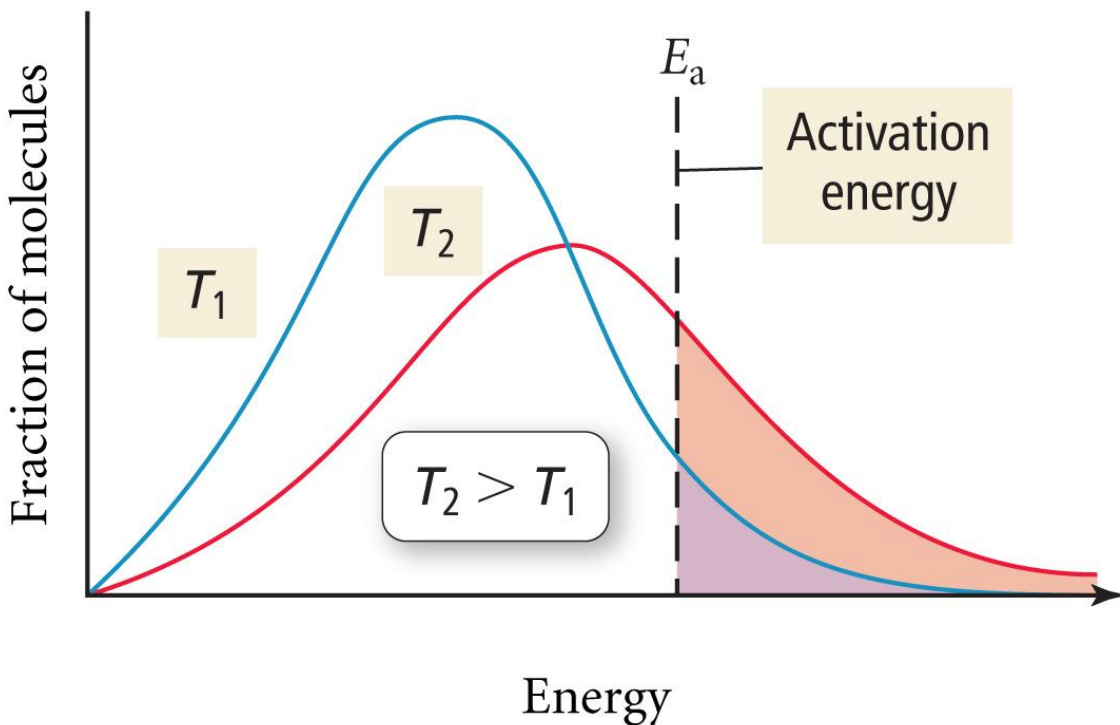the activation energy barrier also increases.

Due to the line shape of the Boltzmann distribution, the fraction of molecules with E_a or greater has an exponential relationship with temperature:

Since the fraction of molecules with the correct orientation (p) is fixed and the frequency of collisions (Z) does not vary significantly for a small change in temperature, these two variables are combined into a single constant called the 'frequency factor' (A):

The Arrhenius Equation
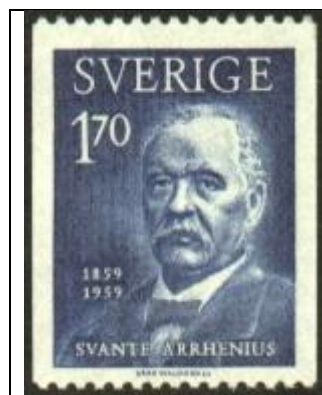
The _Arrhenius Equation_ combines the above variables and, so, relates k to activation energy and temperature for any reaction

$$k = Ae^{-E_a/RT}$$

frequency factor   activation energy   ideal gas constant   Arrhenius Equation

We will return to the Arrhenius equation soon, but first, more on transition state theory and activated complexes….

Definition of an Activated Complex

An unstable grouping of atoms, formed during a fruitful collision, that breaks apart to form reaction product(s)

> **A short lived activated complex (transition state) is formed during a fruitful collision**
>
> **The activated complex, once formed, quickly decomposes to give reaction products**
>
> **The energy needed to form an activated complex is equal to or greater than the respective reaction's activation energy (E_a)**
>
> **"If you think about it, reactions are *really* all about making activated complexes"**

Example: The isomerization of methylisonitrile (see slide and appendix)

$$CH_3NC \text{ (g)} \rightarrow [\text{activated complex }]^{\ddagger} \rightarrow CH_3CN \text{ (g)}$$

Reaction Pathway (coordinate) diagram

Analogy
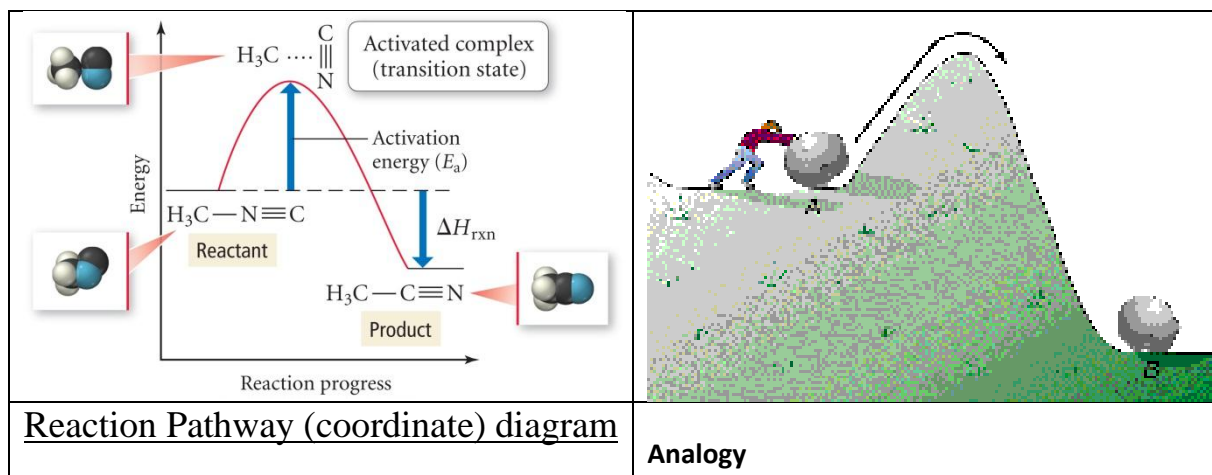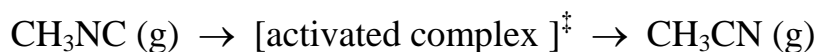
"Activation energy gets you over the 'hump' needed to start a reaction" - think about this in terms of why you have to strike a match or spark your stove.

> **A reaction cannot proceed unless the reactants have achieved or surpassed the necessary activation energy (E_a) for the chemical process**

OK, back to the Arrhenius Equation….

$$k = Ae^{-E_a/RT}$$

frequency factor *activation energy* *ideal gas constant*

Arrhenius Equation

> 🔑 **A LINEAR version of the Arrhenius Equation, in terms of k and T, is required to determine the activation energy (E_a) for a chemical process.**

<u>Derivation</u>: The two linear forms of the Arrhenius equation

<u>Interpretation</u>

$$\ln k = \frac{-Ea}{R}\frac{1}{T} + \ln A \qquad \underline{OR} \qquad \ln k_2 - \ln k_1 = \frac{-Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$y = m \quad x \ + b \qquad\qquad (y_2 - y_1) = m \quad (x_2 - x_1)$$

> 🔑 **A plot of ln k v 1/T (for k determined at different temperatures) for any chemical process will yield a LINEAR plot with slope equal to $-E_a/R$. <u>OR</u>**
>
> **Two points from the Arrhenius data (ln k_1, 1/T_1) and (ln k_2, 1/T_2) may be used to find E_a mathematically**

Generic Arrhenius Plot of ln k v 1/T

ln A

slope = $-E_a/R$

ln k

$\frac{1}{T}(K^{-1})$

©NCSSM 2002
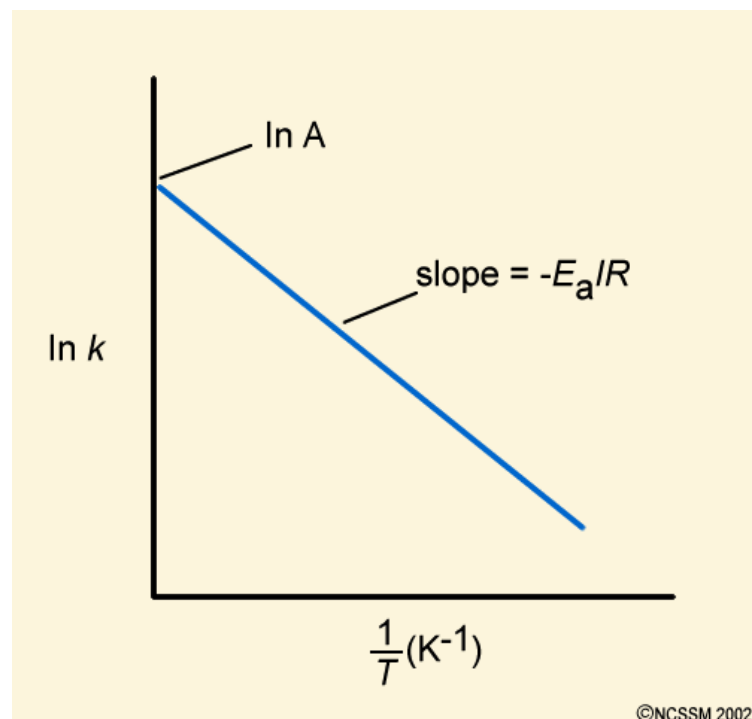
The following data was determined:

Experiment	k	T (K)		
1.	1.05×10^{-3}	759		
2.	2.14×10^{-2}	836		

Questions: What is E_a? What is k at 865 K?

<u>Discussion</u>: How would you solve these problems (there are two general methods)?

<u>Plan and execution</u>:

The rate of a particular reaction is quadrupled when the temperature was increased from $55^oC \rightarrow 60^oC$. What is E_a for this process?

Work in groups of 3 or 4 – try to figure out the 'trick'

Reaction Mechanisms

Definition of Reaction Mechanism: A combination of *elementary steps* resulting in the formation of product(s) from reactant(s)

Example: The following reaction has a single, *bimolecular*, *elementary step*:

$$NO\ (g)\ +\ O_3\ (g)\ \rightarrow\ [NOO_3]^{\ddagger}\ \rightarrow\ NO_2\ (g)\ +\ O_2\ (g)$$

bimolecular – involves the collision of two reactant molecules (NO and O_3)

elementary step – ONE collision or other molecular scale event

molecularity – the number of molecules involved in an elementary step

Note: Reactions can also feature *unimolecular* (e.g. isomerization of methylisonitrile, any nuclear decay) or (rarely, why?) *termolecular* elementary steps.

Elementary Steps and their rate laws (fill in the blanks)

Molecularity	Elementary Step	Rate Law
*Uni*molecular	A → products	Rate = $k[A]^1$
*Bi*molecular	A + A → products	Rate = $k[A]^2$
*Bi*molecular	A + B → products	Rate = $k[A]^1[B]^1$
*Ter*molecular	A + A + A → products	Rate = $k[A]^3$
*Ter*molecular	A + A + B → products	Rate =
*Ter*molecular	A + B + C → products	Rate =

<u>Discussion</u>: For the above reactions, which feature single elementary steps, do you see any correlation between the molecularity and the overall order in each case?

DANGER! DANGER! WILL ROBINSON...

DO NOT assume molecularity (stoichiometry) and reaction order are numerically identical for all reactions. This IS true for elementary steps, but *not* for multi-step reactions (discussed below).

Recall from *Chemical Kinetics 2* that orders of reaction must be determined from initial rate (experimental) data

Multiple Step Reactions

Most reactions feature two or more elementary steps – these are called multi-step reactions

<div style="border: 1px solid black; padding: 10px;">

🔑 The mechanism (and balanced chemical equation) for a multi-step reaction is the sum of its individual elementary steps.

</div>

Example: The formation of NO and CO_2 from NO_2 and CO

Elementary step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ (slow)

Elementary step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

Combine steps: $NO_2 + NO_2 + NO_3 + CO \rightarrow NO_3 + NO + NO_2 + CO_2$

What's that itch??

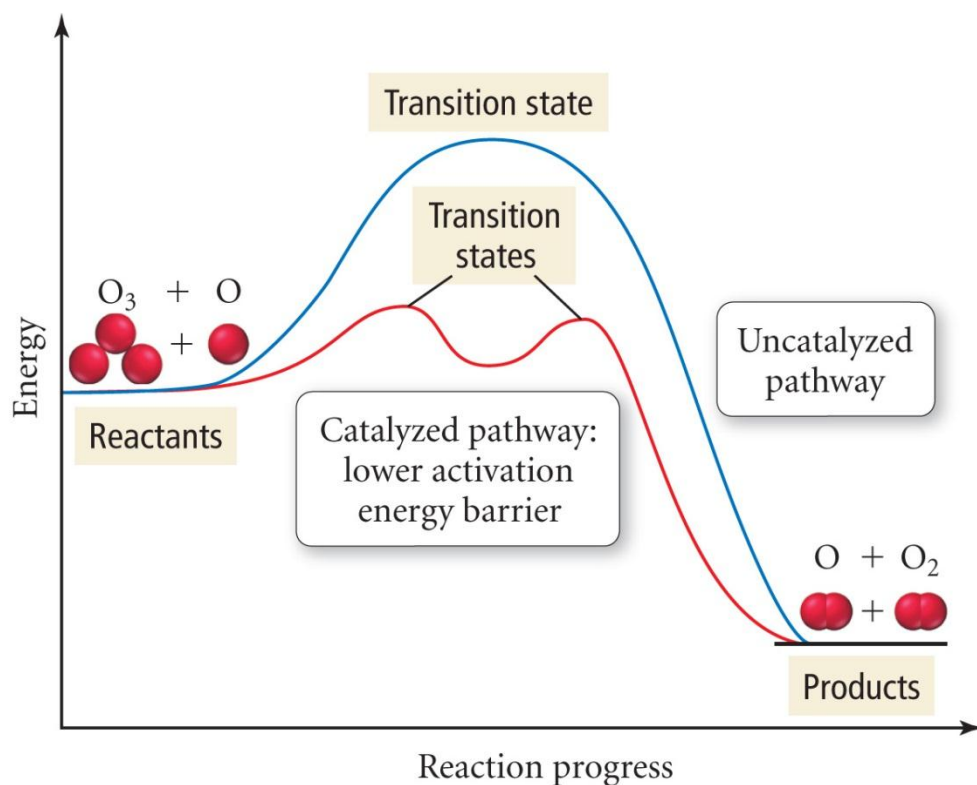Net Reaction:

<table>
<tr>
<td></td>
<td>

The overall rate of a multi-step reaction is limited by its slowest single elementary step (the *rate limiting step*) – this fact was utilized in your recent clock reaction lab. How?

Analogy: A production line is only as fast as its slowest person – "quit showing off Frank, these pies need to go in the oven!"

</td>
</tr>
</table>

Catalysis

Background: As we saw in *Chemical Kinetics 1*, a catalyst speeds up the rate of reaction without being consumed in the process. We discovered that, in part, this is due to the catalyst (be it homogeneous *or* heterogeneous) increasing the *local* reactant concentration. However, this is only part of the story - what's really going on behind the curtain?
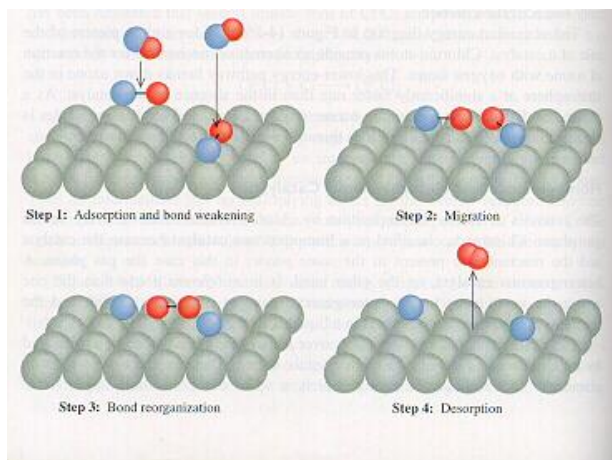

A catalyst provides an ***alternate reaction pathway***, which, in turn, consists of two or more elementary steps.

While the *total* activation energies for the uncatalyzed and catalyzed pathways are the same, that of the catalyzed process is made up from the sum of each elementary step's activation energies.

A greater fraction of molecules (recall the Boltzmann distribution) will have kinetic energy greater than, or equal to, that of the largest E_a for the catalyzed reaction's elementary steps

Case study: The conversion of NO_2 (g)$\rightarrow$ N_2 (g) + O_2 (g) by your car's catalytic converter

Step 1: Adsorption and bond weakening
Step 2: Migration
Step 3: Bond reorganization
Step 4: Desorption

The (catalyzed) reaction is now composed of four(+) individual processes, each with its own E_a, that occur at the catalyst surface:

a. NO_2 (g) $\rightarrow$ NO_2 (ads)
b. 2 NO_2 (ads) $\rightarrow$ O_2(ads) + 2 N (ads)
c. O_2 (ads) $\rightarrow$ O_2(g)
d. 2 N (ads) $\rightarrow$ N_2(ads) (not shown)
e. N_2 (ads) $\rightarrow$ N_2(g) (not shown)

The sum of these reactions E_as equals that of the uncatalyzed reaction

Homogeneous Catalysis

Homogeneous catalysts 'do the same job' as heterogeneous catalysts, *but are in the same phase as the reactants* **– typically in solution.**

Examples of homogeneous catalysts include aqueous ions, such as H^+, or aqueous transition metal complexes, such as $TiCl_4$.
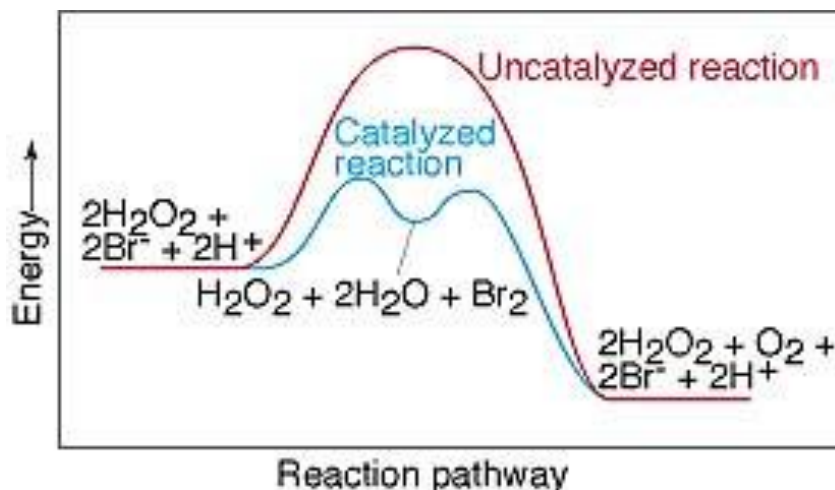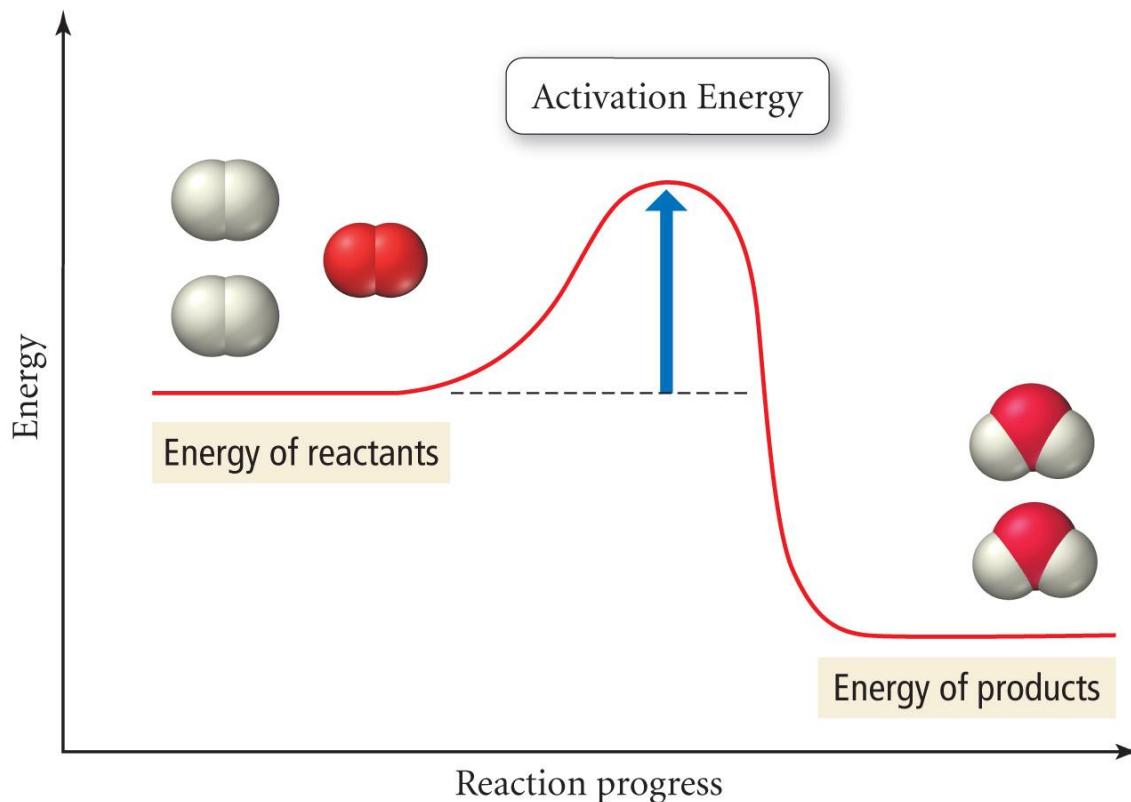
"Arrhenius"

The following question was taken from your 2nd practice midterm:

Question 1 (25 points): The activation energy for a certain reaction is 65.7 kJ/mol. How many times faster will the reaction occur at 50^oC than 0^oC?

Activation Energy

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

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$$k = Ae^{\frac{-E_a}{RT}}$$

Activation energy

Frequency factor

Exponential factor

$CH_3-N\equiv C \longrightarrow CH_3-C\equiv N$
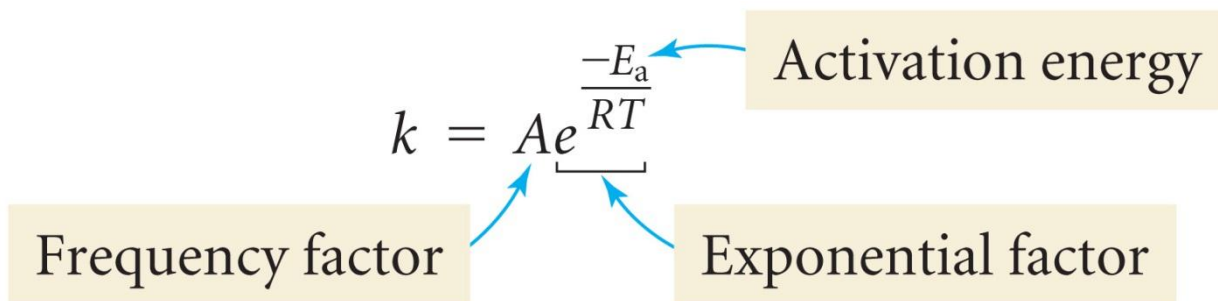
Activated complex (transition state)

$H_3C \cdots \overset{\displaystyle C}{\underset{\displaystyle N}{\parallel\parallel}}$

Activation energy (E_a)

$H_3C-N\equiv C$

Reactant

ΔH_{rxn}

$H_3C-C\equiv N$

Product

Energy

Reaction progress
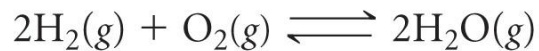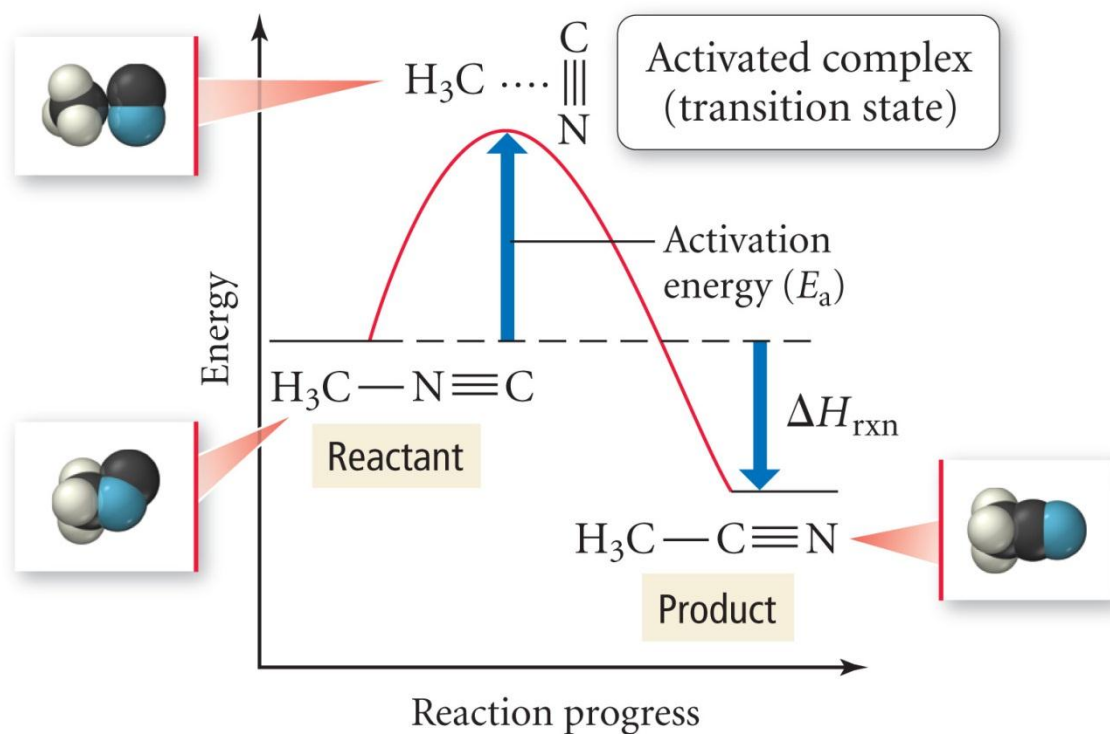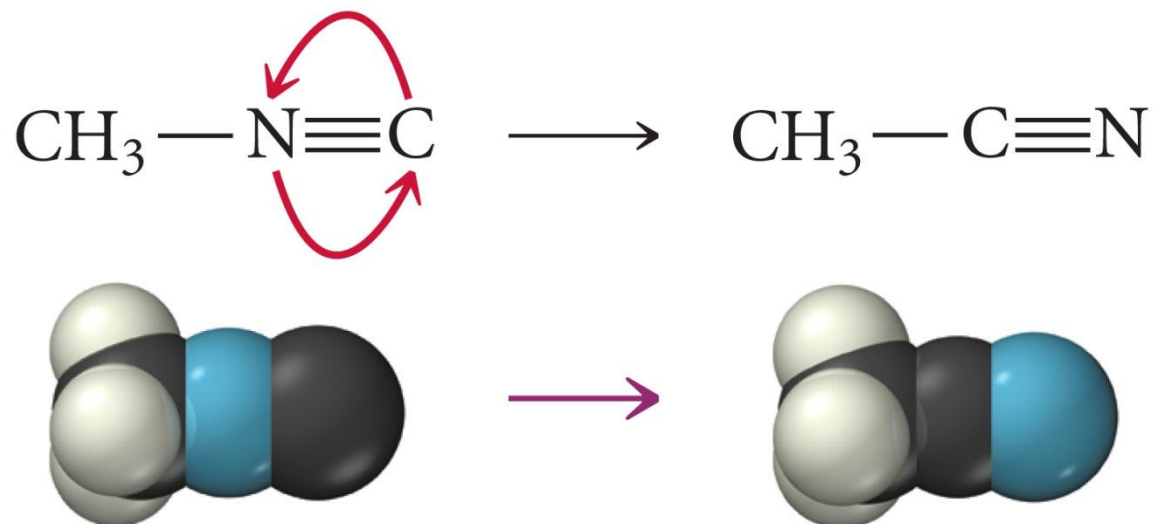
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Bond weakens
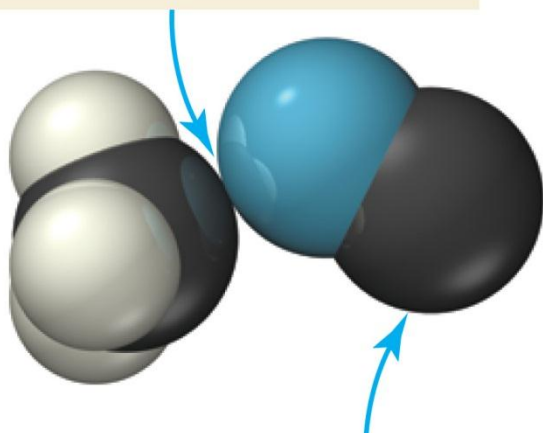
NC group begins to rotate

Activation
energy
(E_a)

Energy

Reaction progress

108
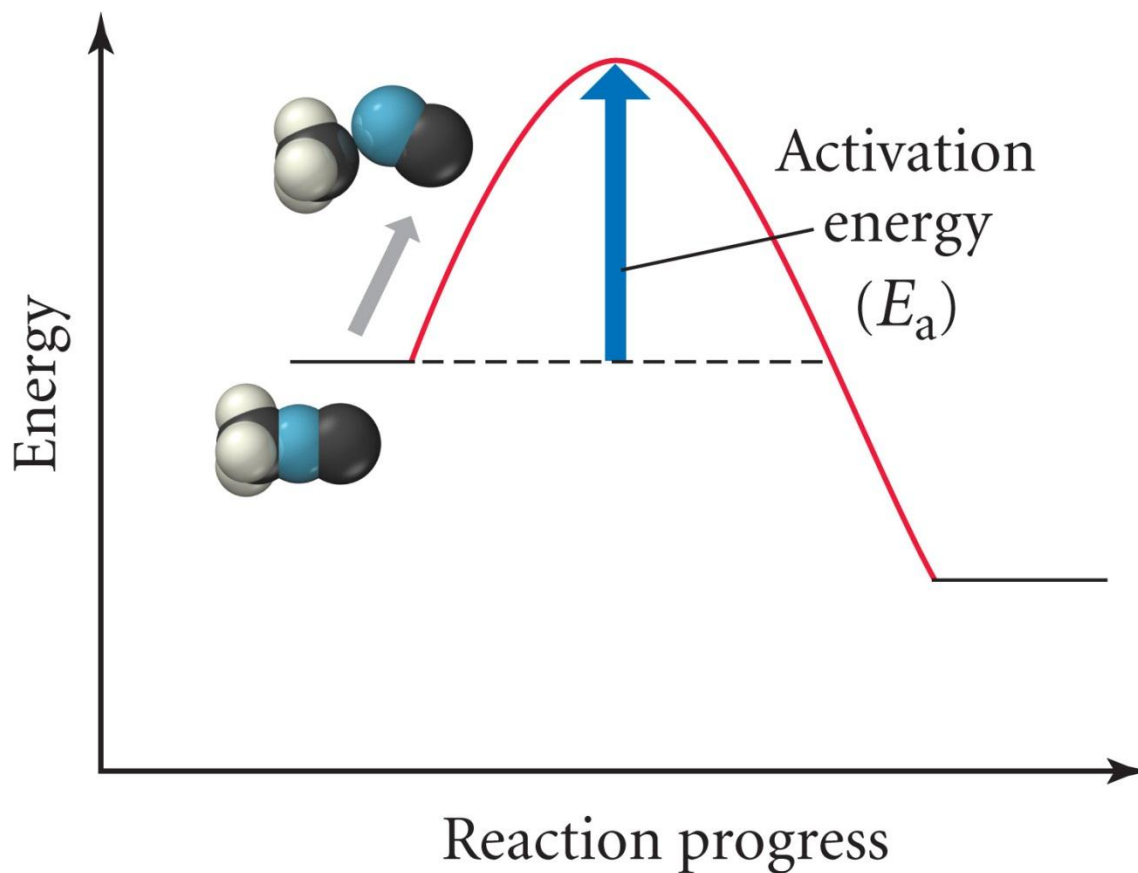
Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.
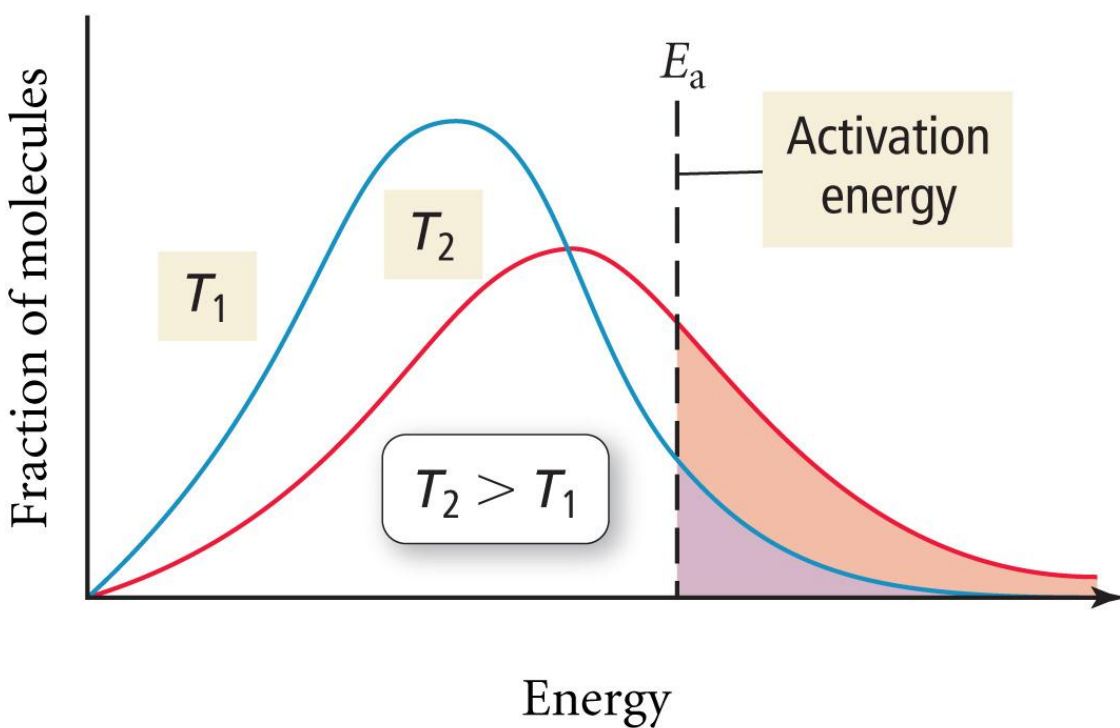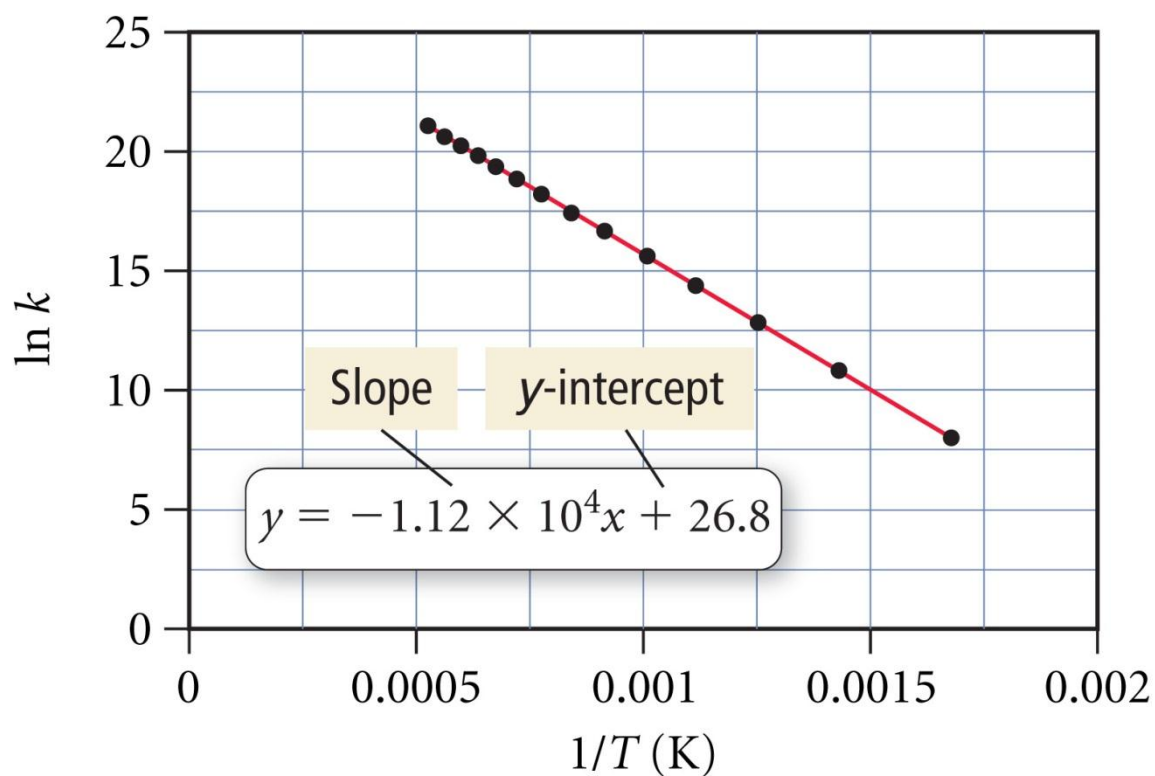
$$k = Ae^{\frac{-E_a}{RT}}$$

$$= pze^{\frac{-E_a}{RT}}$$

Orientation factor   Collision frequency

Energetic collision
leads to product
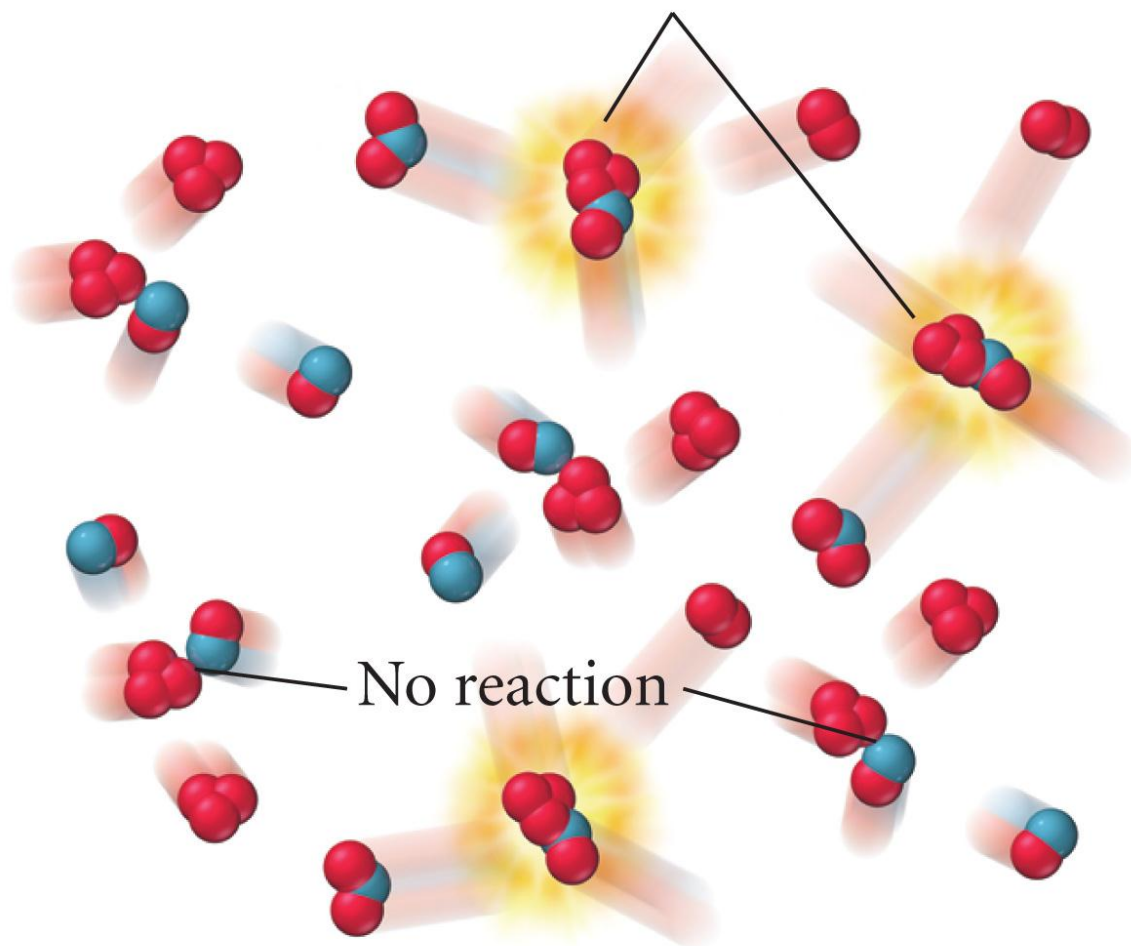
No reaction

$$NOCl(g) + NOCl(g) \longrightarrow 2\ NO(g) + Cl_2(g)$$
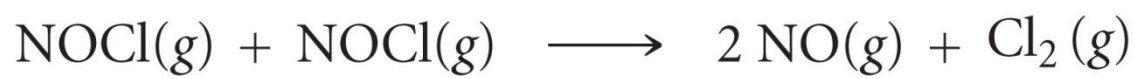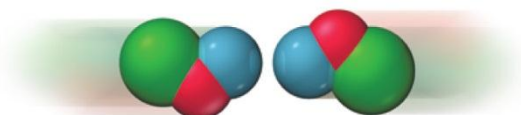
Ineffective collision
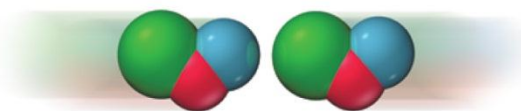
Ineffective collision
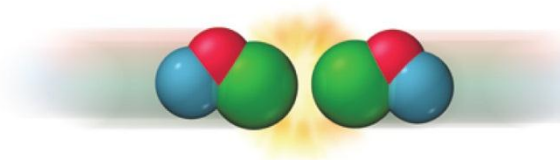
Effective collision

Energy Diagram for a Two-Step Mechanism

Because E_a for step 1 > E_a for step 2, step 1 has the smaller rate constant and is rate-limiting.

Transition states

• Step 1 has higher activation energy.

• Step 1 has smaller rate constant.

• Step 1 determines overall rate.

E_{a1}

E_{a2}

Energy

Reactants

ΔH_{rxn}

Products

Step 1

Step 2

Reaction progress
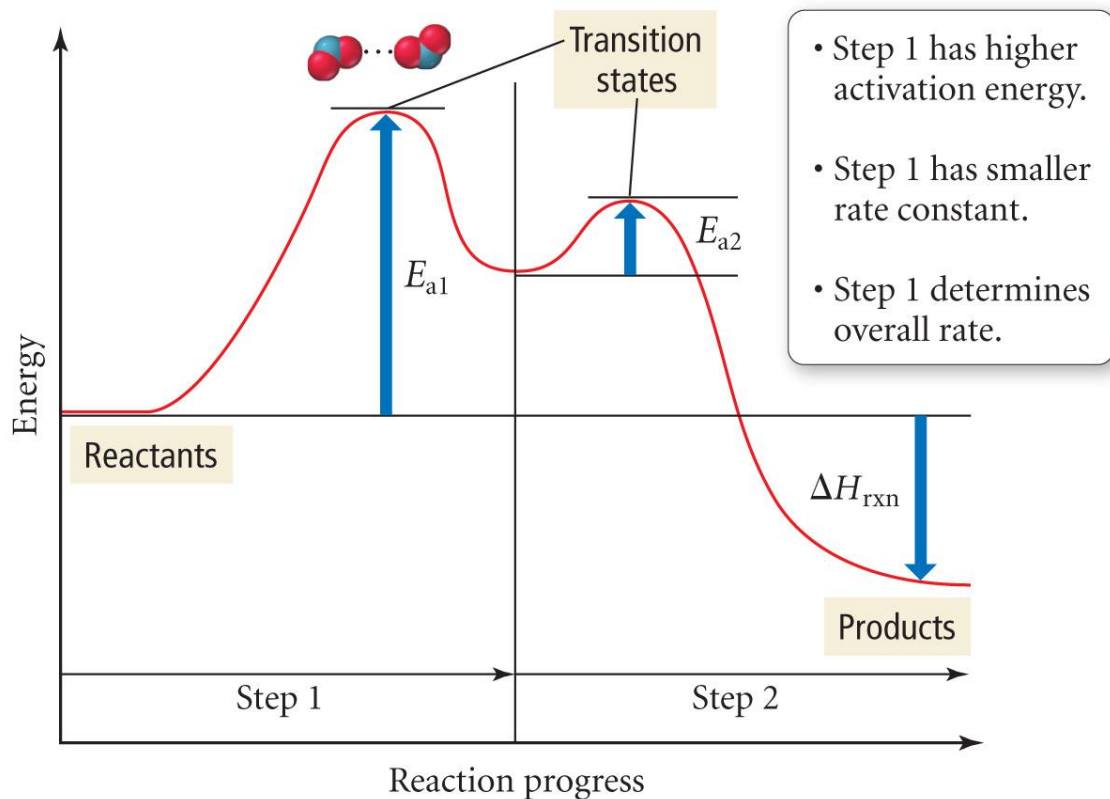
Energy Diagram for Catalyzed and Uncatalyzed Pathways
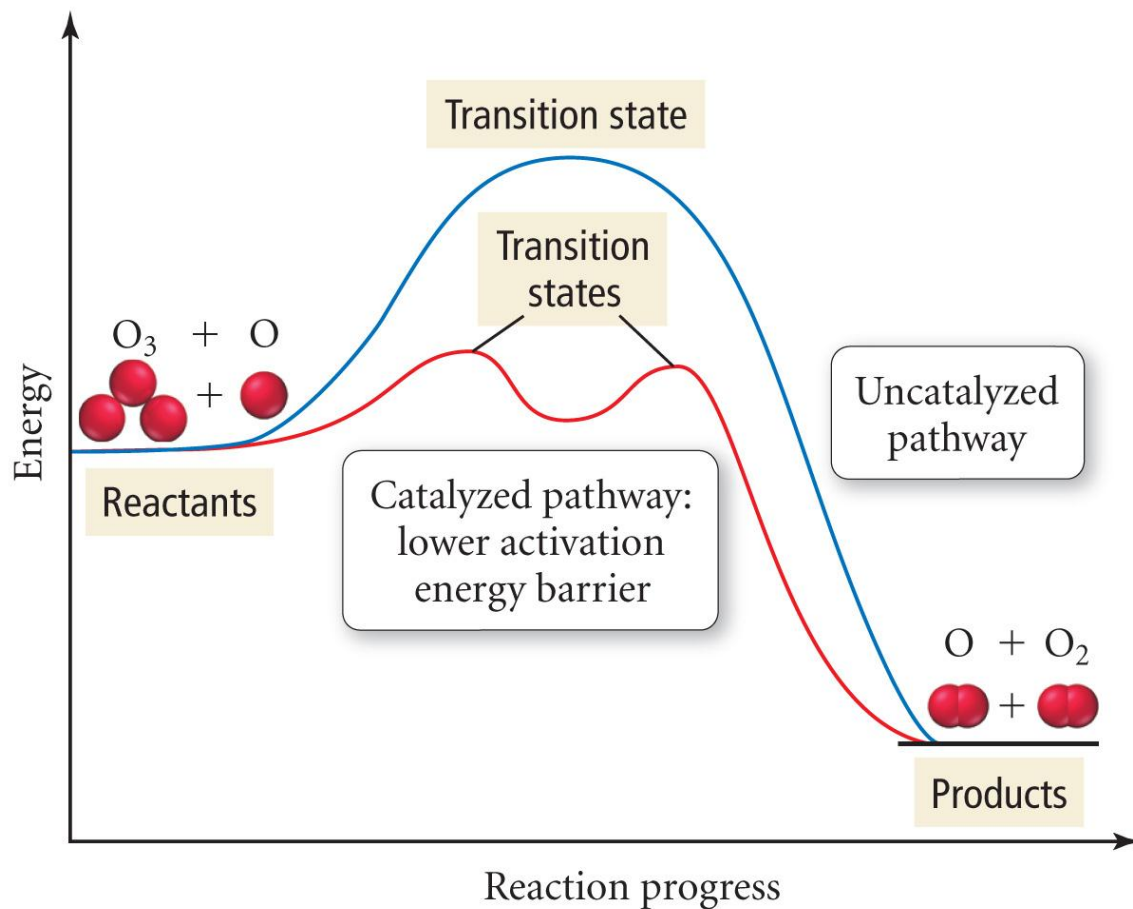
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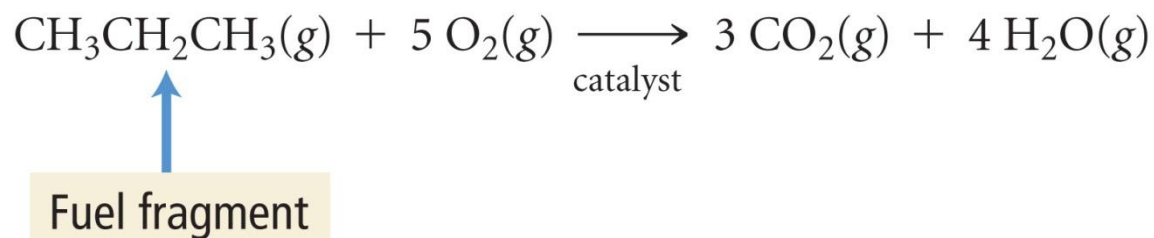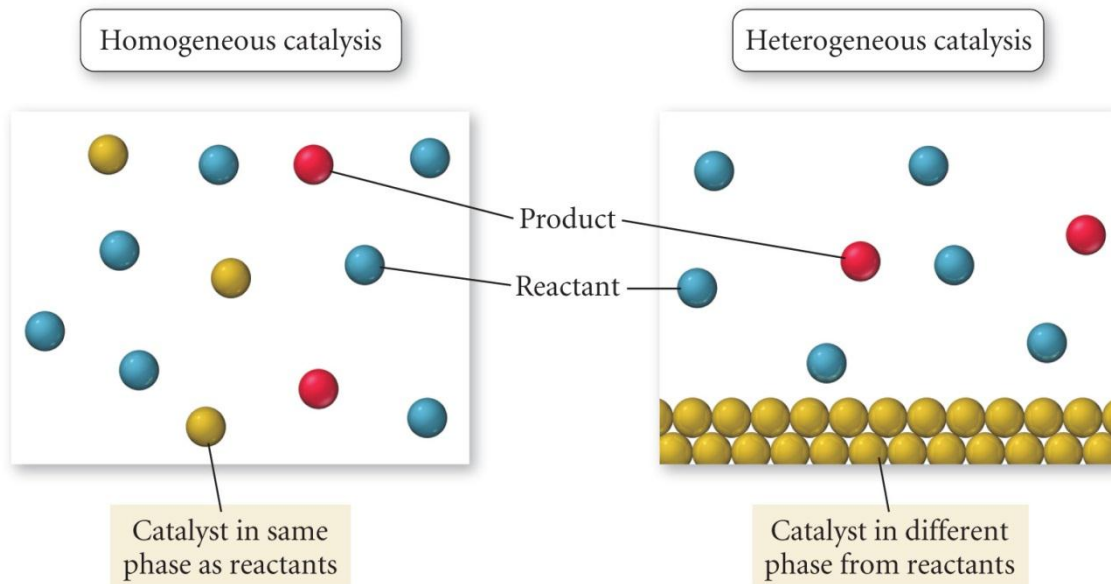
$$CH_3CH_2CH_3(g) \ + \ 5\,O_2(g) \ \xrightarrow{\text{catalyst}} \ 3\,CO_2(g) \ + \ 4\,H_2O(g)$$

Fuel fragment

Homogeneous catalysis

Heterogeneous catalysis

Product

Reactant

Catalyst in same phase as reactants

Catalyst in different phase from reactants

Heterogeneous Catalysis

Hydrogen   Ethene

Adsorption

Diffusion

Reaction

Desorption
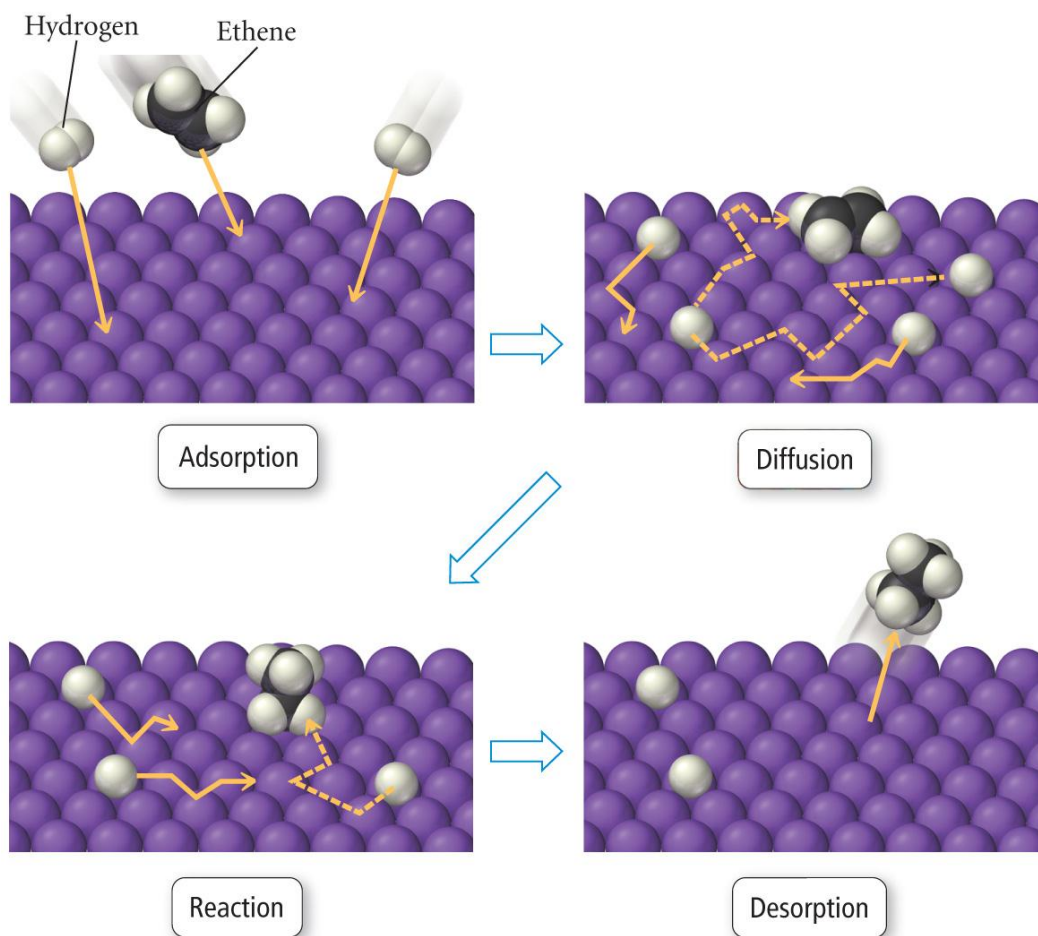
Chemical Equilibria 1

Background: Expressing Equilibria

Discussion: What is a *dynamic* chemical equilibrium?

Analogy: the Vancouver shoe sale

8:59 am: Before reaction starts

9:01 am: Reaction starts

9:10 am: *Dynamic* equilibrium established

Product(s) and reactant(s) have fixed molar ratios at equilibrium.
Therefore:

Forward **rate of reaction** ≡ *Reverse* **rate of reaction for a system at equilibrium**

Example: The Equilibrium between N_2O_4 (g) and the 'smog gas' NO_2 (g) - see slide.

Equilibrium Position

Discussion: Based on the slide (as well as the above picture of the LA skyline), would you say that the equilibrium between N_2O_4 (g) and NO_2 (g) favors reactants or products at room temperature? Why?

$$N_2O_4 \text{ (g)} \Leftrightarrow 2\ NO_2 \text{ (g)}$$

The position (or condition) of a chemical equilibrium is expressed as a ratio of product(s) : reactant(s). This ratio is reported as a single quantity K, the equilibrium constant. Simply:

$$K = \frac{[\text{Product(s)}]}{[\text{Reactant(s)}]}$$

Typically: K > 1 for equilibria that favor product(s)
K < 1 for equilibria that favor reactant(s)

Quantitative Determination of the Equilibrium Constant, K

Task: Based on the basic definition of K, discussed above, *estimate** the value of K for the N_2O_4 (g) $\Leftrightarrow$ 2 NO_2 (g) equilibrium via inspection of the supplied slide. What about the shoe store?

A chemical equilibrium and its respective equilibrium expression are *quantitatively* related via the following generic expression:

$$\underline{\text{For:}} \quad aA + bB \Leftrightarrow cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Important: The concentration of each reactant and product in a chemical equilibrium is raised to the power of its respective stoichiometic constant (balancing number), as found in the appropriate balanced chemical equation.

Task: Use the preceding math in conjunction with the slide to *determine** a more accurate value of K for the N_2O_4 (g) $\Leftrightarrow$ 2 NO_2 (g) equilibrium.

Note: For gas phase reactions, [conc] $\propto$ p. Therefore, partial pressures (e.g. p_{NO2}) may be used in place of [conc] expressions for gas phase processes. See appendix for more examples.

Task: Write an expression for K, involving partial pressures, for:

$$N_2O_4 \text{ (g)} \Leftrightarrow 2\ NO_2 \text{ (g)}$$

Note: It is possible to mix 'n match [conc] and *p* units in a single equilibrium expression – this is an example of a *heterogeneous* equilibrium
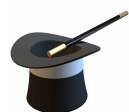
> Pure solids and/or liquids do NOT have a defined concentrations or partial pressures, so do NOT appear in equilibrium expressions

Example: Write an equilibrium expression for:

$$CaCO_3\text{(s)}\ +\ 2\ HCl\text{ (g)}\ \Leftrightarrow\ CaCl_2\text{ (s)}\ +\ H_2O\text{ (l)}\ +\ CO_2\text{ (g)}$$

Example: A mixture of H_2 (g) and N_2 (g) was allowed to come to equilibrium at 472 °C:

$$N_2 \text{ (g)} + 3 H_2 \text{ (g)} \iff 2 NH_3 \text{ (g)}$$
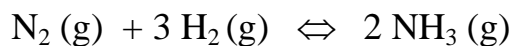
Find K for this system, assuming the partial pressures or each reactant were found to be $p_{N2} = 2.46$ atm, $p_{H2} = 7.38$ atm, and be $p_{NH3} = 0.166$ atm respectively.

If K is known for a chemical process, then the [conc] and/or partial pressures of aqueous and/or gas phase species, respectively, involved in a chemical process may be determined.

Example: At 21.8°C, K for the following equilibrium is known to be 7.0 x 10^{-2}.

$$NH_4HS \text{ (s)} \iff NH_3 \text{ (g)} + H_2S \text{ (g)}$$

Calculate the equilibrium partial pressures of NH_3 (g) and H_2S (g) if a solid sample of NH_4HS is placed in a closed vessel and allowed to decompose until equilibrium is attained. Is this a hetero- or homogeneous equilibrium? See appendix for another example.

The Feasibility of a Reaction – what does the value of K really mean?

Discussion: If K is very *large*, do reactants or products dominate at equilibrium? If K is very *small*, do reactants or products dominate at equilibrium? Hint: Recall the basic definition of K.

> If K is *large*, the equilibrium is said to lie to the *right*.
>
> If K is *small*, the equilibrium is said to lie to the *left*.

Extreme Cases – 'complete' and 'incomplete' reactions

If K $\geq 10^6$, a reaction is said to be 'complete'

If K $\leq 10^{-6}$, a reaction is said to be 'incomplete'

Discussion: Given the above information, is there such a thing as an entirely complete or incomplete chemical reaction??

Products

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Reactants

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$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$
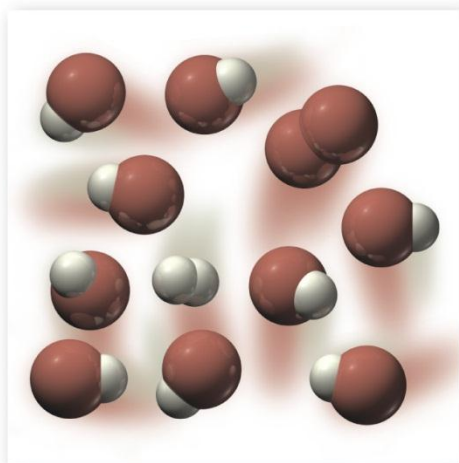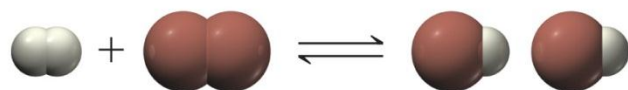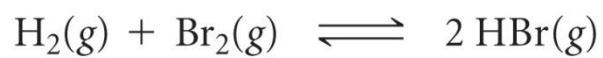
$$K = \frac{[HBr]^2}{[H_2][Br_2]} = \text{large number}$$

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$
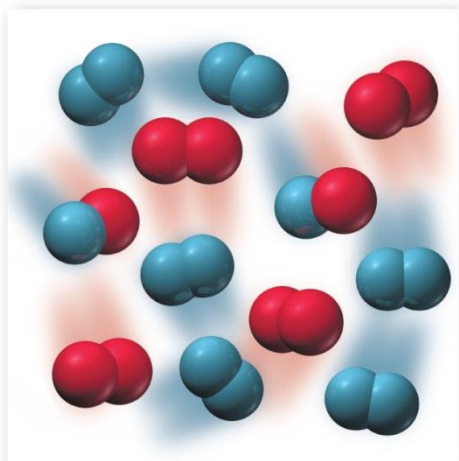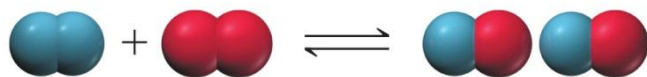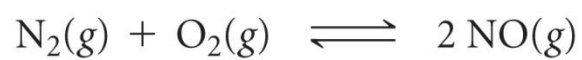
$$K = \frac{[NO]^2}{[N_2][O_2]} = \text{small number}$$

$$2\,CO(g) \;\rightleftharpoons\; CO_2(g) + C(s)$$

Same $[CO_2]$ and $[CO]$

Same temperature

$C(s)$

$C(s)$

Chemical Equilibria 2

Review

A chemical equilibrium and its respective equilibrium expression are *quantitatively* related via the following generic expression:

For: aA + bB ⇔ cC + dD

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
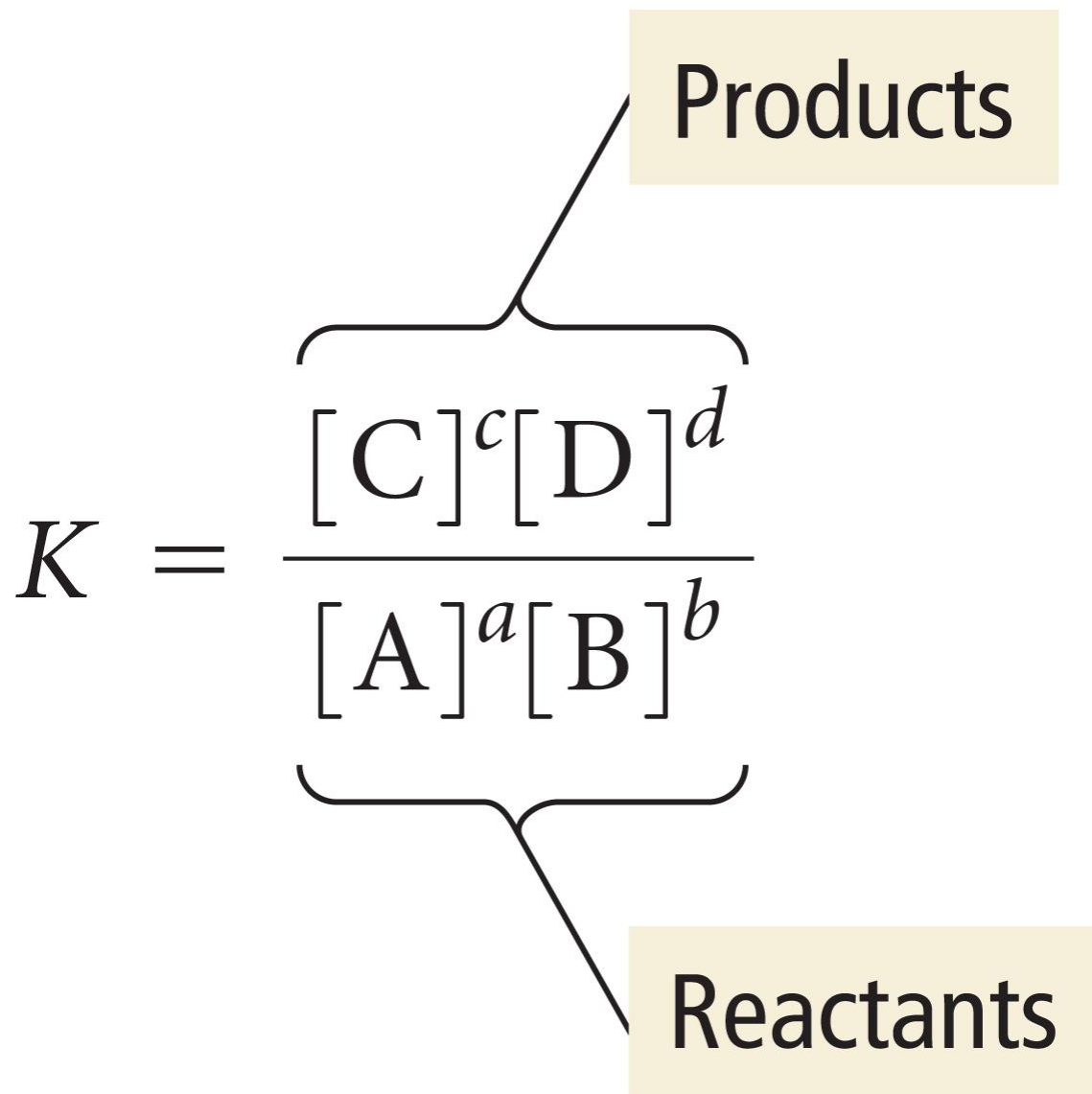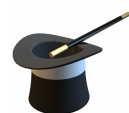
If K is *large*, the equilibrium is said to lie to the *right*.

If K is *small*, the equilibrium is said to lie to the *left*.

Task: Analyze and discuss the following rate plots for chemical processes that attain measurable equilibria. Which equilibrium *lies to the right, to the left*?

125
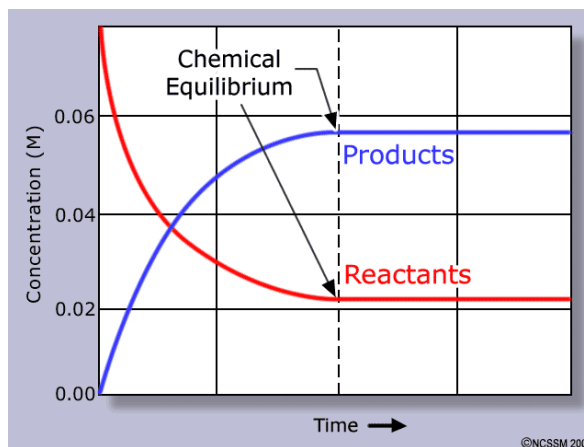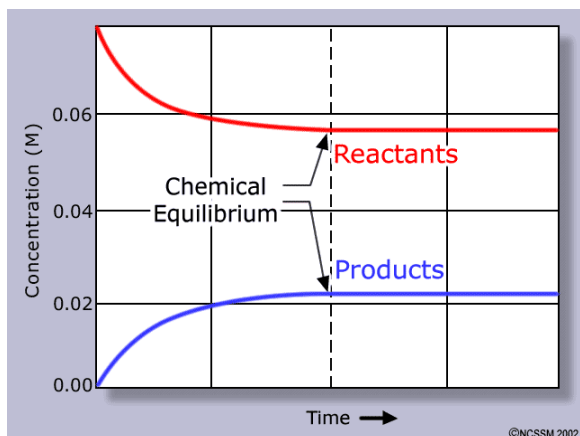
Since the value of K is fixed for a specific temperature and pressure, the ratio of products to reactants is also fixed. Therefore:

A reaction mixture will approach the equilibrium position from either the reactants side (reactants in XS, **forward reaction**) or the products side (products in XS, **reverse reaction**). See slide and appendix table.

Notes

Reverse Reactions

Analogy Is the glass half full or half empty? There are two ways of looking at equilibrium too – *either* from the point of view of the formation of product(s) from reactants (L→R) *or* the formation of reactants from products (L←R).

Question: How are these two processes related?

For the Generic Equilibrium:

A $\Leftrightarrow$ B K_{for} = $\dfrac{[B]}{[A]}$ Derivation

K_{rev} = $\dfrac{[A]}{[B]}$

Example:

$$HF \text{ (aq)} \iff H^+ \text{ (aq)} + F^- \text{ (aq)} ; \ K = 6.4 \text{ x } 10^{-4}$$
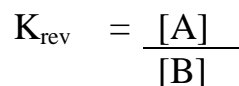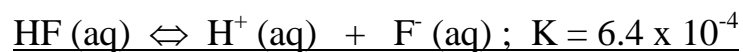
What is K_{rev}?

Do you think HF (aq) is a strong acid? Why?

More Equilibrium Math

If an equilibrium expression is multiplied by a constant value, its 'new' eq^m constant is the original value of K raised to the multiplying power

Example: Given:
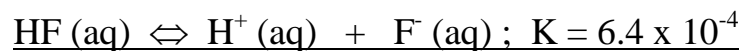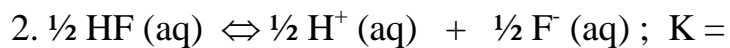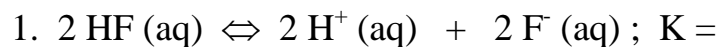
$$HF \text{ (aq)} \iff H^+ \text{ (aq)} + F^- \text{ (aq)} ; \ K = 6.4 \text{ x } 10^{-4}$$

What is K for:

1. $2 HF \text{ (aq)} \iff 2 H^+ \text{ (aq)} + 2 F^- \text{ (aq)} ; \ K =$

2. $\frac{1}{2} HF \text{ (aq)} \iff \frac{1}{2} H^+ \text{ (aq)} + \frac{1}{2} F^- \text{ (aq)} ; \ K =$

Worked Example: Given:

$$2HF \text{ (aq)} \Leftrightarrow 2H^+ \text{ (aq)} + 2F^- \text{ (aq)} \quad ; \underline{K_1 = 4.6 \times 10^{-7}}$$

and

$$2 H^+ \text{ (aq)} + C_2O_4^{\ 2-} \text{(aq)} \Leftrightarrow H_2C_2O_4 \text{ (aq)} \quad ; K_2 = 2.6 \times 10^5$$
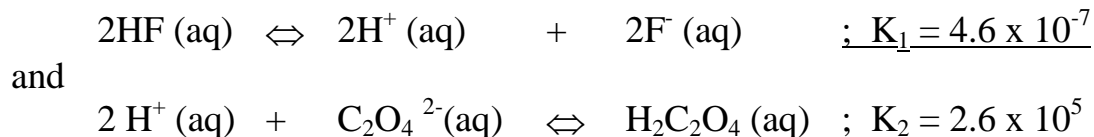
What is K for: $2HF \text{ (aq)} + C_2O_4^{\ 2-} \text{(aq)} \Leftrightarrow 2F^- \text{ (aq)} + H_2C_2O_4 \text{ (aq)}$

Always add equations and multiply Ks first - just to see what you get

Task: What is K for: $CO \text{ (g)} + 2 H_2S \text{ (g)} \Leftrightarrow CS_2 \text{ (g)} + H_2O\text{(g)} + H_2 \text{ (g)}$

Given: $CO \text{ (g)} + 3 H_2 \text{ (g)} \Leftrightarrow CH_4 \text{ (g)} + H_2O \text{ (g)} \quad ; K_1 = 3.92$
$CH_4 \text{ (g)} + 2 H_2S \text{ (g)} \Leftrightarrow CS_2 \text{ (g)} + 4 H_2 \text{ (g)} \quad ; K_2 = 3.3 \times 10^4$

The Equilibrium Constant K_p

> For gas phase reactions it is easier to measure *partial pressures* of reactants and products. This will yield an equilibrium constant in terms of partial pressures *only*, K_p
>
> **K_p is related to the 'regular' equilibrium constant, K_c, (used for expressing molar concs. of reactants and products) by:**
>
> $$K_p = K_c(RT)^{\Delta n}$$

Where: R = molar gas constant (careful with units) =   *or*
          T = Temp. in Kelvin
          $\Delta n = \Sigma$ (coeff gas products) - Σ(coeff gas reactants)

Math:

Example: What is K_p for: PCl_5 (g) $\Leftrightarrow$ PCl_3 (g) + Cl_2 (g) at 191°C, given $K_c =$ 3.26 x10^{-2}

The Reaction Quotient, Q_c

"An expression that has the same form as the eq^m constant (K_c), except that the conc values are not necessarily those at equilibrium"

For: $aA + bB \Leftrightarrow cC + dD$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Given the [conc] of all reactant(s) and product(s) under non-eq^m conditions, the direction of the reaction proceeds in order to establish eq^m can be found

Discussion: What does it really mean, in terms of the [reactants] and [products], when $Q_c > K_c$?

When $Q_c > K_c$, reaction moves to _____

When $Q_c < K_c$, reaction moves to _____

When $Q_c = K_c$, reaction is _____

See appendix

Worked Example: A 10.0 L vessel contains 0.0015 mol. CO_2 (g) and 0.100 mol. CO (g). If:

$$CO_2 \text{ (g)} + C \text{ (s)} \Leftrightarrow 2 \text{ CO (g)} ; K_c = 1.17$$
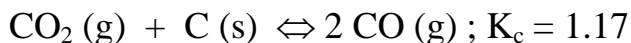
What will happen to the concentrations of the gasses present if a small amount of C (s) is added to the vessel?

Initial $[CO_2]$ =

Initial [CO] =

Q_c =

Q_c K_c, therefore:

Task: A 50.0 L vessel contains 1.00 mol. N_2 (g), 3.00 mol. H_2 (g) and 0.500 mol. NH_3 (g). If:

$$N_2 \text{ (g)} + 3 H_2 \text{ (g)} \Leftrightarrow 2 NH_3 \text{ (g)} ; K_c = 0.5 \text{ under rxn. conditions}$$
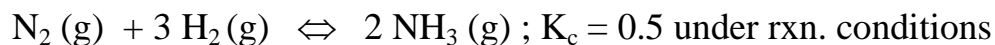
Will more or less NH_3 (g) be present when the system attains equilibrium?

ANS = Less

Le Châtelier's Principle

When a system in eq^m is disturbed by a change in [*conc*], *temperature or pressure*, the eq^m will shift to compensate for this change

"You push me, I push back" - John Rambo, noted physical chemist

Discussion:

For: A $\Leftrightarrow$ B   K $=$ $\dfrac{[B]}{[A]}$ (A constant)
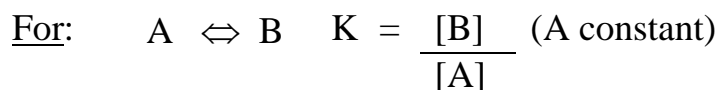
What, then, *must* happen if [B] is reduced by removing this chemical from the reaction mixture?

Answer:

1. Altering Concentration - Removing Products and/or Adding Reactants

For: N_2 (g) $+ 3 H_2$ (g) $\Leftrightarrow$ $2 NH_3$ (g)
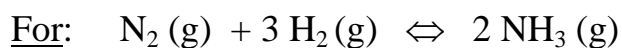
What will happen to the position of the equilibrium if:

A. Some NH_3 (g) is removed from the reaction vessel (its partial pressure is reduced)

B. N_2 (g) and/or H_2 (g) is added to the reaction vessel

C. Some N_2 (g) is added to the reaction vessel (see slide)

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$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \text{Time} \longrightarrow$$

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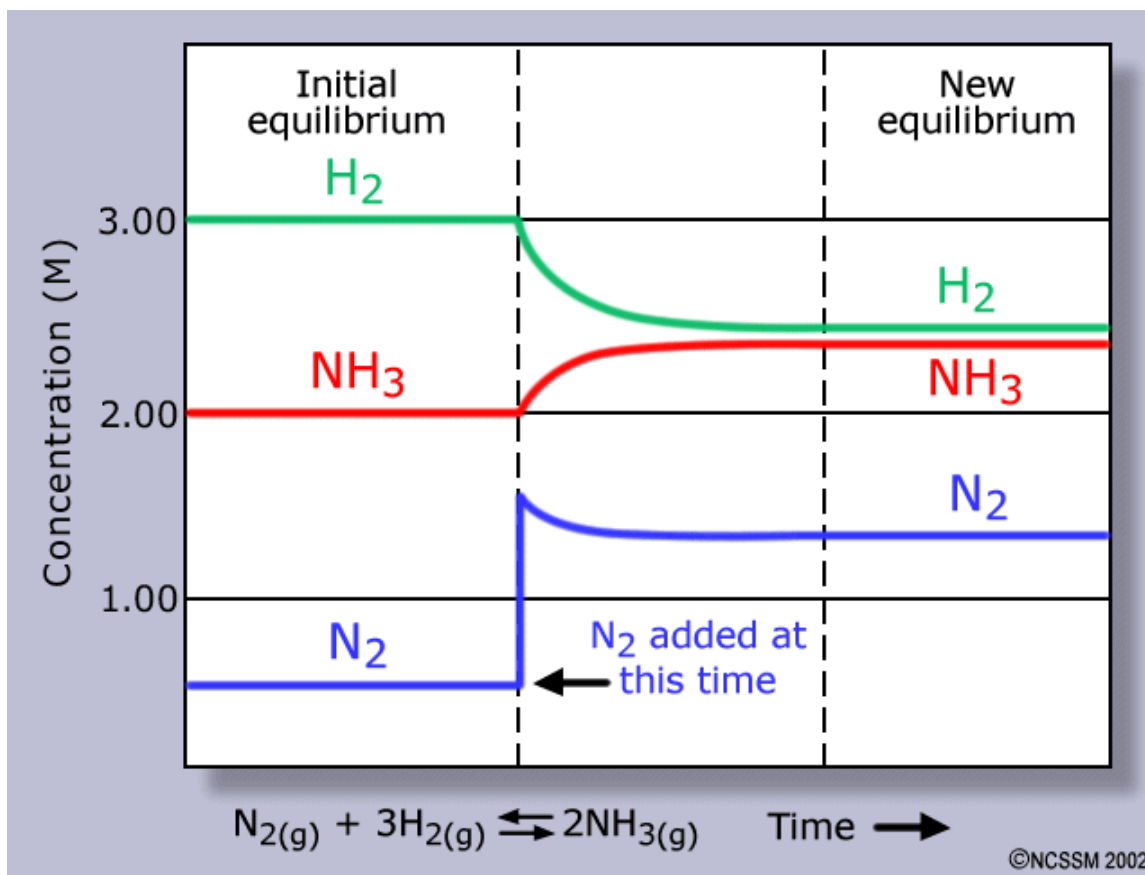
Task: Predict the direction of reaction for:

$$CaCO_3 \text{ (s)} \Leftrightarrow CaO \text{ (s)} + CO_2 \text{ (g)}$$

If the amount (pressure) of CO_2 (g) is increased

If the amount of $CaCO_3$ (s) is doubled

2. Changing Pressure and /or Temperature

<u>Discussion</u>: What exerts more pressure in a fixed volume container – 2 moles of gas or 4 moles of gas?

When an equilibrium involving gasses is stressed by altering the pressure, the equilibrium will shift to either increase (p↑) or decrease (p↓) the number of gasses species present

<u>Thus</u>:

When the pressure is *increased*, the system will remove this stress by _____ the moles of gaseous species present at equilibrium

When the pressure is *decreased*, the system will remove this stress by _____ the moles of gaseous species present at equilibrium

Example: Consider the equilibrium:

$$CO\ (g)\ +\ 3\ H_2\ (g)\ \Leftrightarrow\ CH_4\ (g)\ +\ H_2O\ (g)$$
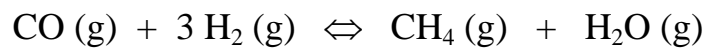
What would happen to the rxn. mixture if the vessel were compressed? (See below fig. for a microscopic view of what happens)

		Key
		⬤ CO
		∞ H₂
		CH₄
		H₂O

Gases at equilibrium

A

After compression, but before equilibrium

B

Compressed gases at equilibrium

C
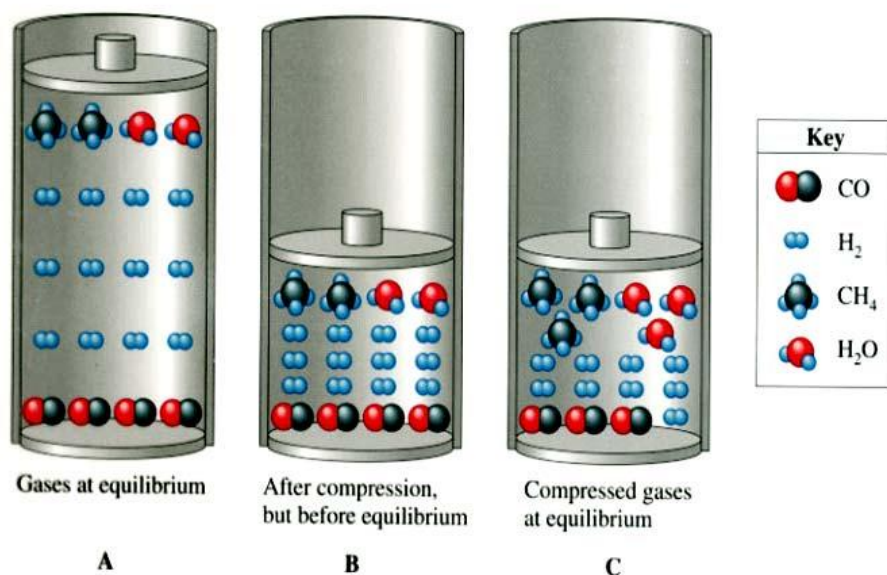
What would happen if the volume of the reaction vessel were doubled?

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Examples: Can the amount of product(s) in the following reactions be increased by increasing the pressure inside the reaction vessel?

a. CO_2 (g) + H_2 (g) $\Leftrightarrow$ CO (g) + H_2O(g)

b. 4 CuO (s) $\Leftrightarrow$ 2 Cu_2O (s) + O_2 (g)

c. 2 SO_2 (g) + O_2 (g) $\Leftrightarrow$ 2 SO_3 (g)
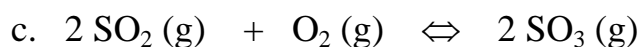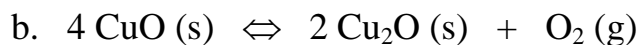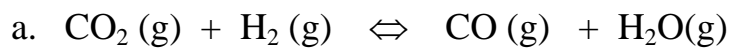
Temperature Effects

Aside: Recall from the 'Thermo' section of Chem. 101:

Discussion: what is an exothermic reaction, what is an endothermic reaction? Hint: think of the roots –(ex, en)

EXOthermic:

ENDOthermic:

Fact: The vast majority of all known reactions are exothermic (heat is evolved). For example, all combustion reactions give out heat.

Type of reaction	Observation	Write heat where?	Sign of ΔH (enthalpy)
Exothermic			-VE
Endothermic			+VE

The amount of heat evolved (exothermic, -ve ΔH) or absorbed (endothermic, +ve ΔH) during a chemical process is expressed in the form of a thermochemical equation – like a regular balanced equation, but with the numerical value of ΔH included

Write 'heat' as a product (on the right) for exothermic reactions (vice versa for endo) – Le Châtelier's Principle can then be applied with regard to heating or cooling the reaction vessel

Example: Consider the following thermochemical process:

$$CO \text{ (g)} + 3 H_2 \text{ (g)} \Leftrightarrow CH_4 \text{ (g)} + H_2O \text{ (g)} ; \Delta H = -206.2 \text{ kJ/mol}$$
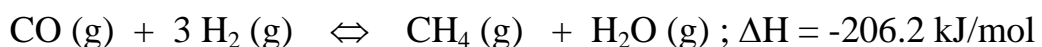
What happens to the position of the equilibrium when the reaction vessel is:

a. Heated up:

b. Cooled down:

Another example: Is a high or low temperature favorable for the formation of CO (g) in the following process? Hint: Remember the previous trick.

$$CO_2 \text{ (g)} + C \text{ (s)} \iff 2 CO \text{ (g)} ; \Delta H = +172 \text{ kJ/mol}$$

Choosing Optimal Reaction Conditions based on Le Châtelier's Principle

Chemists typically want to maximize the formation of products from a chemical reaction. Therefore, choosing the 'right' conditions of P and T (according to Le Châtelier) will allow for the maximum possible yield of product(s)

Example: What conditions of temperature and pressure would maximize the formation of ammonia (NH_3) via the Haber process?

$$N_2 \text{ (g)} + 3 H_2 \text{ (g)} \iff 2 NH_3 \text{ (g)} ; \Delta H = -91.8 \text{ kJ/mol}$$

Temperature: Increase temperature of   OR   Decrease temperature of
                vessel   vessel

Pressure: Increase pressure on   OR   Decrease pressure on
                vessel   vessel

See appendix for figures

Another Example: What conditions of temperature and pressure would maximize the formation of CO (g) for:

$$2\ CO_2\ (g)\ \Leftrightarrow\ 2\ CO\ (g)\ +\ O_2\ (g)\ ;\ \Delta H = +556\ kJ/mol$$
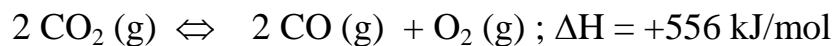
Discussion: What happens to the rate of any exothermic reaction when it is 'optimized' according to Le Châtelier's Principle?
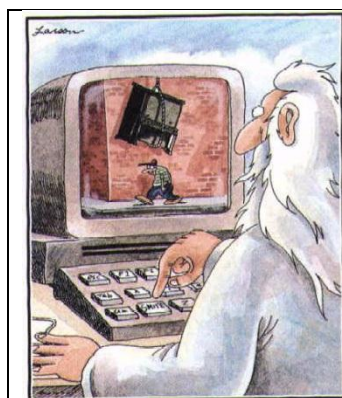
God at His computer

The Great Cosmic Joke – Kinetics v Equilibrium

Increasing the temperature of a reaction increases the rate at which reactants form. However, most reactions are exothermic, so the equilibrium is shifted in favor of reactant and higher temps. IE

You can either make less 'stuff' more quickly (high temp.) or more 'stuff' over a longer period of time (low temp) – you just can't win!

Wrap up: Intro to the ICE method (will be covered in more detail in acid/base equilibria)

Worked Example (Lab question 4): The air pollutant NO (g) is produced in automobile engines from the high temperature reaction below. If the initial concentrations of N_2 (g) and O_2 (g) are both 1.40 M, what is the concentration of each reactant and product at equilibrium. K = 0.0017 at 2300 K.
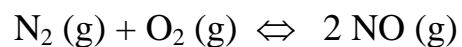
$$N_2 \text{ (g)} + O_2 \text{ (g)} \iff 2 \text{ NO (g)}$$

Question 1 (6 points): Write equilibrium (K) expressions for the following:

1. $MgCO_3(s) \leftrightarrow MgO(s) + CO_2(g)$

2. $N_2(g) + O_2(g) \leftrightarrow 2NO(g)$

3. $Sn(s) + 2H^+(aq) \leftrightarrow Sn^{2+}(aq) + H_2(g)$

Question 2 (5 points): The following equilibrium has a value of $K_p = 0.556$ at 700 K:

$$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$$
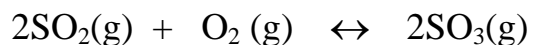
If the partial pressures of $SO_2(g)$ and $O_2(g)$ at equilibrium are 0.175 atm and 0.856 atm, respectively, what is the equilibrium partial pressure of $SO_3(g)$?

TABLE 14.1 Initial and Equilibrium Concentrations for the Reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ at 445 °C

Initial Concentrations			Equilibrium Concentrations			Equilibrium Constant
$[H_2]$	$[I_2]$	$[HI]$	$[H_2]$	$[I_2]$	$[HI]$	$K_c = \dfrac{[HI]^2}{[H_2][I_2]}$
0.50	0.50	0.0	0.11	0.11	0.78	$\dfrac{0.78^2}{(0.11)(0.11)} = 50$
0.0	0.0	0.50	0.055	0.055	0.39	$\dfrac{0.39^2}{(0.055)(0.055)} = 50$
0.50	0.50	0.50	0.165	0.165	1.17	$\dfrac{1.17^2}{(0.165)(0.165)} = 50$
1.0	0.50	0.0	0.53	0.033	0.934	$\dfrac{0.934^2}{(0.53)(0.033)} = 50$
0.50	1.0	0.0	0.033	0.53	0.934	$\dfrac{0.934^2}{(0.033)(0.53)} = 50$

$$A(g) \rightleftharpoons B(g) \qquad Q = \frac{[B]}{[A]}$$

$$Q \longrightarrow \infty \text{ at } [A] = 0, [B] = 1$$

$Q > K$
Reaction runs to left
$(A \longleftarrow B).$

$K = 1.45$

$Q < K$
Reaction runs to right
$(A \longrightarrow B).$

$Q = K$
Reaction is at equilibrium
$(A \rightleftharpoons B).$

[A]	1.00	0.75	0.50	0.25	0.00
[B]	0.00	0.25	0.50	0.75	1.00
	Reactants				Products

Concentration (M)

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Add more NO$_2$.

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Add NO$_2$

Equilibrium is disturbed.

More N$_2$O$_4$ forms.

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

System shifts left.

Le Châtelier's Principle: Graphical Representation
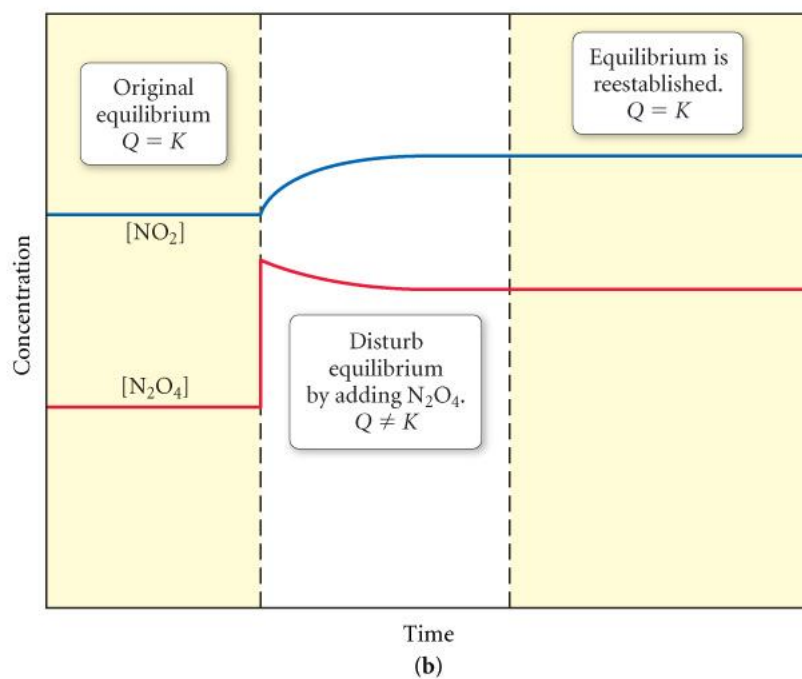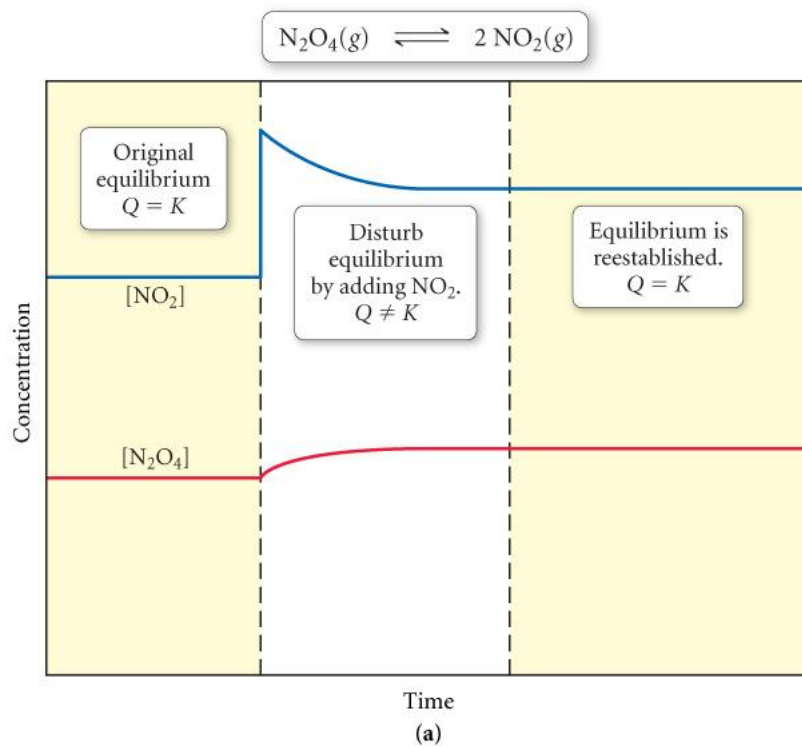
$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Original equilibrium $Q = K$

Disturb equilibrium by adding NO_2. $Q \neq K$

Equilibrium is reestablished. $Q = K$

[NO_2]

[N_2O_4]

Concentration

Time

(a)

Original equilibrium $Q = K$

Equilibrium is reestablished. $Q = K$

[NO_2]

Disturb equilibrium by adding N_2O_4. $Q \neq K$

[N_2O_4]

Concentration

Time

(b)

Add NO_2.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Reaction shifts left.

Add N_2O_4.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Reaction shifts right.

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Le Châtelier's Principle: Changing Pressure
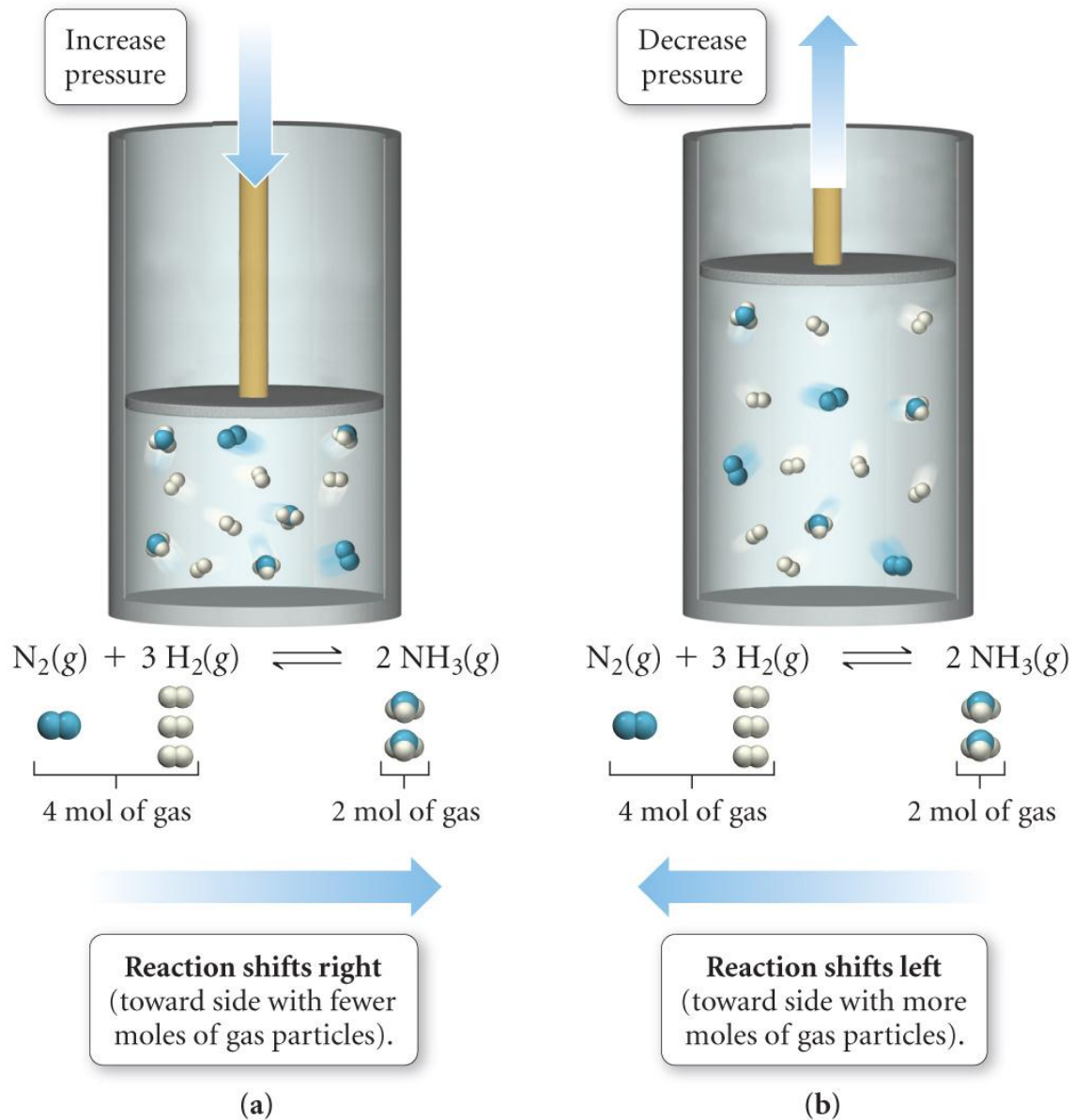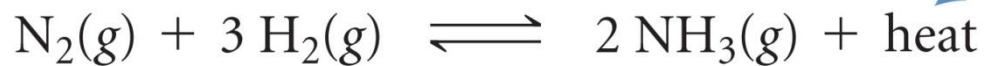
Increase pressure

Decrease pressure

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$

4 mol of gas   2 mol of gas

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$

4 mol of gas   2 mol of gas

Reaction shifts right
(toward side with fewer
moles of gas particles).

Reaction shifts left
(toward side with more
moles of gas particles).

(a)   (b)
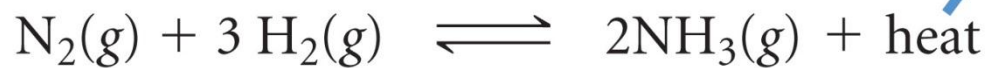
$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + heat$$

Reaction shifts left.
Smaller K

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2NH_3(g) + heat$$

Rection shifts right.
Larger K

Add heat

$$N_2O_4(g) + heat \rightleftharpoons 2\,NO_2(g)$$

colorless   brown

Reaction shifts right.
Larger K

Remove heat

$$N_2O_4(g) + heat \rightleftharpoons 2\,NO_2(g)$$

colorless   brown

Reaction shifts left.
Smaller K

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$$N_2O_4(g) + \text{heat} \;\rightleftharpoons\; 2\,NO_2(g)$$

colorless   brown

Lower temperature:
N_2O_4 favored
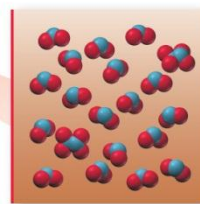
Higher temperature:
NO_2 favored

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Acid - Base Equilibria 1

  Background and Discussion: What is an acid? What is a base? Give some common examples.

 There are three models used to describe acid and base behavior: *Arrhenius, Brønsted – Lowery, and Lewis*

Note: Lewis Acids and Bases: will be discussed later in the course

Arrhenius Acids and Bases:

Arrhenius Acid: "*A substance when dissolved in water increases the* $[H^+]$" - this is a generic definition, true for all three models

Example:

Arrhenius Base:

Example:

<u>Brønsted – Lowery Acids and Bases</u>: - ***the proton transfer model***

🔑 **'Naked' H^+ (aq) ions do not really exist** (even though we often write them in chemical equations). H^+ ions 'piggyback' on H_2O molecules – the resulting H_3O^+ (aq) (*hydronium*) ion is what is actually responsible for acidic behavior

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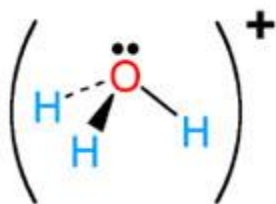
Molecular representation
of the hydronium ion

🎩 Even though we write H^+ (aq) in chemical equations, it is always assumed that this species is actually H_3O^+ (aq)

<u>Aside</u>: Can a completely 'dry' acid cause a chemical burn (like HCl(g)) or just taste acidic (like vinegar)?
<u>Hint</u>: think about sour candies – what is the 'sharp' tasting powdered coating made of?

The Brønsted – Lowery Proton Transfer model

Example: HCl (aq) as a Brønsted – Lowery acid

HCl
(acid, H^+donor)

H_2O
(base, H^+acceptor)

Cl^-

H_3O^+
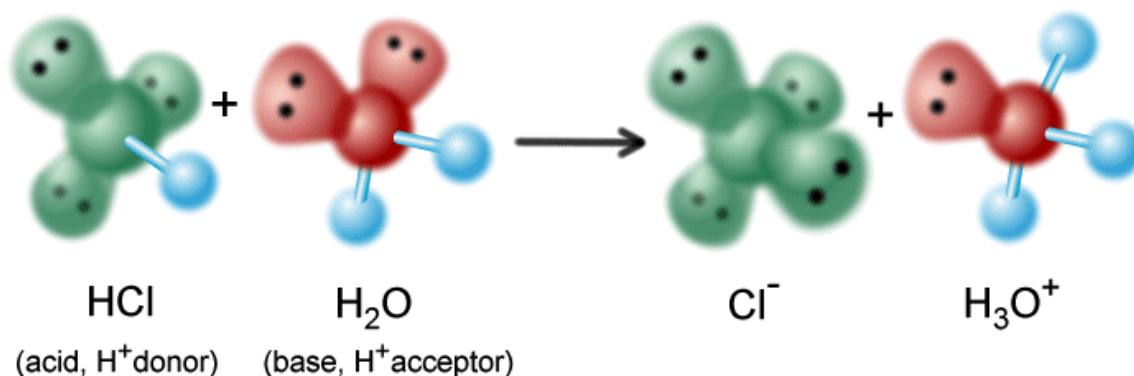
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Task: Identify the B-L acids and B-L bases in the following reactions:

NH_4^+ (aq) + CN^- (aq) → HCN (aq) + NH_3 (aq)

HSO_4^- (aq) + HCO_3^- (aq) → SO_4^{2-} (aq) + H_2CO_3 (aq)

NH_3 (aq) + H_2O (l) → NH_4^+ (aq) + OH^- (aq)

Conjugate Acid – Base Pairs

In an acid base equilibrium, the reacting acid most protonate (by definition) a base. **The (now) de-protonated acid is now known as a *conjugate base* and appears on the products side of the equation.**

Similarly, **the reactant base that accepts proton(s) becomes a *conjugate acid* on the reactants side of the equation.**

Generic Example:

$$HX\ (aq)\ +\ H_2O\ (l)\ \Leftrightarrow\ X^-\ (aq)\ +\ H_3O^+\ (aq)$$

Acid   Base   Conjugate   Conjugate
                                base   acid

Forward reaction: $HX\ (aq)$ and $X^-\ (aq)$ are an acid / conjugate base pair

                               $H_2O\ (l)$ and $H_3O^+\ (aq)$ are a base / conjugate acid pair

Conjugate acids and bases are so named because they act as acids and bases, respectively, *for the reverse reaction*

Example:

$$HNO_2(aq) + H_2O(l) <\!=\!> NO_2^-(aq) + H_3O^+(aq)$$

    Acid   base   conjugate   conjugate
                                   base   acid

Task: Identify the acid / conjugate base and base / conjugate acid pair for above REVERSE reaction

Workshop: Complete the following assignments:

1. Identify acid / conjugate base and base / conjugate acid pairs for the following forward reactions:

HNO_3 (aq) + H_2O (l) $\Leftrightarrow$ NO_3^- (aq) + H_3O^+ (aq)

NH_3 (aq) + H_2O (l) $\Leftrightarrow$ NH_4^+ (aq) + OH^- (aq)
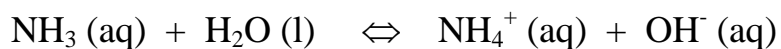
2. What are the conjugate bases of:

$H_2PO_4^-$

H_2S

H_2SO_3

HCO_3^-
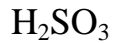
3. What are the conjugate acids of:

$H_2PO_4^-$

SO_4^{2-}

CN^-

HCO_3^-

Amphoteric Behavior

Question: Did you notice anything 'interesting' with regarding the behavior of the poly-protic acids in the previous examples?

Observation:

Answer: Dihydrogen phosphate is *amphoteric*:

> **Amphoteric: "capable as behaving as *either* an acid *or* a base"**

Tasks:

a. Write and equation for the reaction of $H_2PO_4^-$ with water in which it acts as an acid

b. Write and equation for the reaction of $H_2PO_4^-$ with water in which it acts as a base

c. Write a single equilibrium equation that represents what happens when dihydrogen phosphate is dissolved in water

The Relative Strengths of Acids and Bases

  Back to the fish 'n chips: Why can 0.1 M acetic acid (vinegar) be sprinkled on fish 'n chips, while it is *unadvised* to sprinkle 0.1 M HCl on this Scottish staple?

Strong (mineral) acids, such as HCl, *dissociate completely* **in water:**

Weak (organic) acids undergo *partial dissociation* **in water (much more on this later):**

Microscopic View
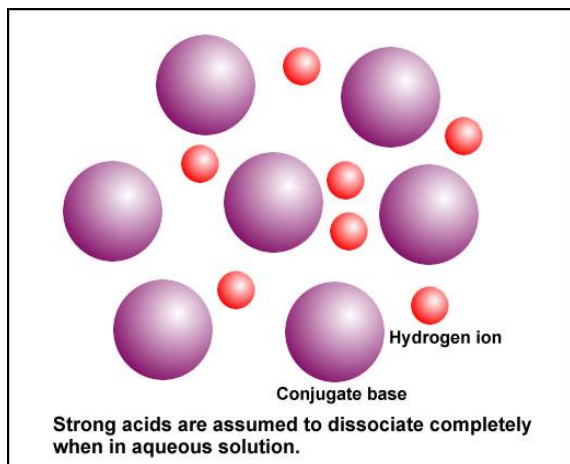
HCl (aq) – 100% dissociation	HA (weak acid) ~ 10% dissociation

Observations from the slide – *Conjugate Acid and Base Pairs*

1.

2.

3.

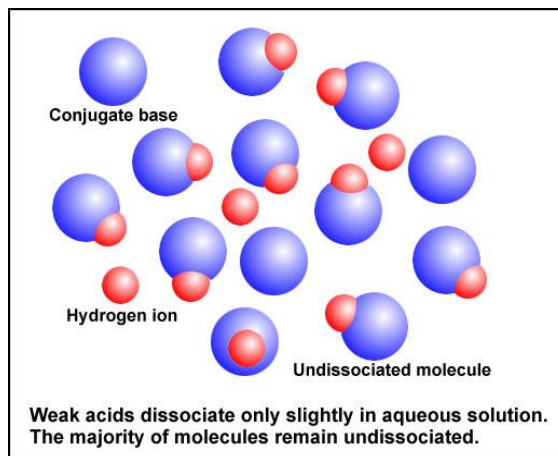|	Acid				Base	
Perchloric acid	HClO₄			ClO₄	Perchlorate ion	
Sulfuric acid	H₂SO₄			HSO₄	Hydrogen sulfate ion	
Hydrogen iodide	HI	Stronger acids than		I	Iodide ion	
Hydrogen bromide	HBr	H₃O⁺; form H₃O⁺ in		Br	Bromide ion	
Hydrogen chloride	HCl	100% yield in H₂O.		Cl	Chloride ion	
Nitric acid	HNO₃			NO₃	Nitrate ion	
Hydronium ion	H₃O⁺			H₂O	Water	
Hydrogen sulfate ion	HSO₄			SO₄	Sulfate ion	
Phosphoric acid	H₃PO₄			H₂PO₄	Dihydrogen phosphate ion	
Hydrogen fluoride	HF			F	Fluoride ion	
Nitrous acid	HNO₂			NO₂	Nitrite ion	
Acetic acid	CH₃CO₂H			CH₃CO₂	Acetate ion	
Carbonic acid	H₂CO₃			HCO₃	Hydrogen carbonate ion	
Hydrogen sulfide	H₂S			HS	Hydrogen sulfide ion	
Ammonium ion	NH₄⁺			NH₃	Ammonia	
Hydrogen cyanide	HCN			CN	Cyanide ion	
Hydrogen carbonate ion	HCO₃⁻			CO₄	Carbonate ion	
Water	H₂O			OH⁻	Hydroxide ion	
Hydrogen sulfide ion	HS			S²	Sulfide ion	
Ethanol	C₂H₅OH	Stronger bases than		C₂H₅O	Ethoxide ion	
Ammonia	NH₃	OH⁻; form OH⁻ in		NH₂	Amide ion	
Hydrogen	H₂	100% yield in H₂O.		H	Hydride ion	
Methane	CH₄			CH₃	Methide ion	

Increasing acid strength (left vertical, upward arrow) — *Increasing base strength* (right vertical, downward arrow)

Task: Use the slide/handout to predict if the following equilibria lie to the left or to the right:

Recall that protonation favors transfer from stronger acid (or weaker base) to stronger base (or weaker acid)

1. PO_4^{3-} + H_2O (l) $\Leftrightarrow$ HPO_4^{2-} + ^-OH (aq)

2. NH_4^+ (aq) + OH^- (aq) $\Leftrightarrow$ NH_3 (aq) + H_2O (l)
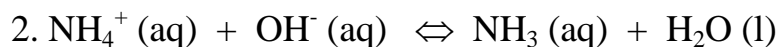
The Autoionization of Water

Water is 'special' – it dissociates to simultaneously give both H_3O^+ (aq) and ^-OH (aq) ions (*autoionization*):

$$2\ H_2O\ (l)\ \Leftrightarrow\ H_3O^+\ (aq)\ +\ ^-OH\ (aq)$$
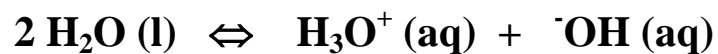
Task: Write an equilibrium (K) expression for the autoionization of water
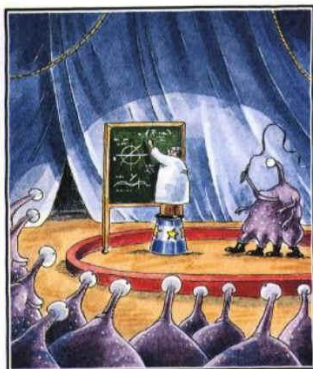
Abducted by an alien circus company,
Professor Doyle is forced to write calculus
equations in center ring.

Derivation of K_w and Other Useful Math

The value of K_w is constant for **ANY** aqueous solution, regardless of how much acid or base is added from external sources. I.E., for any aqueous solution:

$$K_w = 1.0\ x\ 10^{-14} = [H^+][^-OH]\ @\ 25^oC$$

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Applications of K_w - pH, pOH and pK_w

Discussion Questions:

1. If $1.0 \times 10^{-14} = [H^+][^-OH]$, what is the concentration of both H^+ (aq) and OH$^-$ (aq) in *any* neutral solution. <u>Hint</u>: What must always true in terms of the concentrations of $[H^+]$ and $[^-OH]$ for any neutral solution?

2. What is pH, what is it a measure of? What is the relationship between pH and $[H^+]$ for a neutral solution?

> *p* is simply a mathematical function that means: *"take the -log$_{10}$ of the quantity of interest (such as $[H^+]$)"*

Further expressions:

pOH =

pK$_w$ =

There is a *synergic* relationship between pH and pOH (or [H$^+$] and [$^-$OH]) for any solution. I.E., as one rises ↑, one falls ↓:
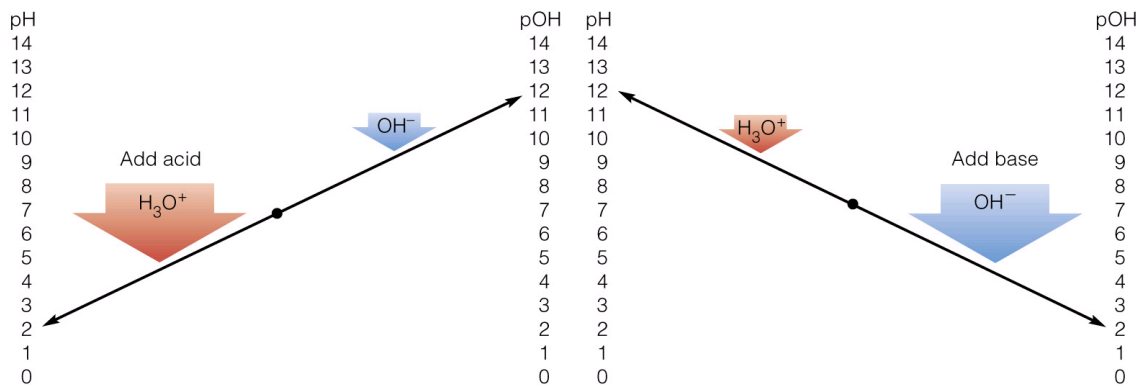
(a) When excess acid is added, pH decreases, and pOH increases.

(b) When excess base is added, pH increases, and pOH decreases.

pH Scale
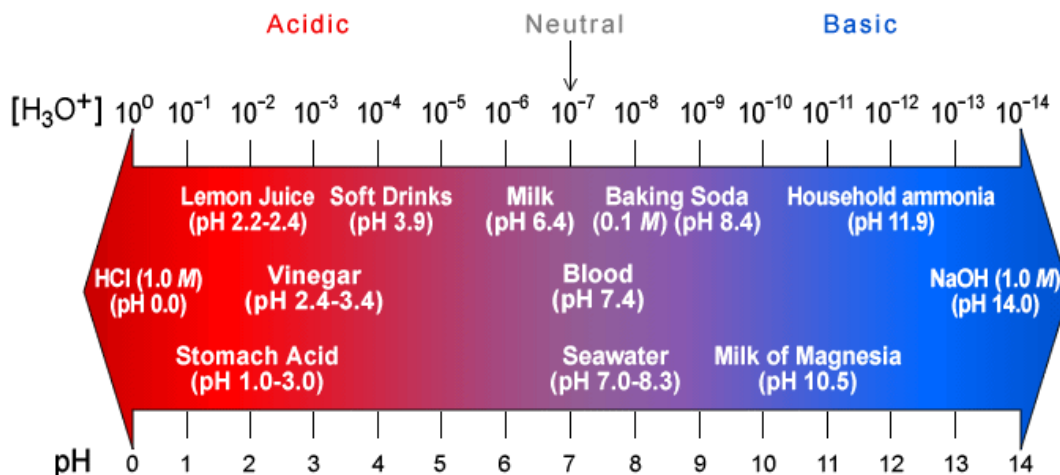
©NCSSM 2002

See the additional slide also

Questions: Determine the pH and pOH of the following strong acid and strong base solutions (assume 100% dissociation in each case):

0.055 M HCl (aq)   0.008 M NaOH (aq)

0.055 M H_2SO_4 (aq)   0.008 M $Ca(OH)_2$ (aq)
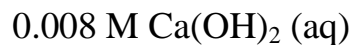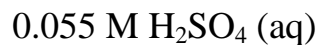
Workshop: Work in small groups to solve the following problems:

Calculate pH, pOH and [$^-$OH] for each of the following solutions. State if each solution is acidic, basic or neutral:

1. [H$^+$] = 0.0041 M

2. [H$^+$] = 3.5 x10^{-9} M

3. A solution where [H$^+$] is 10 times greater than [$^-$OH]

4. If you finish the above, try some homework problems

Acid – Base Indicators

Table of common Indicators
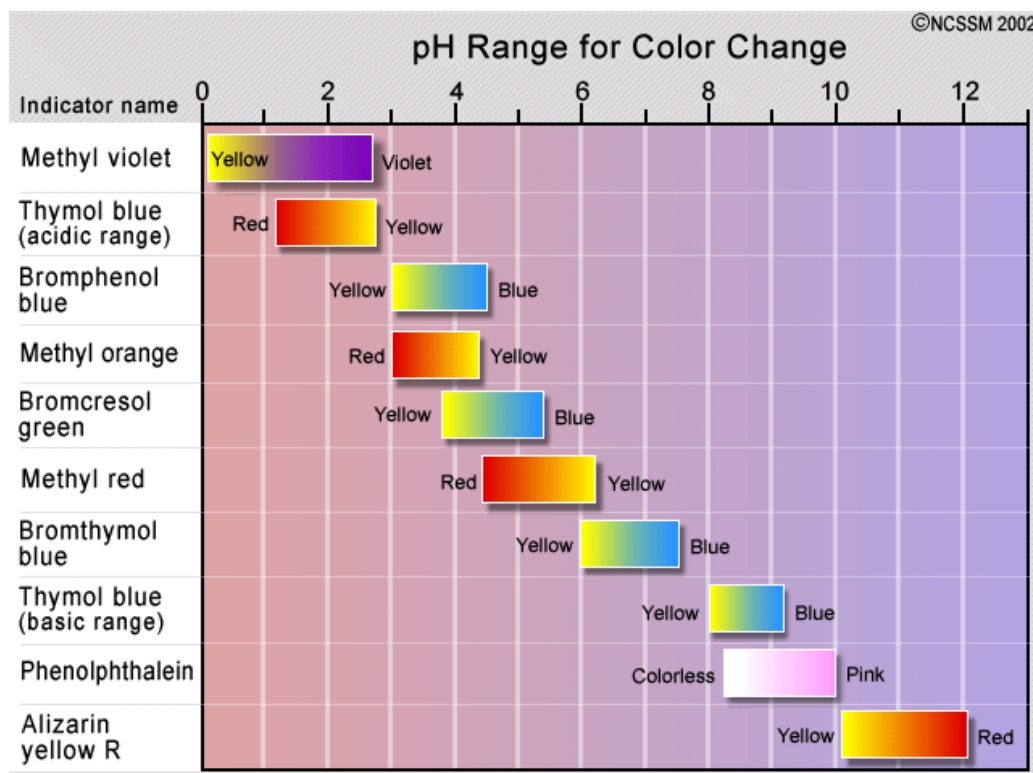
Questions: Which indicator would be best for detecting a titration endpoint that occurs at pH 4.0? What color change would be observed if the acidic sample was titrated with NaOH (aq)?

Why is indicator choice less important for a strong acid / strong base titration??

Arrhenius Acid

HCl

H$^+$ H$^+$
Cl$^-$ Cl$^-$
H$^+$ Cl$^-$
Cl$^-$ Cl$^-$ H$^+$
H$^+$ Cl$^-$ H$^+$

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$
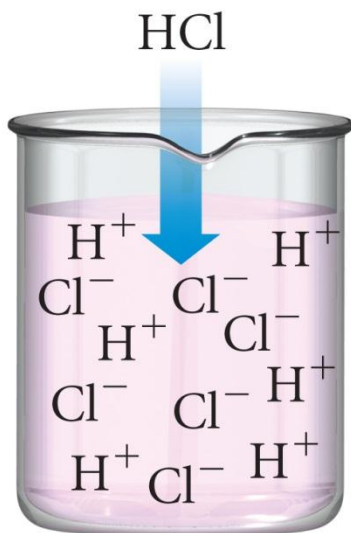
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Arrhenius Base
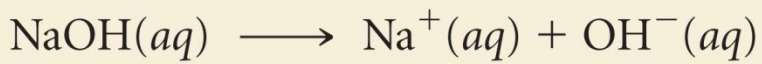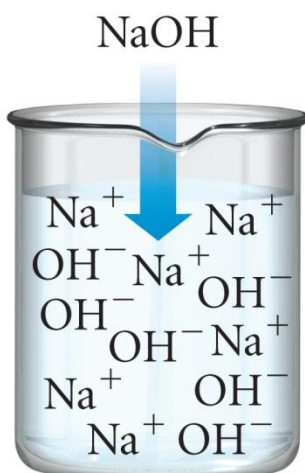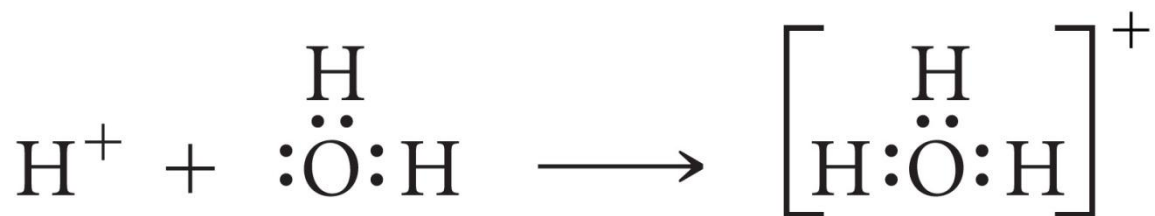
NaOH

Na$^+$ Na$^+$
OH$^-$ Na$^+$
OH$^-$ OH$^-$
OH$^-$ Na$^+$
Na$^+$ OH$^-$
Na$^+$ OH$^-$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

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$$H^+ \ + \ :\overset{\displaystyle H}{\underset{}{\ddot{O}}}:H \ \longrightarrow \ \left[\overset{\displaystyle H}{H:\ddot{O}:H} \right]^+$$

NH$_3$ (base) — Add H$^+$ → NH$_4^+$ (conjugate acid)

Conjugate acid–base pair

H$_2$O (acid) — Remove H$^+$ → OH$^-$ (conjugate base)

Conjugate acid–base pair
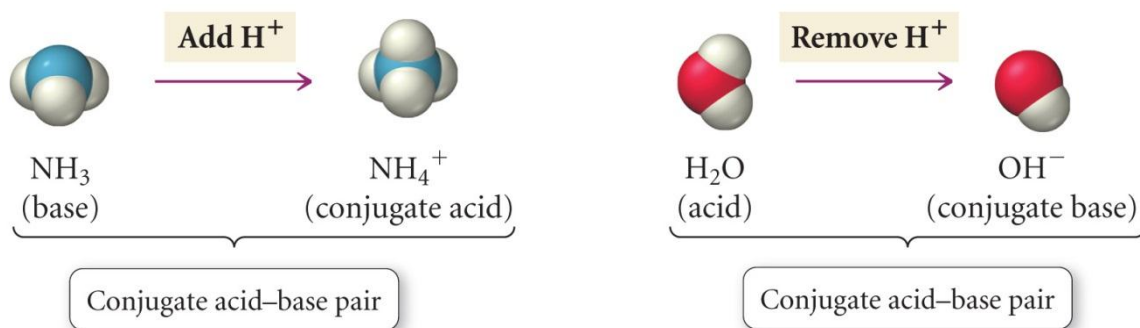
A Strong Acid

When HCl dissolves in water, it ionizes completely.

HCl

H$_3$O$^+$ Cl$^-$
H$_3$O$^+$ H$_3$O$^+$
Cl$^-$ Cl$^-$
H$_3$O$^+$ Cl$^-$
Cl$^-$ H$_3$O$^+$

$SrCl_2$

pH-neutral cation   pH-neutral anion

Neutral solution

$AlBr_3$

acidic cation   pH-neutral anion

Acidic solution

$CH_3NH_3NO_3$

acidic cation   pH-neutral anion

Acidic solution

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CHO$_2^-$

H$_3$O$^+$

HCHO$_2$

(c)

NO$_3^-$

H$_3$O$^+$

(d)

170

OH⁻

NH₃

NH₄⁺

(a)

OH⁻

Na⁺

(b)

171

HCl

Hydrochloric acid

H_2SO_4

Sulfuric Acid

HNO_3

Nitric Acid

$H_3C_6H_5O_7$

Citric acid

$H_2C_4H_4O_5$

Malic acid

	Acid	Base	
Strong	HCl	Cl^-	**Neutral**
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
Weak	HSO_4^-	SO_4^{2-}	**Weak**
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	HCN	CN^-	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible	HS^-	S^{2-}	**Strong**
	OH^-	O^{2-}	

Acid Strength (increasing upward)

Base Strength (increasing downward)

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Acid - Base Equilibria 2

Reading:	Ch 15 sections 8 – 12	Homework:	Chapter 15: 41, 57, 61*, 63, 65*, 67*, 73*, 85, 87*, 89, 91

* = 'important' homework question

Weak Acids

Review / Discussion: What is 'stronger' – HCl (aq) or vinegar (acetic acid)? What are the differences?

🗝 **Strong (mineral) acids, such as HCl, *dissociate completely* in water:**

Weak (organic) acids undergo *partial dissociation* in water (much more on this later):

Because any weak acid and its respective dissociation products (H^+ and conjugate base) are in equilibrium, 'equilibrium math' can be used to define K

Task: Determine an equilibrium expression (K) for the generic weak acid equilibrium:

HA (aq)	+	H_2O (l)	$\Leftrightarrow$	H_3O^+ (aq)	+	A^- (aq)
Weak		Water		Hydronium		Conjugate
Acid				ion		Base
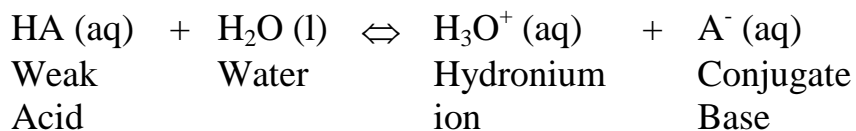
Note: Since, in this case, K pertains to the dissociation of a weak acid only, it is called the *acid dissociation constant* and assigned a suitable subscript:

$$K_a = \frac{[H^+] \ [A^-_{weak}]}{[HA_{weak}]}$$

Discussion: Will strong acids (like HCl) have large or small values for K_a? Will weak acids (like acetic acid) have large or small values for K_a?

Task: Complete the following table:

Acid	Type	Reaction with water	K_a
HCl	strong	$HCl \ (aq) \ \rightarrow \ H^+ \ (aq) \ + \ Cl^- \ (aq)$	'∞'
HNO_3			
HF			$6.8 \ x10^{-4}$
$HC_2H_3O_2$ (acetic)			$1.8 \ x10^{-4}$
HCN			$4.9 \ x10^{-10}$

Discussion: Of all the weak acids listed above, which is the 'strongest', weakest? Why?

The Relationship Between K_a and pH

Overview: Since any weak acid is in equilibrium, a modified I.C.E. method can be used to determine *either* pH *or* K_a

Vanilla I.C.E., noted chemical philosopher

<u>Worked Example</u>: A sample of 0.10 M formic acid ($HCHO_2$) has a pH of 2.38. Determine K_a for formic acid and the % to which formic acid is dissociated.

<u>Plan</u>:

1. Find $[H^+]$

2. Set up and solve an I.C.E. table in order to find the equilibrium concentrations of HA, H^+, A^-. 'Insert and evaluate' to find K_a

3. Find % dissociation

Using K_a to find pH (the 'reverse' problem)

Question: What is the pH of 0.2 M HCN (aq) ($K_a = 4.9 \times 10^{-10}$)

Plan:

Execution:

IMPORTANT: The weak acid approximation: when $K_a \leq 10^{-3}$

$$[HA] - [H^+] \approx [HA]$$

This greatly simplifies the I.C.E. method, which is usually not undertaken unless the above is true (would otherwise require a quadratic equation to be solved)

Group work: Skip ahead to the end of this handout and work through the first two practice exam problems

Weak Bases
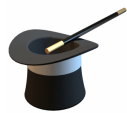
Weak base problems are very similar to the I.C.E. weak acid examples, except that $[OH^-]$ and pOH (rather than $[H^+]$ and pH) are found initially

Generic Equilibrium:

B (aq)   + H_2O (l) $\Leftrightarrow$ HB(aq)   + OH^- (aq)
Weak   Water   Conjugate   Hydroxide
base   Acid   ion
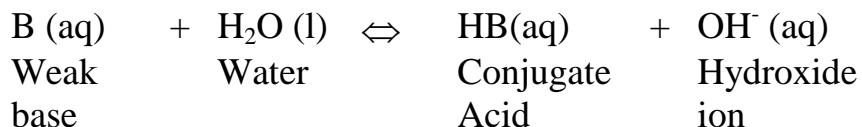
For ammonia dissolved in water:

NH_3 (aq) + H_2O (l) $\rightarrow$ NH_4^+ (aq) + OH^- (aq)
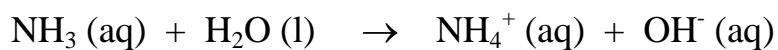
Task: Determine K for the above ammonia equilibrium

Note: Since, in this case, K pertains to the dissociation of a weak base only, it is called the *base dissociation constant* and assigned a suitable subscript:

Task: Complete the following table:

Base	Type	Reaction with water	K_a
NaOH	strong	NaOH (aq) $\rightarrow$ Na$^+$ (aq) + OH$^-$ (aq)	'∞'
KOH			
NH$_3$			1.8×10^{-5}
HS$^-$			1.8×10^{-7}
CO$_3^{2-}$			1.8×10^{-4}

Discussion: Of all the weak bases listed above, which is the 'strongest', weakest? Why?

Example: Find [OH⁻] and pH for 0.15 M NH_3 solution ($K_b = 1.8 \times 10^{-5}$)

Plan:

Recall that [OH-] and pOH can be found initially, then pH can be determined via:

$$pH + pOH = 14$$

Execution:

Group Task: An NH_3 (aq) solution has a pH of 10.50. What is $[NH_3]$ in this solution?

The Relationship between K_a and K_b

Recall: All weak acids and bases are in equilibrium with their respective conjugates. Each will also have an equilibrium (K) expression, e.g.:

NH_4^+ (aq) $\rightarrow$ H^+ (aq) + NH_3 (aq); $K_a =$

NH_3 (aq) + H_2O (l) $\rightarrow$ NH_4^+ (aq) + OH^- (aq); $K_b =$
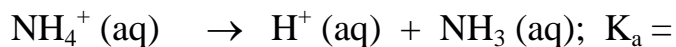
| | 'Equilibrium constant math' can be applied to the above pair of equations. |

Task: Add the above equations and find an expression for K in terms of K_a and K_b. Do you notice something familiar?

	For any weak acid or weak base:
	$$K_aK_b = K_w = 1 \times 10^{-14} = [H^+][OH^-]$$
	Also, since $K_aK_b = K_w$:
	$$pK_a + pK_b = pK_w$$

Quick Question: What is K_a for NH_3 (aq)?

Group work: Skip ahead to the last page of this handout and work through the practice exam problem 'Weak Base'

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"What's the pH?"

Question 2 (25 points): Calculate the pH of each of the following solutions:

1. 0.015 M HCl (aq) (assume complete dissociation)

2. 0.015 M H_2SO_4 (aq) (assume complete dissociation)

3. 0.015 M NaOH (aq) (assume complete dissociation)

4. 0.015 M $HC_2H_3O_2$ (aq), $K_a = 1.8 \times 10^{-5}$

"Weak Acid"

<u>Question 3</u> (25 points): A 0.200 M solution of a weak acid HA (aq) is 9.4 % ionized (dissociated) at equilibrium. Use this information to calculate $[H^+]$, $[HA]$ and K_a for HA.

"Weak Base"

Codeine ($C_{18}H_{21}NO_3$) is a weak organic base. A 5.0 x 10^{-3} M solution of codeine has a pH of 9.95.

<u>Question 4a</u> (20 points): Calculate K_b for codeine.

<u>Question 4b</u> (5 points): Calculate pK_a for codeine.

A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.

HF

HF   HF

F$^-$

HF

HF

H$_3$O$^+$ F$^-$

HF   H$_3$O$^+$

H$_3$O$^+$ ——

HF ——

F$^-$ ——

(a)

CHO$_2^-$ ——

H$_3$O$^+$ ——

HCHO$_2$ ——

(c)

A Weak Base

NH_3

NH_3 OH^-
NH_4^+
NH_3
NH_3
NH_3
OH^- NH_4^+

OH^-

NH_3

NH_4^+

(a)

	Acid	Base	
Strong	HCl	Cl^-	**Neutral**
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
Weak	HSO_4^-	SO_4^{2-}	**Weak**
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	HCN	CN^-	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible	HS^-	S^{2-}	**Strong**
	OH^-	O^{2-}	

Acid Strength

Base Strength

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TABLE 15.5 Acid Ionization Constants (K_a) for Some Monoprotic Weak Acids at 25°C

Acid	Formula	Structural Formula	Ionization Reaction	K_a
Chlorous acid	$HClO_2$	H—O—Cl$=$O	$HClO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + ClO_2^-(aq)$	1.1×10^{-2}
Nitrous acid	HNO_2	H—O—N$=$O	$HNO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + NO_2^-(aq)$	4.6×10^{-4}
Hydrofluoric acid	HF	H—F	$HF(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + F^-(aq)$	3.5×10^{-4}
Formic acid	$HCHO_2$	H—O—C(=O)—H	$HCHO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + CHO_2^-(aq)$	1.8×10^{-4}
Benzoic acid	$HC_7H_5O_2$	H—O—C(=O)—C₆H₅	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.5×10^{-5}
Acetic acid	$HC_2H_3O_2$	H—O—C(=O)—CH₃	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous acid	$HClO$	H—O—Cl	$HClO(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + ClO^-(aq)$	2.9×10^{-8}
Hydrocyanic acid	HCN	H—C$\equiv$N	$HCN(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol	HC_6H_5O	HO—C₆H₅	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

TABLE 15.10 Common Polyprotic Acids and Ionization Constants
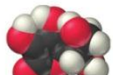
Name (Formula)	Structure	K_{a_1}	K_{a_2}	K_{a_3}
Sulfuric Acid (H_2SO_4)		Strong	1.2×10^{-2}	
Oxalic Acid ($H_2C_2O_4$)		6.0×10^{-2}	6.1×10^{-5}	
Sulfurous Acid (H_2SO_3)		1.6×10^{-2}	6.4×10^{-8}	
Phosphoric Acid (H_3PO_4)		7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Citric Acid ($H_3C_6H_5O_3$)		7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Ascorbic Acid ($H_2C_6H_6O_6$)		8.0×10^{-5}	1.6×10^{-12}	
Carbonic Acid (H_2CO_3)		4.3×10^{-7}	5.6×10^{-11}	

TABLE 15.8 Some Common Weak Bases

Weak Base	Ionization Reaction	K_b
Carbonate ion (CO_3^{2-})*	$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$	1.8×10^{-4}
Methylamine (CH_3NH_2)	$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$	4.4×10^{-4}
Ethylamine ($C_2H_5NH_2$)	$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$	5.6×10^{-4}
Ammonia (NH_3)	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	1.76×10^{-5}
Pyridine (C_5H_5N)	$C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$	1.7×10^{-9}
Bicarbonate ion (HCO_3^-)* (or hydrogen carbonate)	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$	1.7×10^{-9}
Aniline ($C_6H_5NH_2$)	$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$	3.9×10^{-10}

*The carbonate and bicarbonate ions must occur with a positively charged ion such as Na^+ that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate ($NaHCO_3$) basic. We look more closely at ionic bases in Section 15.8.

Acid - Base Equilibria 3

Additional Aspects of Acid-Base Equilibrium

Salts and Polyprotic Acids

Discussion: What happens, on a molecular level, when sodium acetate (or any salt of a weak acid and a strong base) is dissolved in water?

Equation 1:

Would you expect the resulting solution to be acidic, basic or neutral? What's the trick??
(K_a $HC_2H_3O_2 = 1.8$ x 10^{-5}).

Equation 2:

Task: Calculate the pH of a solution made by dissolving 10.0 grams of $NaC_2H_3O_2$ (s) in water, making the final solution volume equal 1.0 L

Discussion: What is the difference between a *mono*protic and a *poly*protic acid? Give an example of each.

Recall your lab: Polyprotic acids are *amphoteric*, so will have *several equivalence points* when titrated - each acidic proton is either removed (NaOH titration of the acid form) or added (HCl titration of the base form).

Each *de*protonation step will have a specific K_a (or pK_a) value associated with it (see slide / handout)
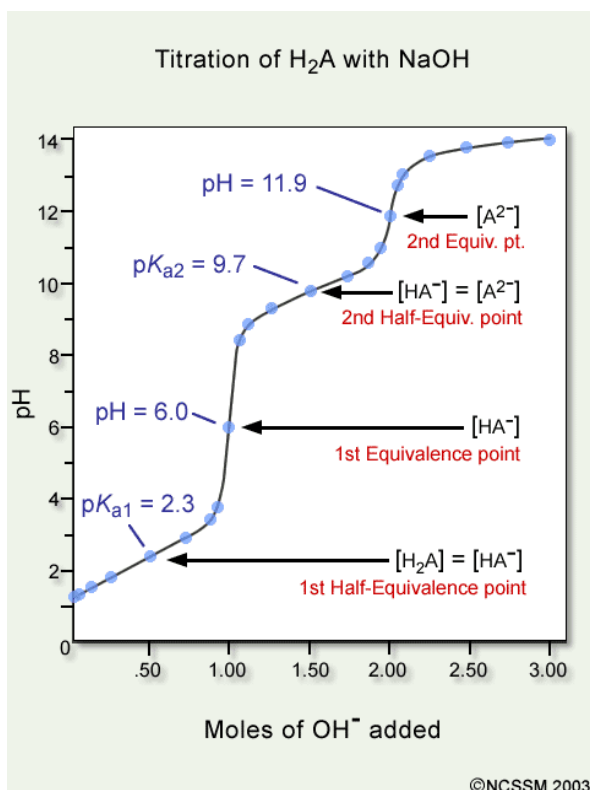
Generic titration plot for a diprotic acid (H_2A) with a strong base

Equivalence Point 1

$$H_2A \Leftrightarrow H^+ + HA^-$$

$$pK_{a1} = 2.3$$

$$K_{a1} = _____$$

Equivalence Point 2

$$HA^- \Leftrightarrow H^+ + A^-$$

$$pK_{a2} = 9.7$$

$$K_{a2} = _____$$

Note: Titration plots can be used to determine K_a values – this will be covered in more detail below.

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Questions: Which indicators would be best for detecting the two titration endpoints, observed for H_2A (above), when this diprotic acid is titrated with NaOH (aq)? What color changes would be observed?
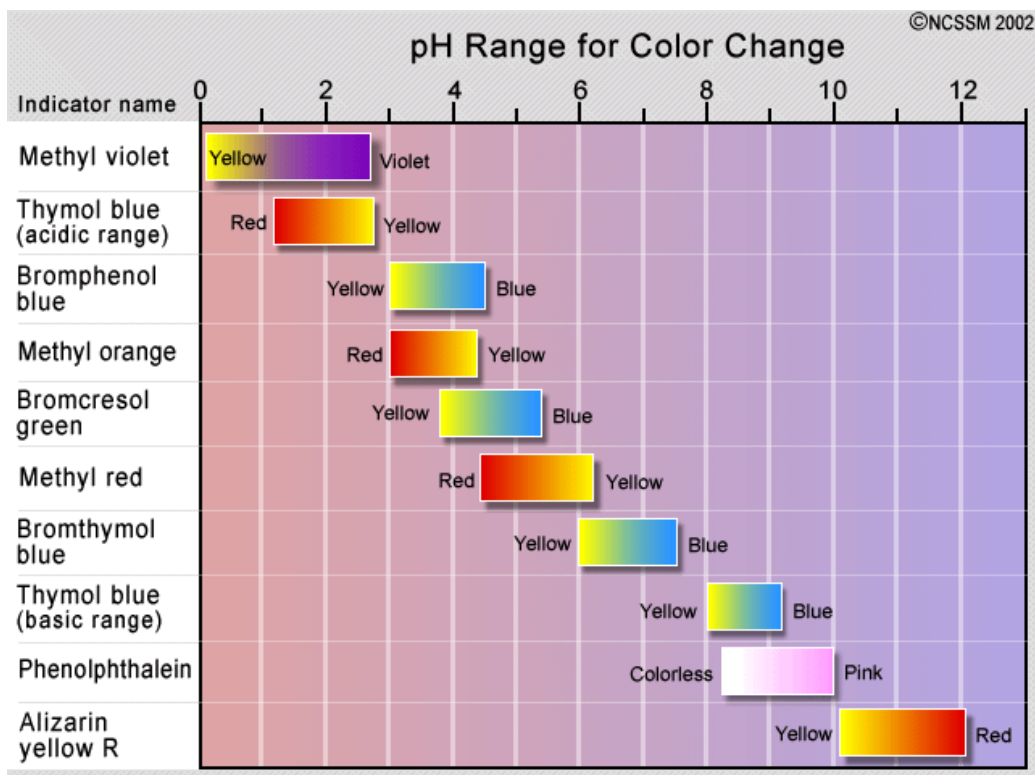
The common Ion effect

Consider the following equilibrium for acetic acid:

$$HC_2H_3O_2 \text{ (aq)} \iff H^+ \text{ (aq)} + C_2H_3O_2^- \text{ (aq)}$$

Discussion: according to Le Châtelier's Principle, what would happen to the position of the above equilibrium if a large amount of $C_2H_3O_2^-$ (aq) (from, for example, $NaC_2H_3O_2$) were added?

Your description:
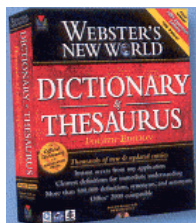
(an unnecessarily wordy) Dictionary Description

*The extent of ionization of a weak electrolyte is decreased by adding a strong electrolyte (such as a salt) that has a **common ion** with the weak electrolyte in solution*

Weak acid

Conjugate base

Buffer solution

Acetic acid
$HC_2H_3O_2$

Sodium acetate
$NaC_2H_3O_2$
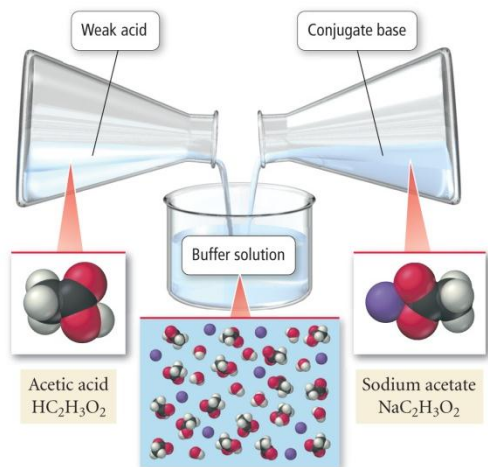
Worked Example: What is the pH of a solution made by adding 0.125 mol. of $HC_2H_3O_2$ and 0.075 mol. of $NaC_2H_3O_2$ to enough water to make a 1.0 L solution? K_a acetic acid $= 1.8 \times 10^{-5}$

Use the standard I.C.E. method for weak acids, BUT include the (*now non-zero*) initial concentration of the conjugate base introduced via dissolving it's salt.

	[HA]	[H₃O⁺]	[A⁻]
Initial	0.125	≈0.00	0.075
Change	$-x$	$+x$	$+x$
Equil	$0.125 - x$	x	$0.075 + x$

From stoichiometry calculation

ANS =

Task: Calculate [F⁻] and pH of a solution that is simultaneously 0.20M in HF (aq) and 0.10 M in HCl (aq). K_a for HF = 6.8 x10⁻⁴

ANS: [F⁻] = 1.4 x10⁻³ M
pH = 1.0

Comment:

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Buffered Solutions

Discussion / Background: consider the following generic weak acid /conjugate base equilibrium (see appendix):

$$HA \ (aq) \ \Leftrightarrow \ H^+ \ (aq) \ + \ A^- \ (aq)$$

According to Le Châtelier's Principle, what would happen to the position of the above equilibrium if:

1. A large amount of H^+ (aq) from an external source (such as a strong acid like HCl (aq)) were added?

   Equation:

2. A large amount of OH^- (aq) from an external source (such as a strong base like NaOH (aq)) were added?

   Equation:

Buffering capacity and Buffer pH

A buffer will resist changes in pH (i.e. increases in either $[H^+]$ or $[OH^-]$) by 'reacting away' these chemical species.

The buffering capacity of the buffer is determined by the relative concentrations of the weak acid (HA) and conjugate base (A^-) at equilibrium. For example, a buffer with HA: A^- in a 10:1 ratio will be able to 'react away' x10 more OH^- than can H^+ before the buffer becomes exhausted.

The chemical makeup of the buffer (i.e. K_a or K_b for the weak acid/base system) determines the 'natural' pH the buffer. Buffers of virtually any pH between ~2 and 13 can be constructed.

Titration curves for non-buffered and buffered systems (see appendix)

Titration of a strong acid with NaOH (non-buffered)	Titration of a weak acid /conjugate base buffer with NaOH
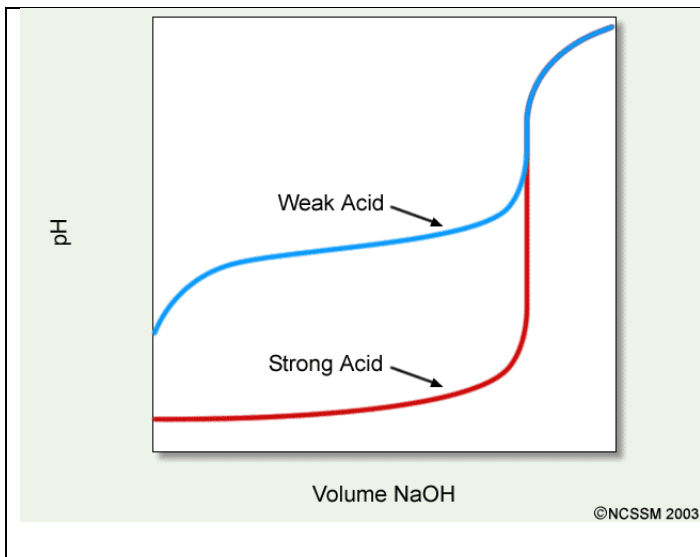
Diagram illustrating the 'buffer region' for a weak acid undergoing titration with NaOH (aq).

Recall:

$$HA + OH^- \rightarrow A^- + H_2O$$
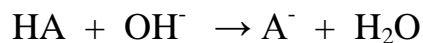
Equivalence is reached when moles HA present = moles OH added. Before equivalence, the 'natural' pH of the buffer is maintained
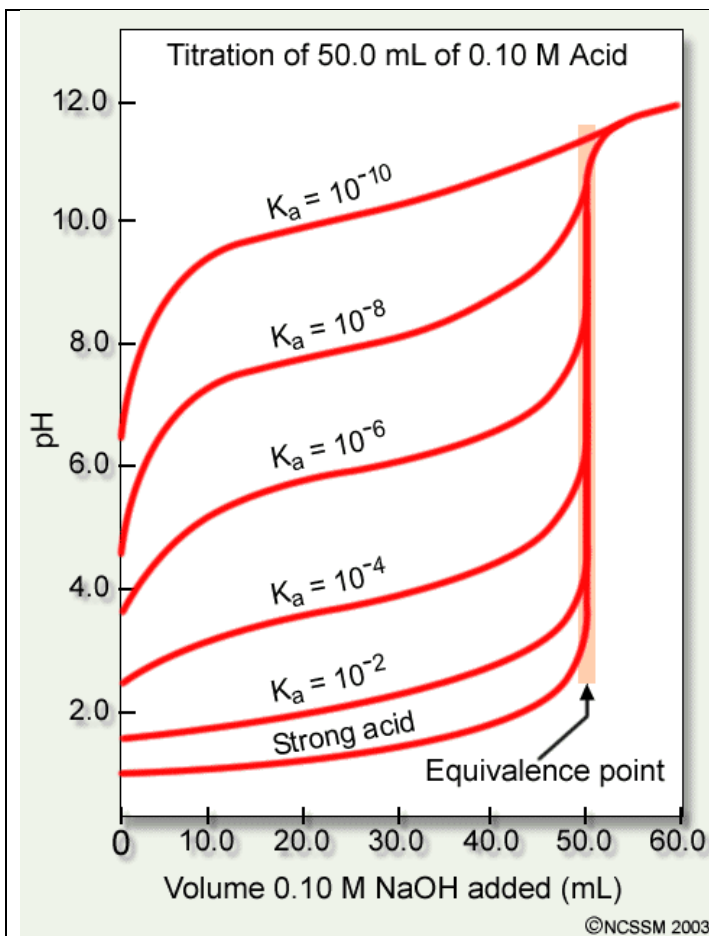
Diagram illustrating the 'buffer region' for weak acids of specific Ka values undergoing titration with NaOH (aq).

Discussion: What do you notice with regard to the relationship between K_a and the 'natural' pH of the buffer?

Note: The mathematical relationship between pH and K_a is discussed further below

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Because buffers are essentially just either a weak acid or a weak base and their respective conjugate in equilibrium, a standard 'common ion' I.C.E. approach can be used to find the 'natural' pH of a buffer (recall the $HC_2H_3O_2$ / $NaC_2H_3O_2$ system discussed previously).

Example (group work): What is the pH of a buffer that is 0.12 M in lactic acid $(HC_3H_5O_3)$ and 0.10M in sodium lactate? $K_a = 1.4 \times 10^{-4}$.

The *Verve* had a good handle on weak acid / base equilibria. Kind of….

Drugs are typically either weak acids or weak bases (more on this later), so their pH - which relates to solubility, and ultimately if the drug should be taken orally or intravenously – is of great interest to MCAT and PCAT examiners!

Problem: Do you think 'they' intend for you to employ a time consuming modified I.C.E. methodology on the 'CAT' test?

Answer:

Solution: There is a quicker and much more convenient method to find the pH of a buffer solution: the Henderson – Hasselbalch equation.
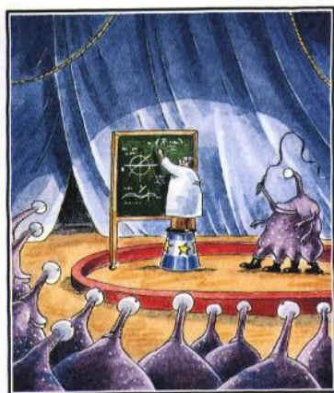
Abducted by an alien circus company, Professor Doyle is forced to write calculus equations in center ring.

Derivation of the Henderson –Hasselbalch equation

Since, for any weak acid conjugate base buffer:

$$ K_a = \frac{[H^+]\,[A^-_{weak}]}{[HA_{weak}]} $$

Then:

Henderson –Hasselbalch equation

$$pH = pK + \log\left(\frac{[A^-]}{[HA]}\right)$$

Task: Assume you are taking the PCAT or MCAT- use the H-H equation to quickly answer the previous lactic acid buffer question:

What is the pH of a buffer that is 0.12 M in lactic acid ($HC_3H_5O_3$) and 0.10M in sodium lactate? $K_a = 1.4 \times 10^{-4}$.

Discussion: When you perform a titration, what is true in terms of the moles of acid and base present at equivalence? What then must be true at half- equivalence?

What happens to the H-H equation at half-equivalence for the titration of a weak acid with NaOH? (i.e. when moles HA unreacted = moles A⁻ formed)?

$pH = pK_a$ for a buffer at half- equivalence (i.e. when $[HA] = [A^-]$)

(see titration cure examples, above (H_2A), and in Appendix)

Mr. Buffer's buffer (buffers in the body)

Blood has a regulated (buffered) pH of 7.4. The buffer responsible for maintaining the pH of blood is the carbonic acid / hydrogen carbonate system – i.e. the same one studied in your recent lab:
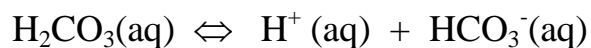
$$H_2CO_3(aq) \Leftrightarrow H^+(aq) + HCO_3^-(aq)$$

Group work: If $H_2CO_3(aq)$ has a concentration of 0.0012 M in human blood, what is $[HCO_3^-]$ in blood? Is blood better at resisting changes in $[H^+]$ or $[OH^-]$? $K_a = 4.3 \times 10^{-7}$

Lewis acids/bases and more about Drugs

The Lewis lone–pair transfer model

In the Lewis model:

Lewis Acids are identified as lone pair electron acceptors

Lewis Bases are identified as lone pair electron donors

Just like proton transfer, but viewed in terms of what the proton 'sticks to'

Example: NH_3 (aq) as Lewis base

NH_3 H_2O NH_4^+ OH^-
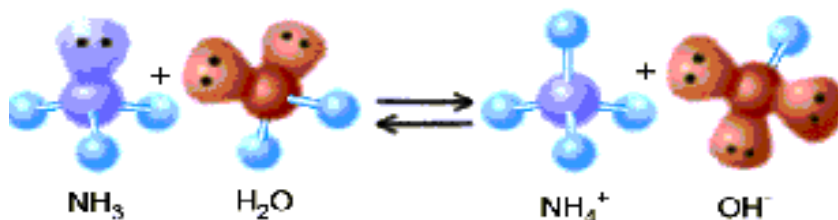
Question: Why worry about Lewis base behavior, when it is essentially just B-L theory from a different point of view?

Answer: Most 'interesting' drugs (be they legal or illegal) are Lewis bases – they contain N**:** group(s) (just like ammonia).

Problem: Most 'free bases' (where have you heard that term before?) are volatile and not too soluble in water – not good candidates for turning into oral (or other) medication.

Solution: Turn 'free bases' into acids salts – acid salts are soluble and non-volatile, so have long shelf lives and can be taken orally.

Generic example of forming the acid salt of a 'free base'

$$D\text{:} \ + \ HCl\,(aq) \ \rightarrow \ [D\text{:}H]^+[Cl]^-$$
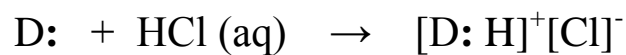
A great many drugs, both legal and illegal, are manufactured and sold as the acid or other salts

Levitra (vardenafil HCl):

'Crack' (cocaine sodium hydrogen carbonate):

Social commentary: I don't want to go off on a rant here, but…

Solubility Equilibria

Background: What is a saturated solution?

Official definition: *A solution in which undissolved solute and dissolved solute are present in equilibrium*

Most *apparently* insoluble solids (such as chalk, for example) are *sparingly soluble* – they dissolve to a tiny degree:

$$CaCO_3 \text{ (s)} \Leftrightarrow Ca^{2+} \text{ (aq)} + CO_3^{2-} \text{ (aq)}$$
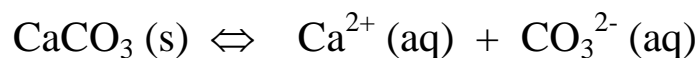
Task: Derive a simple 'products over reactants' expression for the above equilibrium featuring solid chalk (calcium carbonate) and it's dissolved ions. What 'cancels'?

Any sparingly soluble salt (ionic compound) will have a related solubility product (K_{sp}) expression. K_{sp} values are known for most compounds at 25^oC. For chalk (calcium carbonate):

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.5 \times 10^{-9}$$

Since the ionic materials we are dealing with are *sparingly* soluble, their K_{sp} values are necessarily *very* low

Compound	K_{sp}	Compound	K_{sp}
$BaSO_4$	5.0×10^{-9}	CaF_2	3.9×10^{-11}
Ag_2SO_4	1.5×10^{-5}	$AgCl$	1.8×10^{-10}

See the Appendix for a more complete list

Task: Write solubility product *expressions* for the following equilibria

1. Dissolution of barium sulfate

2. Dissolution of calcium fluoride

3. Dissolution of silver sulfate

As with all other equilibria, the concentration of a reactant is raised to the power of its stoichiometic coefficient in the expression

Solubility and K$_{sp}$

Group work: You drop a stick of chalk into some pure water. What will the concentration of the Ca^{2+} (aq) ions be in the resulting *saturated* solution after the solid and its aqueous ions have attained equilibrium? Hint: Use the K$_{sp}$ expression

Harder example: A saturated solution of magnesium hydroxide has a pH of 10.17. Find K$_{sp}$ for Mg(OH)$_2$. See appendix for equation.

Solubility

> **The solubility (*s*) of any sparingly soluble salt (ionic compound)** *is expressed in terms of the solvated metal cation*

For the dissolution of AgCl:

$$AgCl\ (s) \Leftrightarrow Ag^+\ (aq)\ +\ Cl^-\ (aq)$$
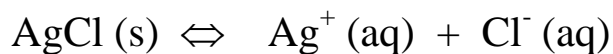
solubility (s) $= [Ag^+]$ (which also $= [Cl^-]$ in this example)

Task: Derive an expression for *s* in terms of K_{sp}, given that, for silver chloride:

$$K_{sp} = [Ag^+][\ Cl^-]$$

Group Task: Determine K_{sp} and solubility (s) expressions for the following equilibrium:

$$CaF_2 \text{ (s)} \iff Ca^{2+} \text{ (aq)} + 2F^- \text{ (aq)}$$
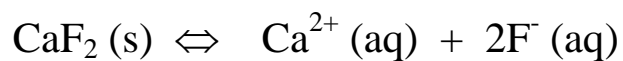
Worked (quantitative) Example: What is the solubility of calcium fluoride in g/L? $K_{sp} = 3.9 \times 10^{-11}$

Plan:

Note: Solubilities (especially in the biochemical and medical fields) are often quoted in g/L or mg/mL

K_{sp} and the Common Ion Effect

Recall: According to Le Châtelier's Principle, increasing the concentration of a dissolved reactant or product in equilibrium will cause the equilibrium to shift in order to remove that material. The same is true for K_{sp} equilibria

Worked Example: Calculate the molar solubility (s, in mol/L) of CaF_2 in a solution that is 0.010M in $Ca(NO_3)_2$ (aq)

Plan: set up a modified I.C.E. grid, then insert and evaluate in the K_{sp} expression.

Notice that any compound that undergoes partial dissociation (weak acids, weak bases, buffers, and now sparingly soluble salts) can be modeled using the I.C.E. method coupled with the appropriate equilibrium expression – *it's just a case of same math, different application….*
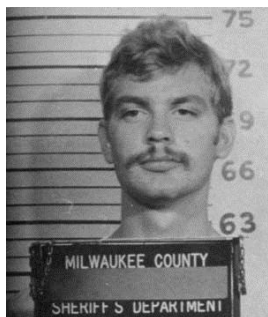
Discussion / Observation: As the infamous serial killer Jeffery Dahmer would have told you, the easiest way to get sparingly soluble salts (like calcium phosphate (bone)) into solution is to dissolve them in an acid.

Jeffery obviously paid attention in Gen. Chem., as this is a standard lab 'trick':

Example: Consider the dissolution equilibrium of the sparingly soluble salt material magnesium carbonate:

$$MgCO_3 \text{ (s)} \iff Mg^{2+} \text{ (aq)} + CO_3^{2-} \text{ (aq)}$$
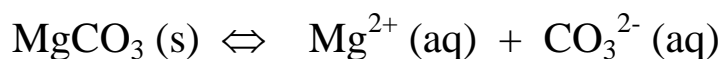
If HCl (aq) is used as a solvent, then:

$$HCl \text{ (aq)} \rightarrow H^+ \text{ (aq)} + Cl^- \text{ (aq)} \quad \text{(complete dissociation)}$$

Now, the H^+ ions will enter into equilibrium with the carbonate anion, which is the conjugate base of the weak acid HCO_3^-:

$$H^+ \text{ (aq)} + CO_3^{2-} \text{ (aq)} \iff HCO_3^- \text{ (aq)}$$
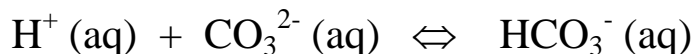
Question: What happens to the original magnesium carbonate equilibrium when carbonate ions are removed in this way? What will happen to the value of $[Mg^{2+}]$ (s) and the amount of sold magnesium carbonate present?

"Common Ion"

Question 2 (25 points): A solution contains 2.5×10^{-4} M Ag^+(aq) and 1.7×10^{-3} M Pb^{2+}(aq).

A. If NaI (aq) is added, will AgI ($K_{sp} = 8.3 \times 10^{-17}$) or PbI_2 ($K_{sp} = 7.9 \times 10^{-9}$) precipitate first?

B. Specify the concentration of I^- (aq) needed to begin precipitation of the material you determined would precipitate first in part A.

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Formation of a Buffer

Weak acid

Conjugate base

Buffer solution

Acetic acid
$HC_2H_3O_2$

Sodium acetate
$NaC_2H_3O_2$
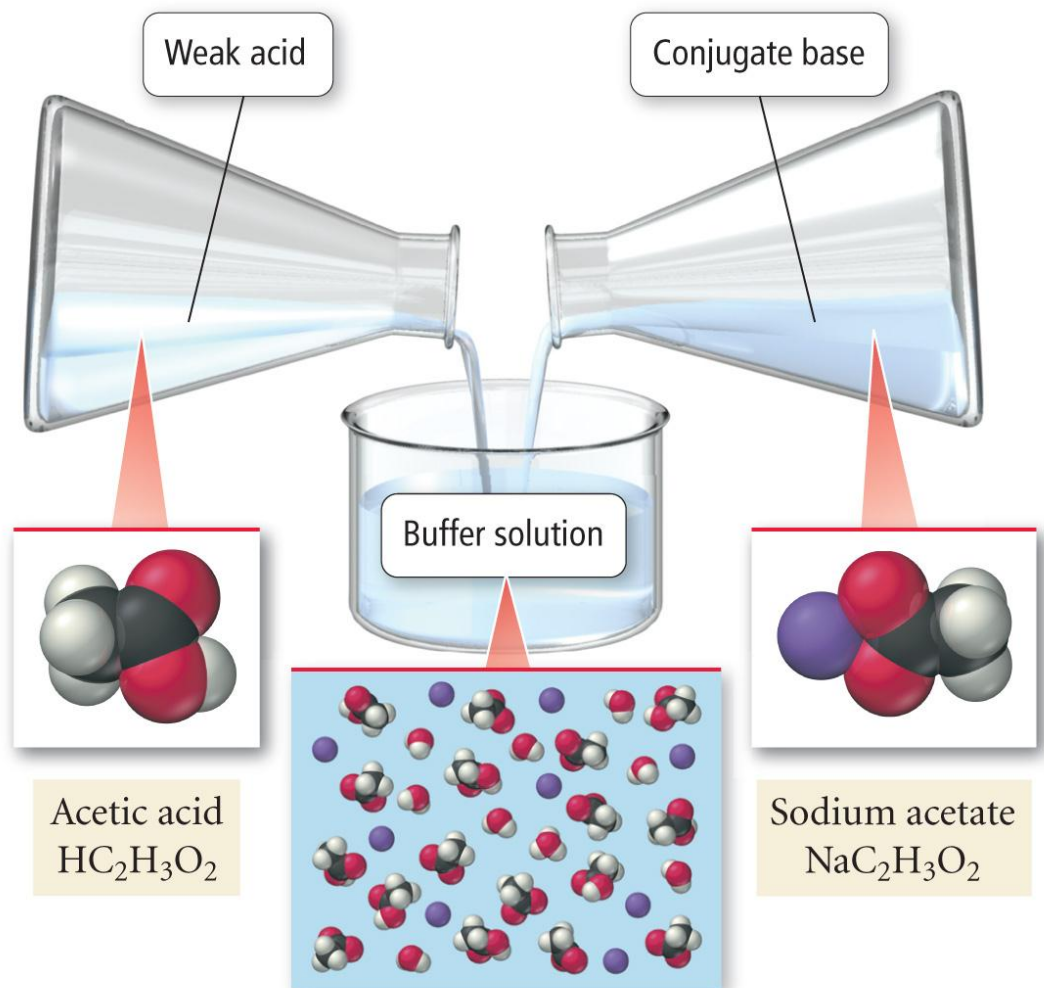
	[HA]	[H₃O⁺]	[A⁻]	
	$[HA]$	$[H_3O^+]$	$[A^-]$	From stoichiometry calculation
Initial	0.125	≈0.00	0.075	
Change	$-x$	$+x$	$+x$	
Equil	$0.125 - x$	x	$0.075 + x$	

Formation of a Buffer

Weak base

Conjugate acid

Ammonia
NH_3

Buffer solution

Ammonium chloride
NH_4Cl
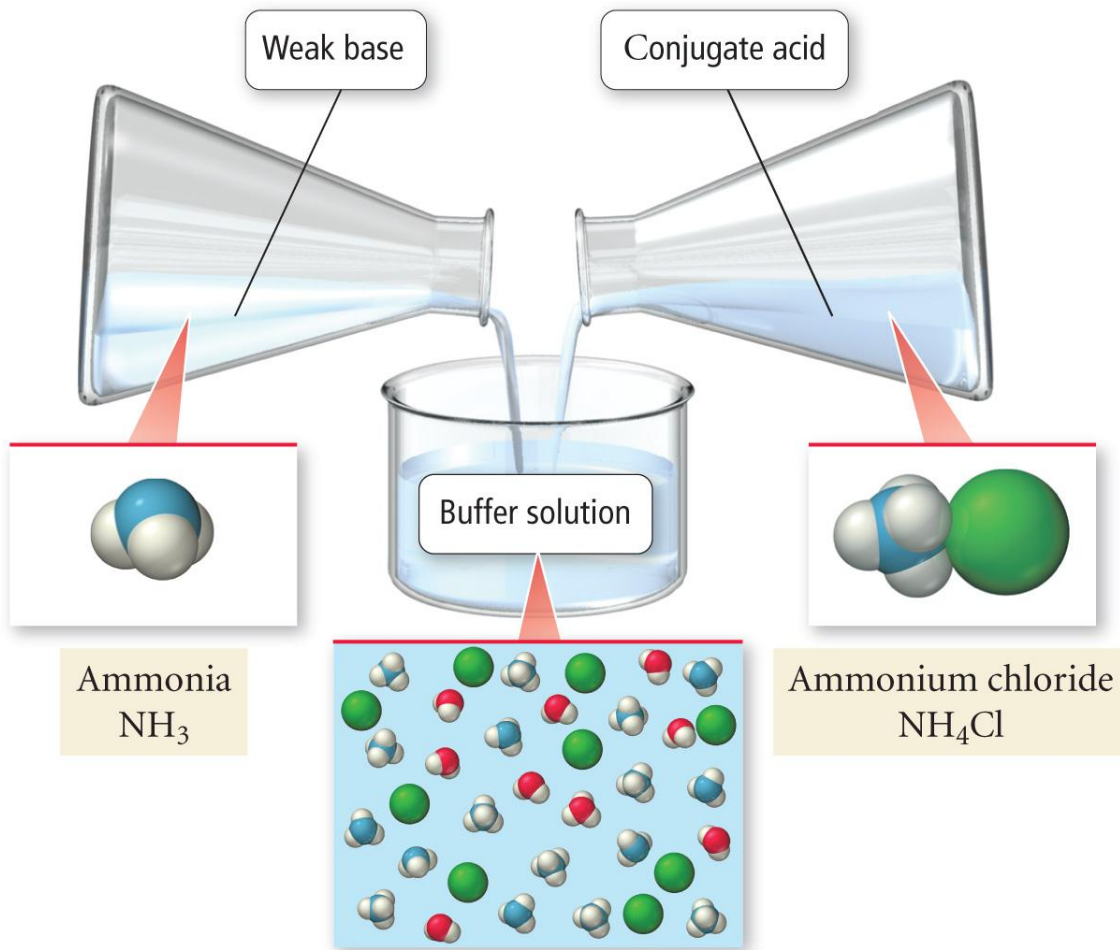
Copyright © 2008 Pearson Prentice Hall, Inc.

Action of a Buffer

After addition of H⁺   Equal concentrations of weak acid and conjugate base   After addition of OH⁻
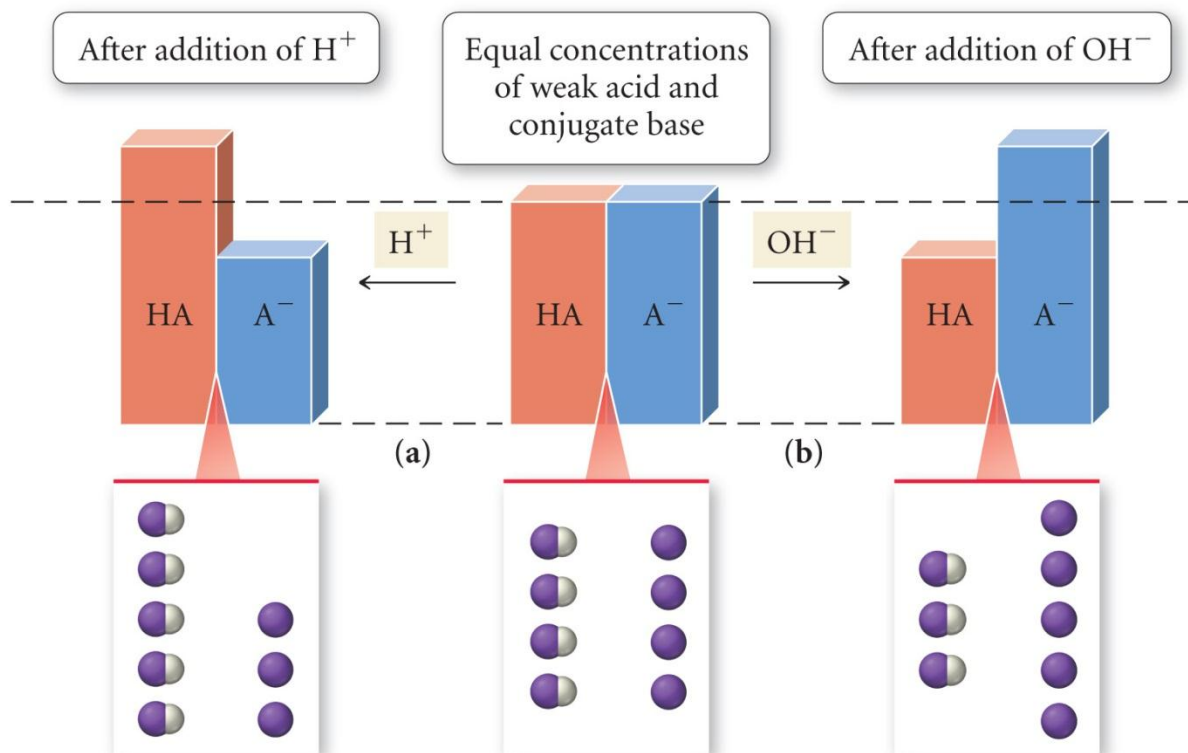
Strong Base & Strong Acid

pH vs. Volume of HCl added (mL)

Equivalence point

220
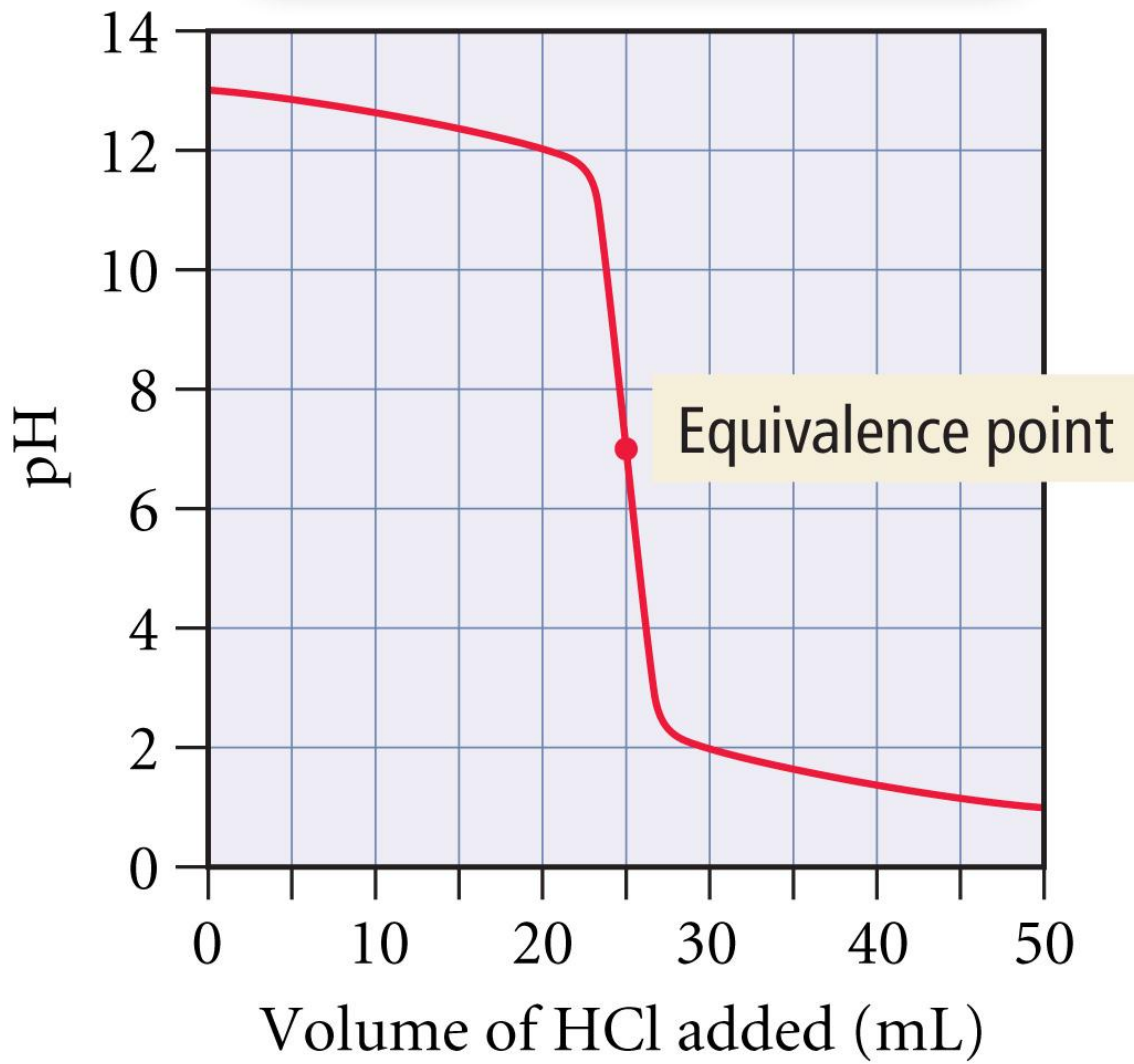
Weak Base & Strong Acid

0.10 M NH_3
pH = 11.12

Half-equivalence point
$[NH_3] = [NH_4^+]$
pH = 9.24

Equivalence point
pH = 5.26

pH

Volume of HCl added (mL)
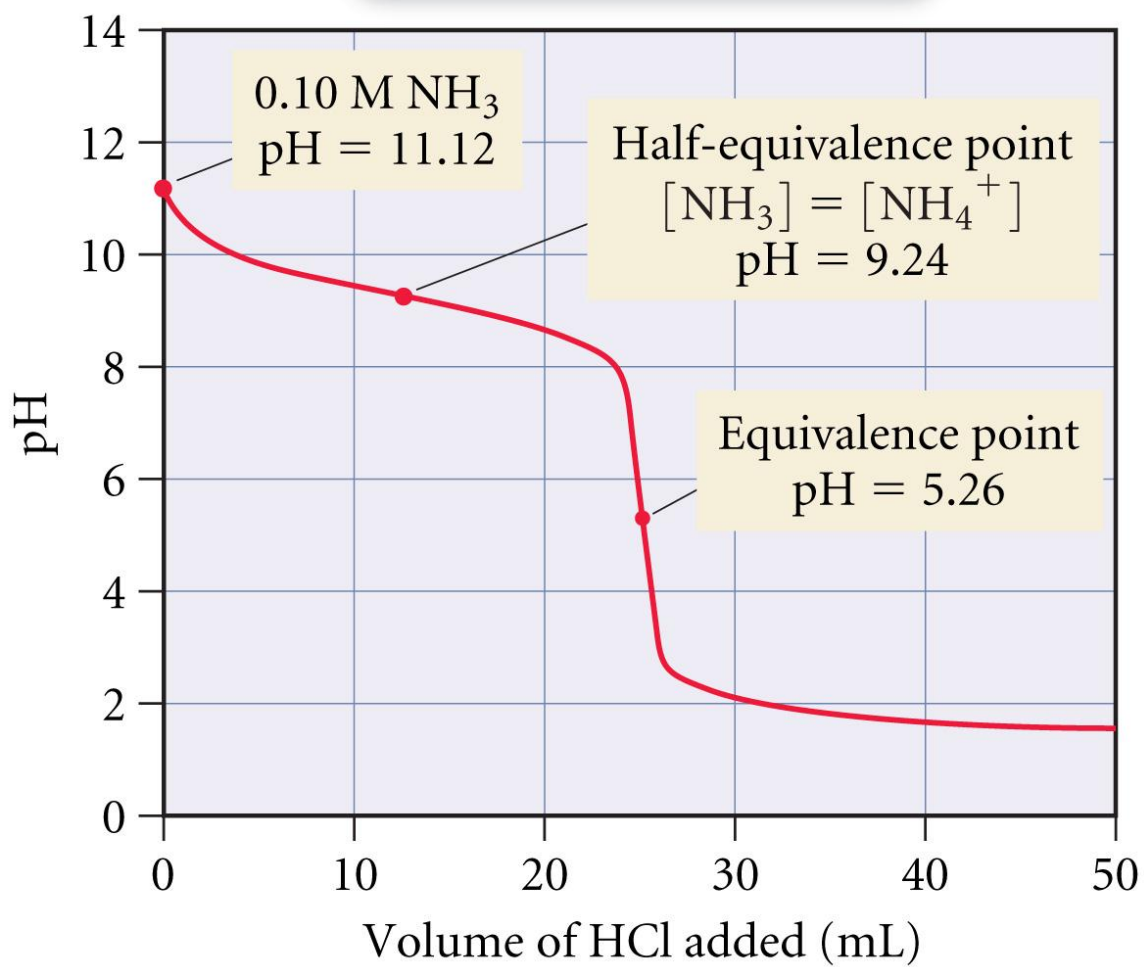
Titration of a Polyprotic Acid
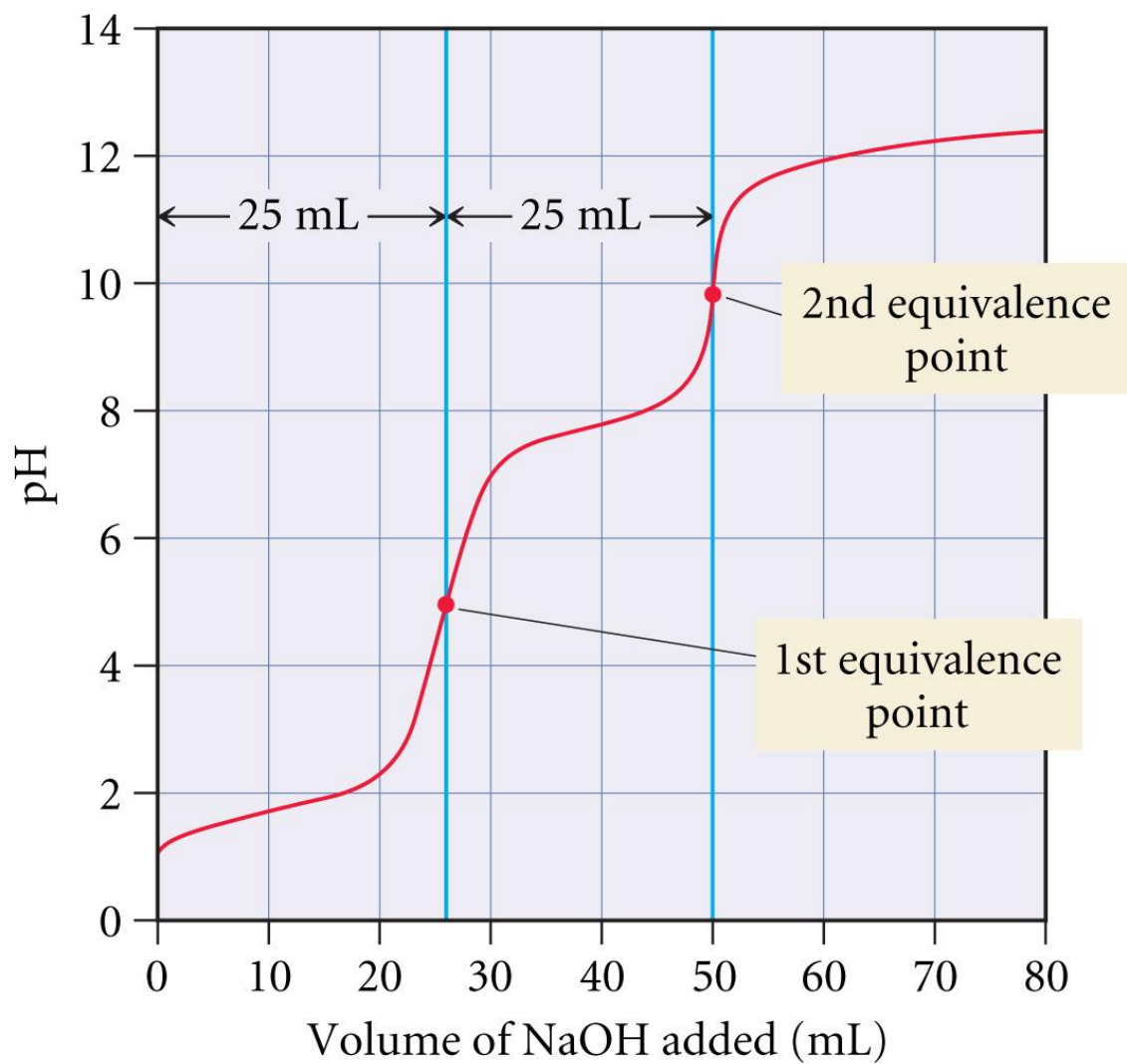
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Common ion
0.100 M $F^-(aq)$

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Equilibrium shifts left

High $[OH^-]$

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Equilibrium shifts left

H_3O^+ reacts with OH^-

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Equilibrium shifts right

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TABLE 16.2 Selected Solubility Product Constants (K_{sp})

Compound	Formula	K_{sp}	Compound	Formula	K_{sp}
Barium fluoride	BaF_2	2.45×10^{-5}	Lead(II) chloride	$PbCl_2$	1.17×10^{-5}
Barium sulfate	$BaSO_4$	1.07×10^{-10}	Lead(II) bromide	$PbBr_2$	4.67×10^{-6}
Calcium carbonate	$CaCO_3$	4.96×10^{-9}	Lead(II) sulfate	$PbSO_4$	1.82×10^{-8}
Calcium fluoride	CaF_2	1.46×10^{-10}	Lead(II) sulfide	PbS	9.04×10^{-29}
Calcium hydroxide	$Ca(OH)_2$	4.68×10^{-6}	Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Calcium sulfate	$CaSO_4$	7.10×10^{-5}	Magnesium hydroxide	$Mg(OH)_2$	2.06×10^{-13}
Copper(II) sulfide	CuS	1.27×10^{-36}	Silver chloride	$AgCl$	1.77×10^{-10}
Iron(II) carbonate	$FeCO_3$	3.07×10^{-11}	Silver chromate	Ag_2CrO_4	1.12×10^{-12}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}	Silver bromide	$AgBr$	5.35×10^{-13}
Iron(II) sulfide	FeS	3.72×10^{-19}	Silver iodide	AgI	8.51×10^{-17}
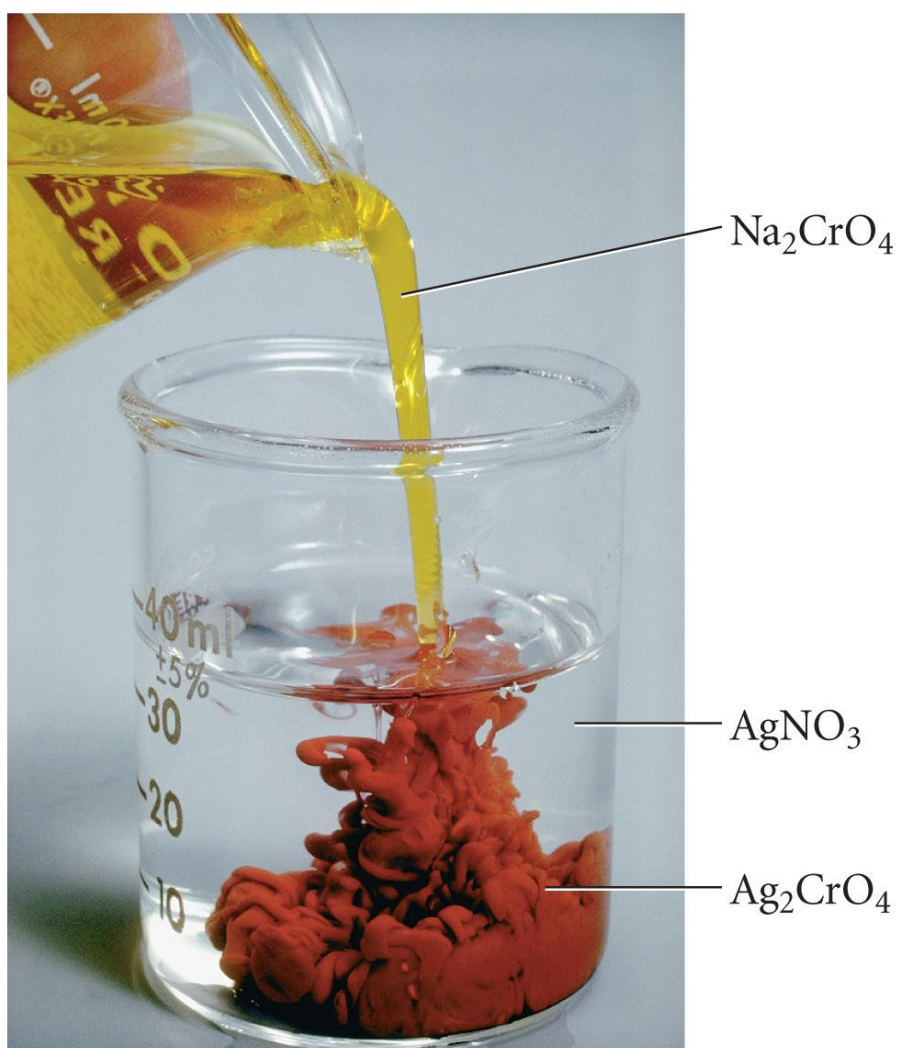
Na_2CrO_4

$AgNO_3$

Ag_2CrO_4

Chemical Thermodynamics

The Second Law of Thermodynamics - ENTROPY

"We don't like the idea of an increasingly disordered universe"
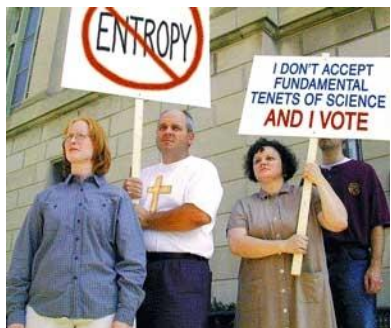
Key Idea and Definitions

The ENTROPY (note spelling), *S*, of the Universe increases (ΔS = +ve) for a *spontaneous* process.

Discussion: What is a spontaneous process? 'Being spontaneous' is a somewhat accurate analogy…

Entropy (S): A measure of the amount of disorder in a system, Symbol *S*.

Discussion: What is *disorder*? Example, which has a higher degree of disorder (entropy) - a rack of pool balls before or after a break off??
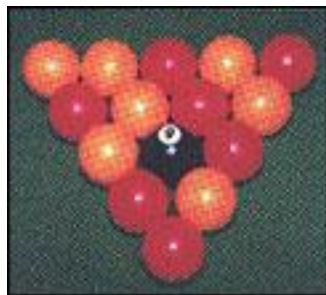
Before

After

Entropy: Entropy:

$$\Rightarrow \Delta S \ = \ S_{(final)} - S_{(initial)} \ =$$

Examples: Based on Entropy arguments alone, would you expect the following processes to be spontaneous (i.e. experience an increase in entropy upon completion)? Briefly explain.

1. H_2CO_3 (aq) $\rightarrow$ H_2O (l) + CO_2 (g)
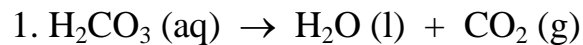
Observation

2. The air drying of washing up or clothes on a washing line

$$H_2O \text{ (l)} \rightarrow H_2O \text{ (g)}$$
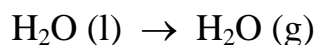
Observation

"The 2nd law will take care of it"...

3. NaCl (s) $\rightarrow$ NaCl (aq)
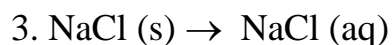
Observation (see more detailed figure below)

Dissolution of NaCl increases entropy

Less randomness (less entropy)

More randomness (more entropy)

H_2O

$\Delta S > 0$

$\Delta S < 0$

H_2O

NaCl

NaCl(s) + H_2O(l)

Na^+(aq) + Cl^-(aq)

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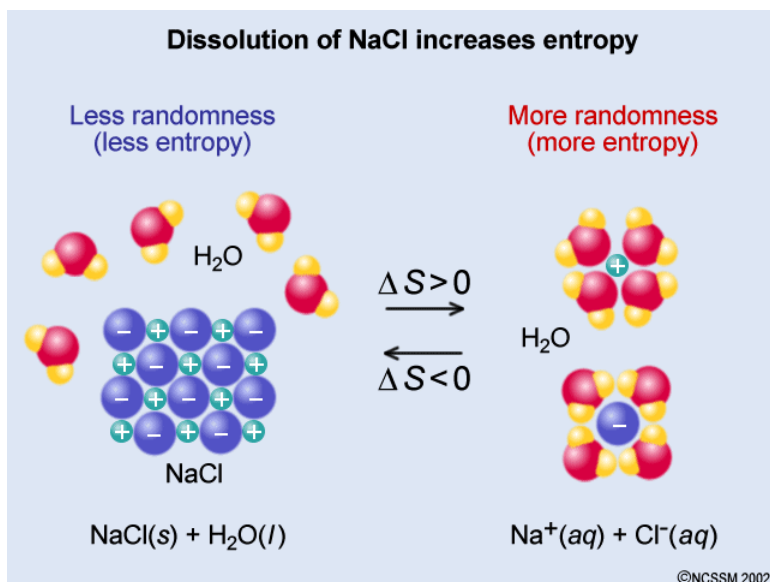
4. The diffusion of any gas

<u>Observation</u>

<u>Task</u>: List at least three entropy driven processes (see appendix for examples)
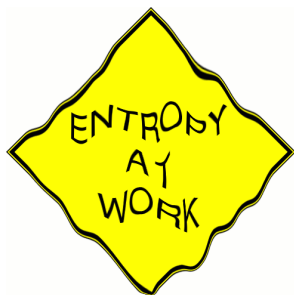
Just like with Enthalpy (H), each material has an inherent amount of entropy. All S values are measured in J/mol K and are always positive. **The magnitude of S indicates the relative amount of disorder for the material**.

Standard Entropy values can be used (in a similar way to ΔH_f values) to find ΔS for any reaction. See Appendix.

<u>Example</u>: Calculate ΔS for the following reaction:

$$CCl_4 \text{ (l)} \rightarrow CCl_4 \text{ (g)}; \quad \Delta S = \underline{\hspace{3cm}}$$
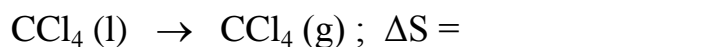
Given: CCl_4 (g), S = 309.4 J/molK
            CCl_4 (l), S = 214.4 J/molK

What conclusion can you make regarding the evaporation of CCl_4 (l)?

Math considerations – the second law of thermodynamics

Entropy is temperature dependant – the hotter a material is the more entropy it has (standard entropies form Appendix C are calculated at 25°C, 1.00 atm). This fact is conveyed in the formal mathematical description of the 2nd law:

$$S = \frac{q_{rev}}{T}$$

For chemical systems that do not do 'PV' work, $\Delta H = q$ (first law), therefore:

$$S = \frac{\Delta H}{T}$$

Wrap up Discussion: If all spontaneous processes result in an increase in entropy, how can processes that result in a decrease in entropy (such as the freezing of water) for a material ever occur??
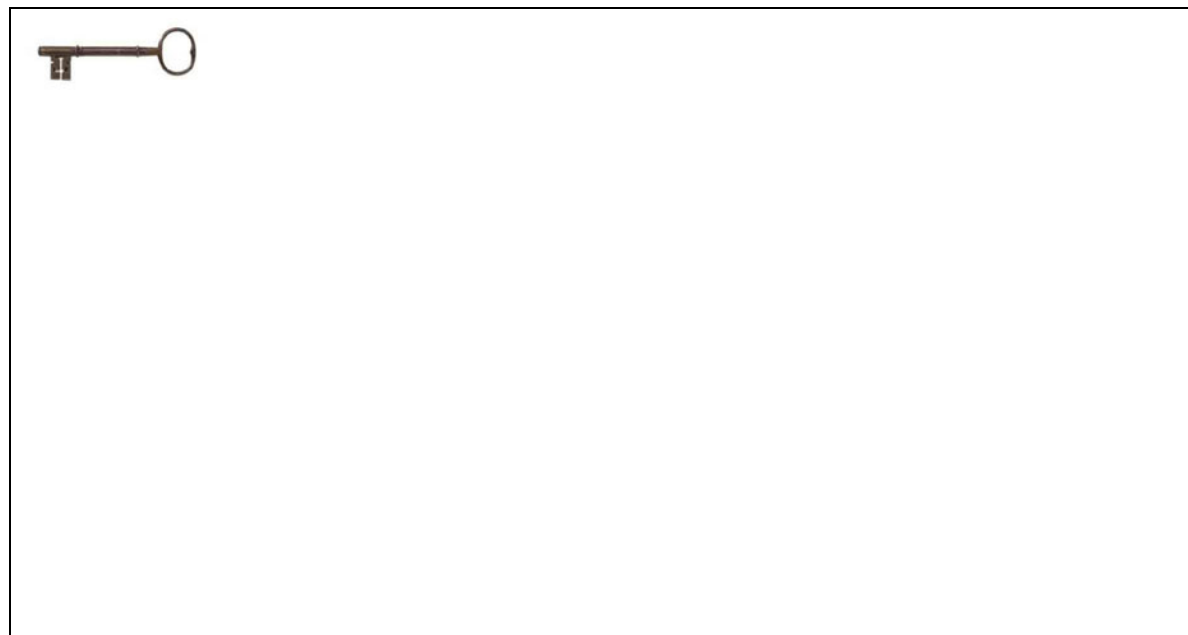
Gibbs Free Energy

> **Gibbs free energy (ΔG) for a reaction relates ΔH and ΔS for that reaction.**
>
> **Simply, the mathematical sign of ΔG, determined via the Gibbs equation, determines if a reaction will ever work (is spontaneous); will never work (in non-spontaneous) or at equilibrium.**
>
> **Spontaneous: ΔG < 0   Non-spontaneous: ΔG > 0   Equilibrium: ΔG = 0**

Gibbs Free Energy Equation:

$$\Delta G = \Delta H - T\,\Delta S$$

The sign of ΔG (and, therefore, if a reaction is spontaneous) depends on the signs of ΔH and ΔS. See appendix.

Task: Complete the following table / determine the sign of ΔG

ΔH	ΔS	ΔG	spontaneous
-ve	-ve		
-ve	+ve		
+ve	-ve		
+ve	+ve		

> **As with ΔH and ΔS, ΔG is a state function.**
>
> **ΔG values follow the same 'state function' math rules as the ΔH and ΔS, so can be determined from these quantities. Slides**

'Huge' worked Example: The thermite reaction is used to weld railway tracks:

$$Fe_2O_3 \text{ (s)} + 2\,Al \text{ (s)} \rightarrow 2\,Fe \text{ (s)} + Al_2O_3 \text{ (s)}$$
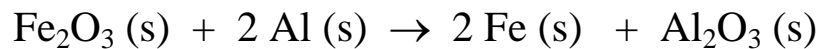
Based on the below data, determine if this reaction is spontaneous at 25^oC and quote the value of ΔG in kJ/mol

Given:

ΔH_f Fe_2O_3 (s) $= -822.16$ kJ/mol

ΔH_f Al_2O_3 (s) $= -1669.9$ kJ/mol

S Fe_2O_3 (s) $= +89.96$ J/molK

S Al_2O_3 (s) $= +51.00$ J/molK

S Fe (s) $= +27.15$ J/molK

S Al (s) $= +25.32$ J/molK

Plan: Find ΔH, ΔS, and then find ΔG

Free Energy and Equilibrium

Recall: For and equilibrium, $\Delta G = 0$. In terms of the equilibrium constant K and other variables

$$\Delta G = \text{-RT lnK}$$

Where: K = equilibrium constant (no units)
            ΔG = Gibbs Free energy (kJ/mol)
            R = 8.314 J/molK
            T = temperature in Kelvin

Task: Rearrange the above equation to find an expression for K in terms of ΔG

Group activity: Use the standard ΔG values in appendicies to find K at 25°C for:

$$N_2 \text{ (g)} + 3 \, H_2 \text{ (g)} \rightarrow 2 \, NH_3 \text{ (g)}$$

Plan: Find ΔG, find K

"Gibbs"

Question 1 (25 points): Using the thermodynamic information given in the data sheet, calculate ΔG^o for the following reaction:

$$Fe_2O_3 \text{ (s)} + 6 \text{ HCl (g)} \rightarrow 2 \text{ FeCl}_3 \text{ (s)} + 3 \text{ H}_2O \text{ (g)}$$

Appendix

H$_2$O(s)

Increasing entropy

H$_2$O(l)

H$_2$O(g)

Increasing entropy

H$_2$O(l)

CAUTION

WET FLOOR

NaCl(*aq*)

Increasing
entropy

NaCl(*s*)

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Gas

Evaporation
of liquid

Liquid

Solid   Melting of solid

0

Temperature (K)

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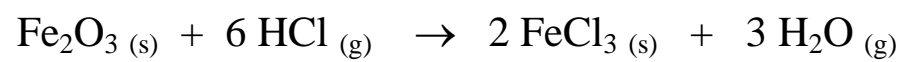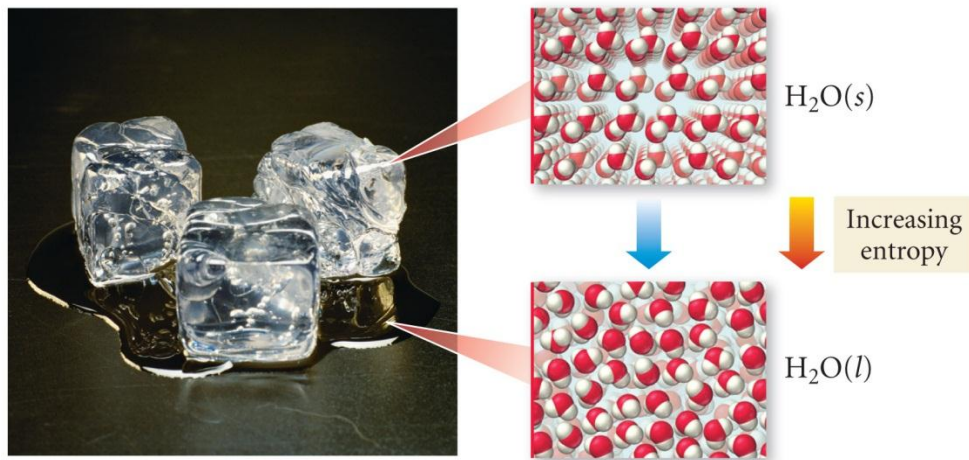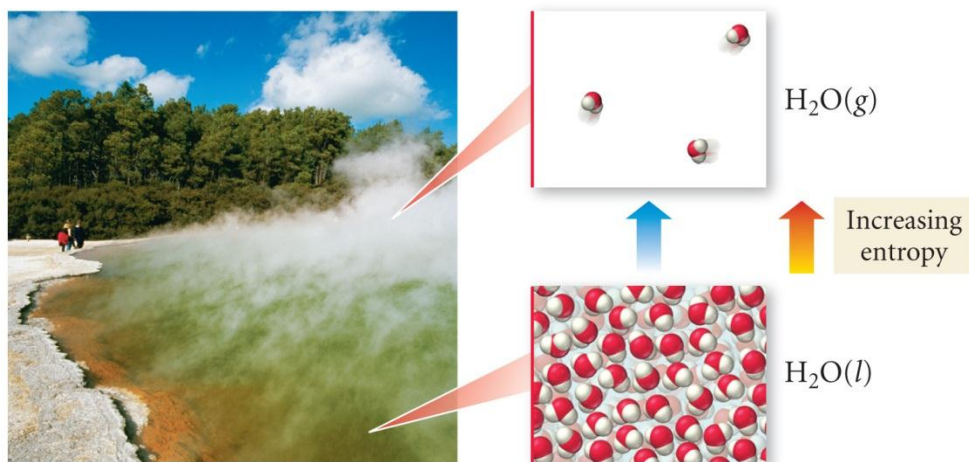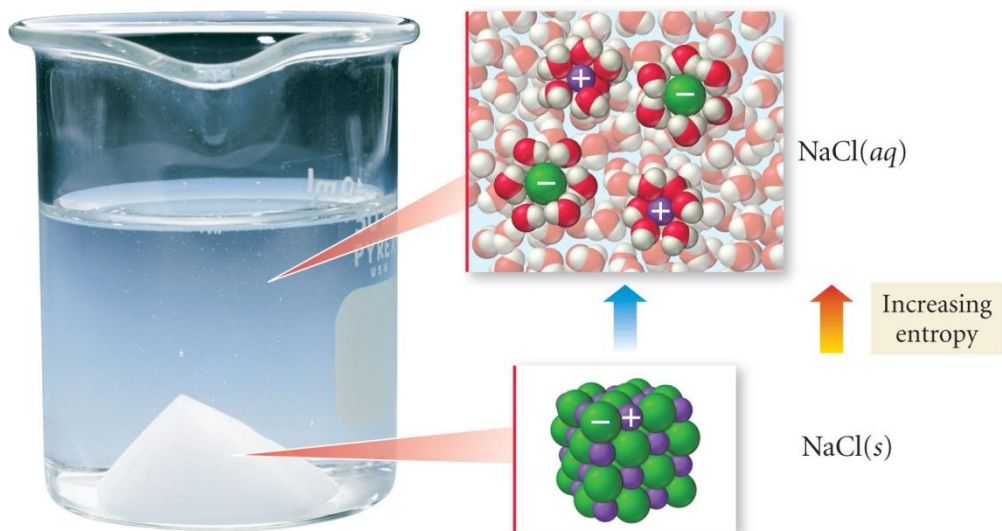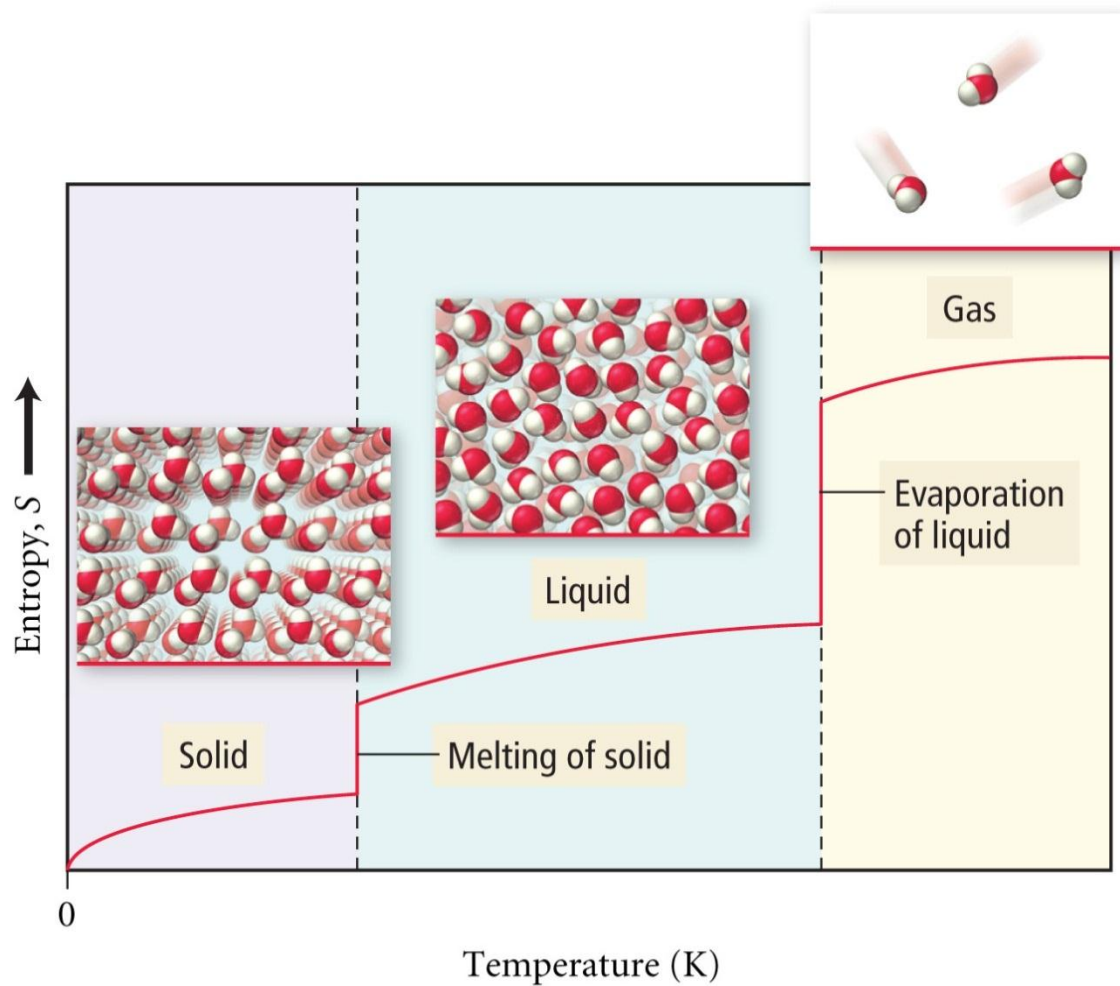
TABLE 17.2 Standard Molar Entropy Values ($S°$) for Selected Substances at 298 K

Substance	$S°$ (J/mol·K)	Substance	$S°$ (J/mol·K)	Substance	$S°$ (J/mol·K)
Gases		**Liquids**		**Solids**	
$H_2(g)$	130.7	$H_2O(l)$	70.0	$MgO(s)$	27.0
$Ar(g)$	154.8	$CH_3OH(l)$	126.8	$Fe(s)$	27.3
$CH_4(g)$	186.3	$Br_2(l)$	152.2	$Li(s)$	29.1
$H_2O(g)$	188.8	$C_6H_6(l)$	173.4	$Cu(s)$	41.6
$N_2(g)$	191.6			$Na(s)$	51.3
$NH_3(g)$	192.8			$K(s)$	64.7
$F_2(g)$	202.8			$NaCl(s)$	72.1
$O_2(g)$	205.2			$CaCO_3(s)$	91.7
$Cl_2(g)$	223.1			$FeCl_3(s)$	142.3
$C_2H_4(g)$	219.3				

TABLE 17.1 The Effect of ΔH, ΔS, and T on Spontaneity

ΔH	ΔS	Low Temperature	High Temperature	Example
−	+	Spontaneous ($\Delta G < 0$)	Spontaneous ($\Delta G < 0$)	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$
+	−	Nonspontaneous ($\Delta G > 0$)	Nonspontaneous ($\Delta G > 0$)	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	Spontaneous ($\Delta G < 0$)	Nonspontaneous ($\Delta G > 0$)	$H_2O(l) \longrightarrow H_2O(s)$
+	+	Nonspontaneous ($\Delta G > 0$)	Spontaneous ($\Delta G < 0$)	$H_2O(l) \longrightarrow H_2O(g)$
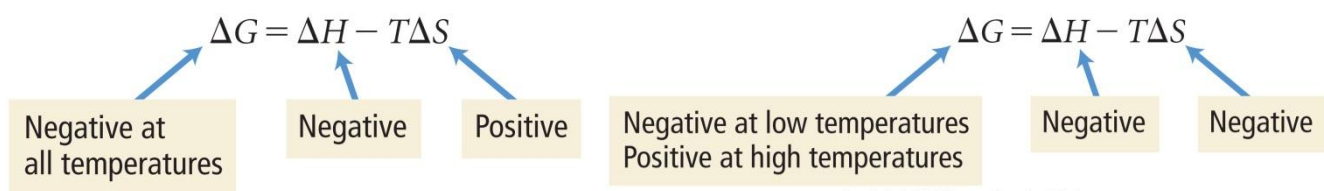
$$\Delta G = \Delta H - T\Delta S$$

Negative at all temperatures   Negative   Positive

$$\Delta G = \Delta H - T\Delta S$$

Negative at low temperatures Positive at high temperatures   Negative   Negative

$$\Delta G = \Delta H - T\Delta S$$

Positive at all temperatures   Positive   Negative

$$\Delta G = \Delta H - T\Delta S$$

Positive at low temperatures Negative at high temperatures   Positive   Positive

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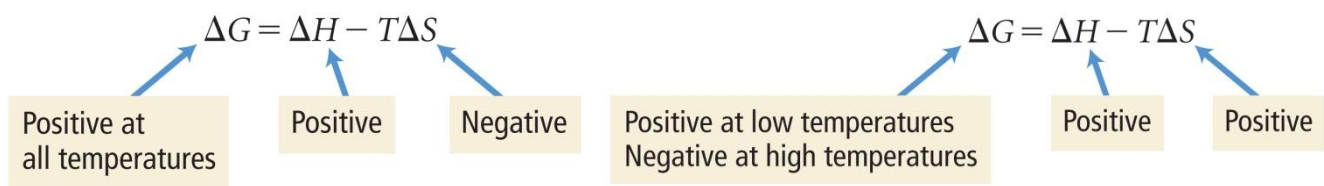
TABLE 17.3 Standard Molar Free Energies of Formation (ΔG_f°) for Selected Substances at 298 K

Substance	ΔG_f° (kJ/mol)	Substance	ΔG_f° (kJ/mol)
$H_2(g)$	0	$CH_4(g)$	−50.5
$O_2(g)$	0	$H_2O(g)$	−228.6
$N_2(g)$	0	$H_2O(l)$	−237.1
$C(s, graphite)$	0	$NH_3(g)$	−16.4
$C(s, diamond)$	2.900	$NO(g)$	+87.6
$CO(g)$	−137.2	$NO_2(g)$	+51.3
$CO_2(g)$	−394.4	$NaCl(s)$	−384.1
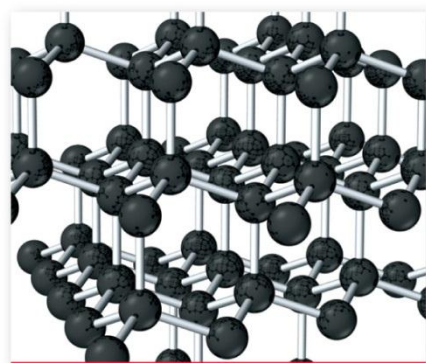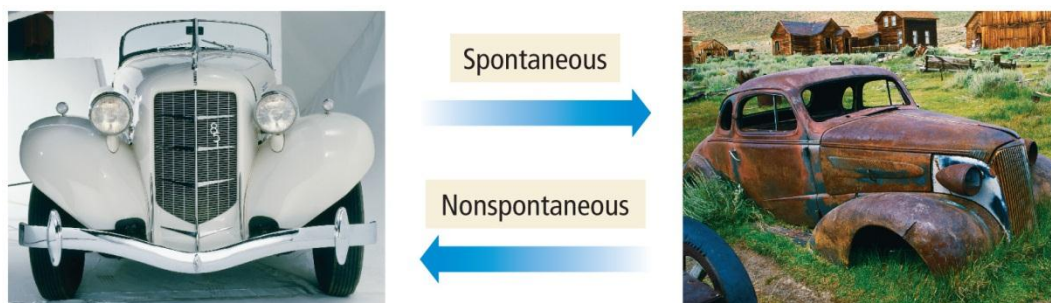
Spontaneous
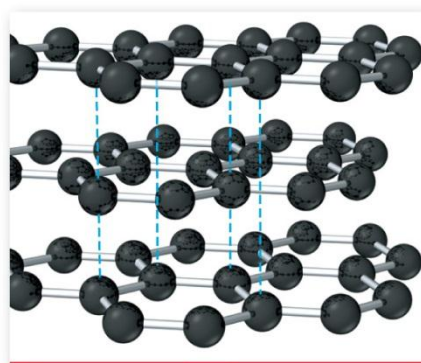
Nonspontaneous

Spontaneous

Slow rate

Diamond

Graphite

(a)

(b)

(c)

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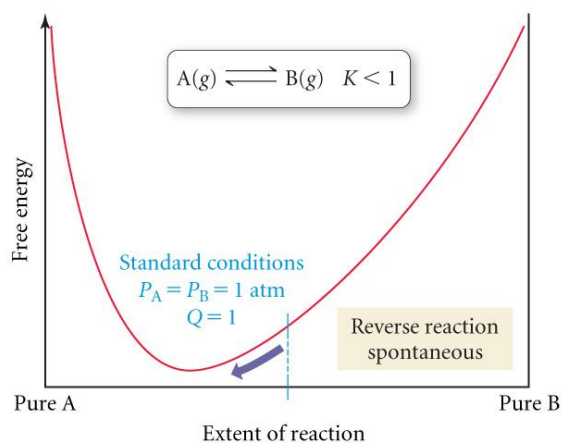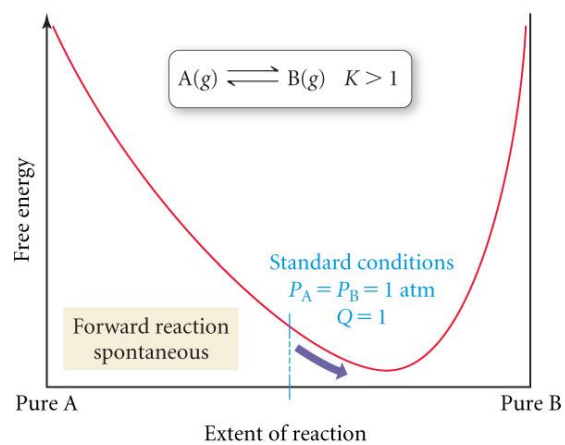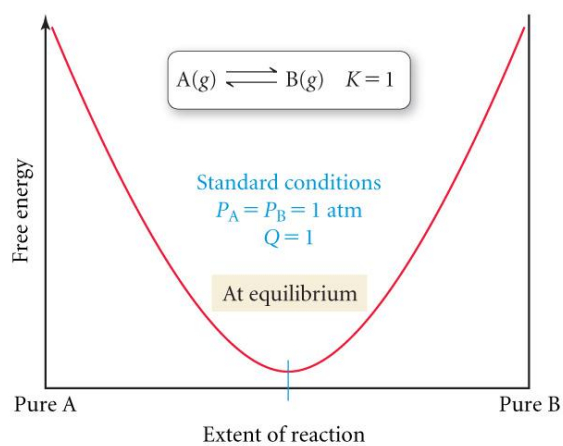
Free Energy Determines the Direction of Spontaneous Change

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$

Pure
$N_2 + H_2$

Free energy

Spontaneous

Spontaneous

Pure NH_3

$Q < K$

$Q > K$

Equilibrium
mixture
$(Q = K)$
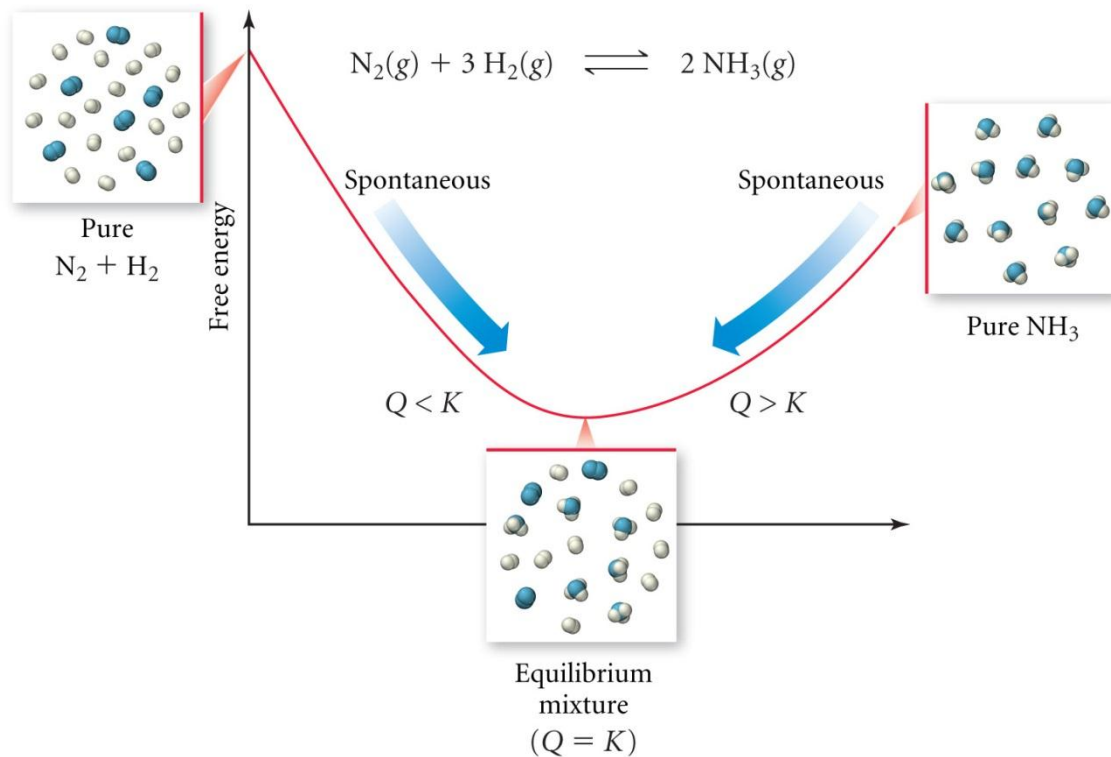
Electrochemistry

Reading:	Ch 18, sections 1 – 9	Homework:	Chapter 18: 37, 39*, 43, 45*, 47, 53, 55, 61, 63, 65*, 67, 69, 73, 77

* = 'important' homework question

Review of REDOX Reactions

Background

'REDOX' reactions are chemical processes in which REDuction and OXidation simultaneously occur

Oxidation Is Loss of electrons. **An element or compound that *loses* electron(s) during a chemical process is said to be OXIDIZED**

Reduction Is Gain of electrons. **An element or compound that *gains* electron(s) during a chemical process is said to be REDUCED**

TRICK: Remembering the difference between oxidation and reduction is easy, just remember….

OIL RIG of electrons

Oxidation Is Loss, Reduction Is Gain *of electrons*

Example of a Simple REDOX reaction:

$$Na \ + \ Cl \ \rightarrow \ NaCl$$

Discussion: Which chemical species has lost electrons during this process (i.e. been oxidized)? Which has gained electrons (been reduced)? How can you figure this out?

An overall REDOX equation is the sum of two half equations – one for oxidation, one for reduction

Oxidation ½ Eqn. $$Na \ \rightarrow \ Na^+ \ + \ 1 \ e^-$$

Reduction ½ Eqn. $$1 \ e^- \ + \ Cl \ \rightarrow \ Cl^- \qquad +$$

Summary: All REDOX equations are balanced by combining their two respective ½ equations, just like in the above example. We will learn how to perform this task for more complex reactions in the following pages

Oxidation Numbers

Oxidation Number or Oxidation State – the 'charge' on an atom in a substance as if it were a monatomic ion

A *change* in oxidation state during a chemical process indicates that a specie has either been *oxidized* (number goes up), or *reduced* (number goes down). **Recall the previous NaCl example.**

Rules for assigning oxidation numbers

1. For materials that form atomic ions, the oxidation state is the same as the 'regular' ionic charge

Task: State the oxidation state of the following:

Na in NaCl		Cl in $AlCl_3$	
Mg in $MgCl_2$		Fe in Fe_2O_3	

Since you know the charge of a great many atomic ions, you also know their oxidation states, i.e.:

Group I = I (Li^+, Na^+…)   **Group VII = -I (F^-, Cl^-…)**
Group II = II (Mg^{2+}, Ca^{2+}…)   Group VI = -II (O^{2-}, S^{2-}…)

Note: Oxidation states / numbers are expressed with Roman Numerals (this differentiates them from 'pure' ionic charges)

2. For ANY elemental atom, its oxidation state is ZERO. Why?

E.g. Elemental chlorine, Cl_2

$$Cl — Cl$$
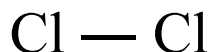
Any atom bonded to other *identical* atom(s) must have an oxidation state (oxidation number) of ZERO

ALL ELEMENTS must by definition posses zero oxidation states

Examples: Any diatomic element (O_2, F_2), any metallic element (Pb(s), Al(s)) etc.

3. All other atoms' oxidation states must be determined mathematically using the 'Sum of Oxidation States' Rule:

For molecules: The sum of the molecule's component atoms individual oxidation numbers = ZERO

Example: Nitric acid, HNO_3

For polyatomic ions ('charged molecules'): The sum of the polyatomic ion's component atoms individual oxidation numbers = overall ionic charge

Example: The nitrate ion, NO_3^-

Exceptions:

- **Oxygen always has a -II oxidation state, except when bonded to either fluorine or itself**. Why? <u>Hint</u>: Think of the periodic trend in electronegativity (slide, appendix).

Examples:

H_2O_2 OF_2

- **F always has a –I oxidation state, except when bonded to itself. Other Halogens (Cl, Br, I) are also –I, except when bonded to F or O**. Why?

Examples:

ClO_2 ClO_3^-

More Examples: Calculate the oxidation state of:

S in SO_3 Xe in XeF_6

S in SO_4^{2-} Cr in CrO_4^-

Na in NaH (Hint: think electronegativity)   N in Mg_3N_2
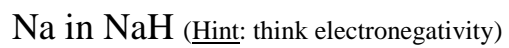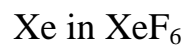
Balancing 'harder' REDOX reactions

Worked example

Balance the following REDOX process:

$$MnO_4^- \text{ (aq)} + C_2O_4^{2-} \text{ (aq)} \rightarrow Mn^{2+} \text{ (aq)} + CO_2 \text{ (g)}$$
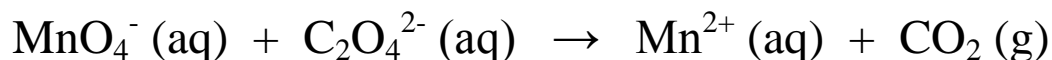
Question: Why cant we just balance these equations 'normally'

Answer:

Step 1: Split the overall reaction into a pair of ½ equations and balance atoms OTHER THAN H and O.

Trick: assign oxidation numbers to the original unbalanced equation in order to see which species were oxidized and reduced.

___ MnO_4^- (aq) $\rightarrow$ ___ Mn^{2+} (aq)   (reduction)

___ $C_2O_4^{2-}$ (aq) $\rightarrow$ ___ CO_2 (g)   (oxidation)
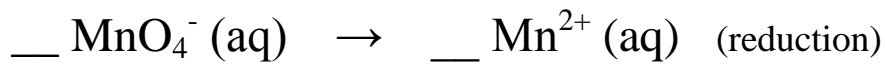
Step 2: Balance the amount of O (oxygen atoms) in each ½ equation by adding H_2O (l) where necessary.

Step 3: **Balance the amount of H (hydrogen atoms) in each ½ equation by adding H$^+$ (aq) where necessary.**

Step 4: **Balance the NET charges on both sides of each ½ equation by adding e^- (electrons) where necessary.**

	Trick: Electrons have a -1 charge, so add them to the more positive side of each ½ equation until the charge on both sides IS THE SAME

Step 5: **Equalize the amount of e^- in each ½ equation by multiplying through by the appropriate LCF.**

> Recall: REDOX reactions are really electron exchange reactions. By completing this step you ensure that an *equal number* of e^- are transferred (lost and gained respectively) during the two ½ equations. This is the goal of the procedure(!)

Step 6: **Add the two ½ equations, cancel any similar terms. Ensure that the conservation of mass law (same # and type of atoms b.s.) is obeyed**

Background: ALL batteries utilize REDOX processes, with the electrons transferred between each ½ reaction being passed through a circuit in order to provide electrical power. Your cell phone most likely uses a 'NiCad' (Nickel/Cadmium) battery – take a look!

Task: Balance the following 'NiCad battery' REDOX reaction:

$$Cd \ (s) \ + \ NiO_2 \ (s) \ \rightarrow \ Cd(OH)_2 \ (s) \ + \ Ni(OH)_2 \ (s)$$

	Trick: Write the initial pair of ½ equations ONCE, but leave space for each balancing step

The Reactivity Series

Background: For batteries featuring similar ½ reactions (such as in the Cu-Zn battery), it is often difficult to know which metal undergoes oxidation and which reduction

> This information is contained within the *Reactivity Series*

K	Potassium	most
Na	Sodium	reactive
Ca	Calcium	
Mg	Magnesium	
Al	Aluminium	
C	*Carbon*	
Zn	Zinc	
Fe	Iron	
Sn	Tin	
Pb	Lead	
H	*Hydrogen*	
Cu	Copper	
Ag	Silver	least
Au	Gold	reactive
Pt	Platinum	
(added for comparison)		

> The MOST reactive metals are those which LOSE electrons (i.e. become oxidized) the most easily. These (e.g. K) are at the TOP of the reactivity series

Discussion: Which of the following is the correct REDOX reaction for the Cu-Zn battery? See slide / handout.

$Cu + Zn(NO_3)_2(aq) \rightarrow Zn + Cu(NO_3)_2(aq)$

or

$Zn + Cu(NO_3)_2(aq) \rightarrow Cu + Zn(NO_3)_2(aq)$

Task: Write a REDOX reaction for the Ag(s) / Ag(NO$_3$)(aq) : Cu(s) / Cu(NO$_3$)$_2$(aq) battery. Hint: Decide on two ½ reactions, then follow 'the rules'.

Quantitative Electrochemistry – Cell EMF

	Reduction Half-Reaction		E^o (V)	
Stronger oxidizing agent	$F_2(g) + 2 e^-$	$\longrightarrow 2 F^-$ (aq)	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\longrightarrow 2 H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^-$	$\longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
	$Cl_2(g) + 2 e^-$	$\longrightarrow 2 Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$	$\longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(l)$	1.23	
	$Br_2(l) + 2 e^-$	$\longrightarrow 2 Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2 e^-$	$\longrightarrow 2 I^-(aq)$	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^-$	$\longrightarrow 4 OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2 e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2 e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2 H^+(aq) + 2 e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2 e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2 e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2 e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2 e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2 H_2O(l) + 2 e^-$	$\longrightarrow H_2(g) + 2 OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3 e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2 e^-$	$\longrightarrow Mg(s)$	−2.37	
Weaker oxidizing agent	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	Stronger reducing agent
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

Recall your lab – the EMF (voltage or potential difference) of an electrochemical cell (voltaic cell or battery) is simply the DIFFERENCE (potential difference, get it!?) in the two half cell reduction potentials.

<u>Task</u>: Determine the *magnitude* of the voltage for a Cu-Zn battery

> Problem: Working out the *magnitude* of a battery's EMF is straight forward, but determining if this voltage difference is 'positive' or 'negative' requires further consideration.
>
> Recall the complication of having to 'reverse the leads' in your lab – *this was the manifestation of this issue in practice*.

Quantitative analysis of the 'Duracell' reaction

1. Recall: Since zinc is higher in the reactivity series that copper it will be oxidized, while copper ions are reduced:

$$\textbf{Zn} + \textbf{Cu}^{2+} \ \rightarrow \ \textbf{Cu} + \textbf{Zn}^{2+}\textbf{(aq)}$$
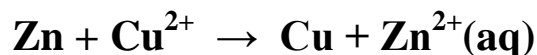
2. Using a 'number line' approach, we know that the *absolute* EMF of this cell (from above) is 0.34 V + 0.76V = 1.1 V

3. Electrochemical conventions must now be used to determine which half –cell makes up the anode and which the cathode of the cell. This will determine the sign (+ or -) of the cell voltage.

Remember that *Oxidation* occurs at the *Anode* (**-ve** electrode) and **R**eduction at the **C**athode (**+ve** electrode)
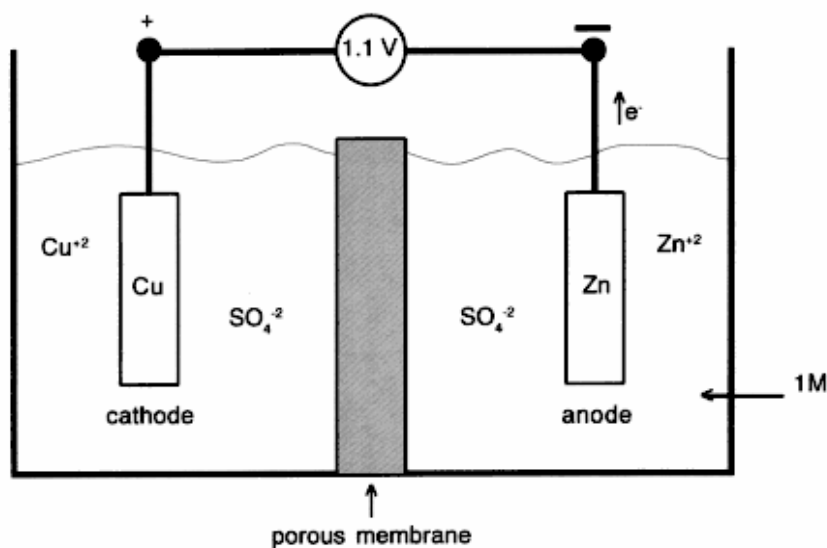
Now, we must use the following equation to find both the magnitude and sign of the cell EMF (must remember):

$$\mathbf{E^o_{cell} = E^o_{red} \, (cathode) - E^o_{red} \, (anode)}$$

Where: E^o_{cell} = cell EMF, with correct sign
E^o_{red} (cathode) = standard reduction potential of the reduction process (at the cathode)
E^o_{red} (anode) = standard reduction potential of the oxidation process (at the anode)

Determine which half-cells make up the anode and cathode, respectively.

Recall, **Oxidation at the Anode** – the half-cell highest in the reactivity series (lowest in the reduction potential table) will be the anode.

'Insert and evaluate' in the above equation, once anode and cathode reduction potentials have been assigned.

For the Zn-Cu battery:

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq)$ E^o_{red} = -0.76 V

Reduction: $Cu^{2+}(aq) \rightarrow Cu(s)$ E^o_{red} = +0.34 V

Since $E^o_{cell} = E^o_{red}$ (cathode) $- E^o_{red}$ (anode):

$$E^o_{cell} = (+0.34 \text{ V}) - (-0.76 \text{V}) = +1.10 \text{ V}$$

Note: The Zn-Cu battery has a positive sign for E^o_{cell} - *this is only true (for any voltaic cell) if the anode and cathode are correctly assigned.*

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Group Task: Determine the magnitude and sign of the EMF for the following voltaic cells, constructed from the half-cells shown (also see appendix E or slide for standard potentials)

1. $2 H^+ (aq) + 2e \rightarrow H_2 (g)$ $E^o_{red} = 0.00$ V (anode)

    $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ $E^o_{red} = +0.34$ V (cathode)

2. $H_2 (g) + F_2(g) \rightarrow 2H^+ (aq) + 2 F^- (aq)$

3. $3 Fe^{2+} (aq) \rightarrow Fe (s) + 2Fe^{3+} (aq)$ (disproportionation reaction)
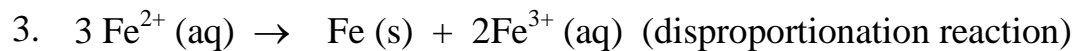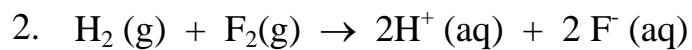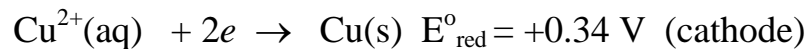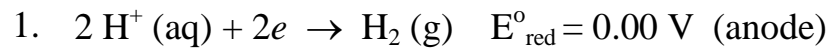
EMF and Gibbs Free Energy
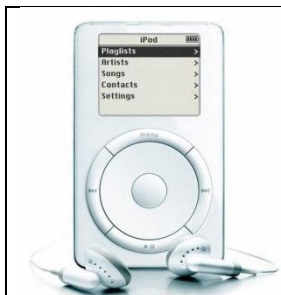
Clearly, voltaic cells feature *spontaneous processes* – the electrons transferred between the two half-cells do so *upon demand* in order to power your I-pod, CD player etc. This relationship is *directly proportional* in terms of EMF and ΔG:

$$\Delta G \propto E$$

The quantitative version of the above relationship is:

$$\Delta G^o = -nFE^o$$

Where: ΔG^o = standard Gibbs free energy of the REDOX process

n = number of electrons transferred in the redox process (from the balanced REDOX equation)

F = The Faraday constant (the charge of 1 mole of electrons), where 1 F = 96,500 Coulombs/mole

E^o = standard cell potential of the REDOX process

Micheal Farady – Scientific idol of Margaret Thatcher, ex Prime Minister of Great Britain

Margaret Thatcher – the only British Prime Minister to hold a bachelors degree in chemistry. 'Maggie' also shares a birthday with Dr. Mills (err, scary!)

Task: Determine ΔG^o for:

$$3\ Fe^{2+}\ (aq)\ \rightarrow\ Fe\ (s)\ +\ 2Fe^{3+}\ (aq)$$

Is this process spontaneous?

Cell EMF Under Non-Standard Conditions

Discussion: The voltage of an AA Duracell Zn-Cu battery is 1.5 V, whereas the standard electrode potential for this pair of half-cells is only 1.1 V. Why is this?

The Nernst Equation relates the EMF of a cell to that at under standard conditions (E^o_{cell}) and Q, (the reaction quotient). Recall from the equilibria topic that Q = [products]/[reactants].

Nernst Equation:

$$\Delta G = \Delta G^o + RT\ \ln Q \quad or \quad E = E_o\ \frac{-RT}{nF}\ \ln Q$$

Since $\Delta G = 0$ at equilibrium (or E_{cell} = zero when the battery goes 'flat', i.e. at *equilibrium**:

$$\Delta G = -RTlnK$$

*This new equation will allow for evaluation of K (equilibrium constant) for any Redox process at any temperature.

Group Task: Use your new equation to answer the following question: What is the value of the equilibrium constant, K, for the following REDOX process? See Appendix E of your notes for standard reduction potentials.
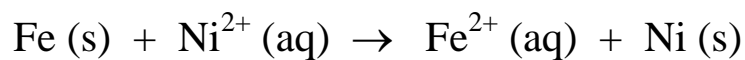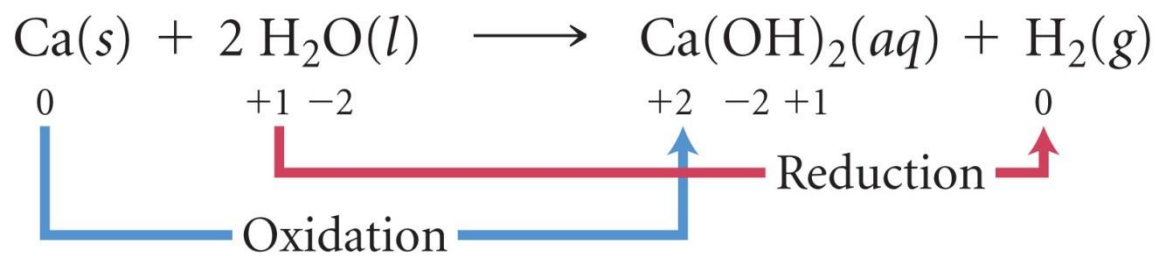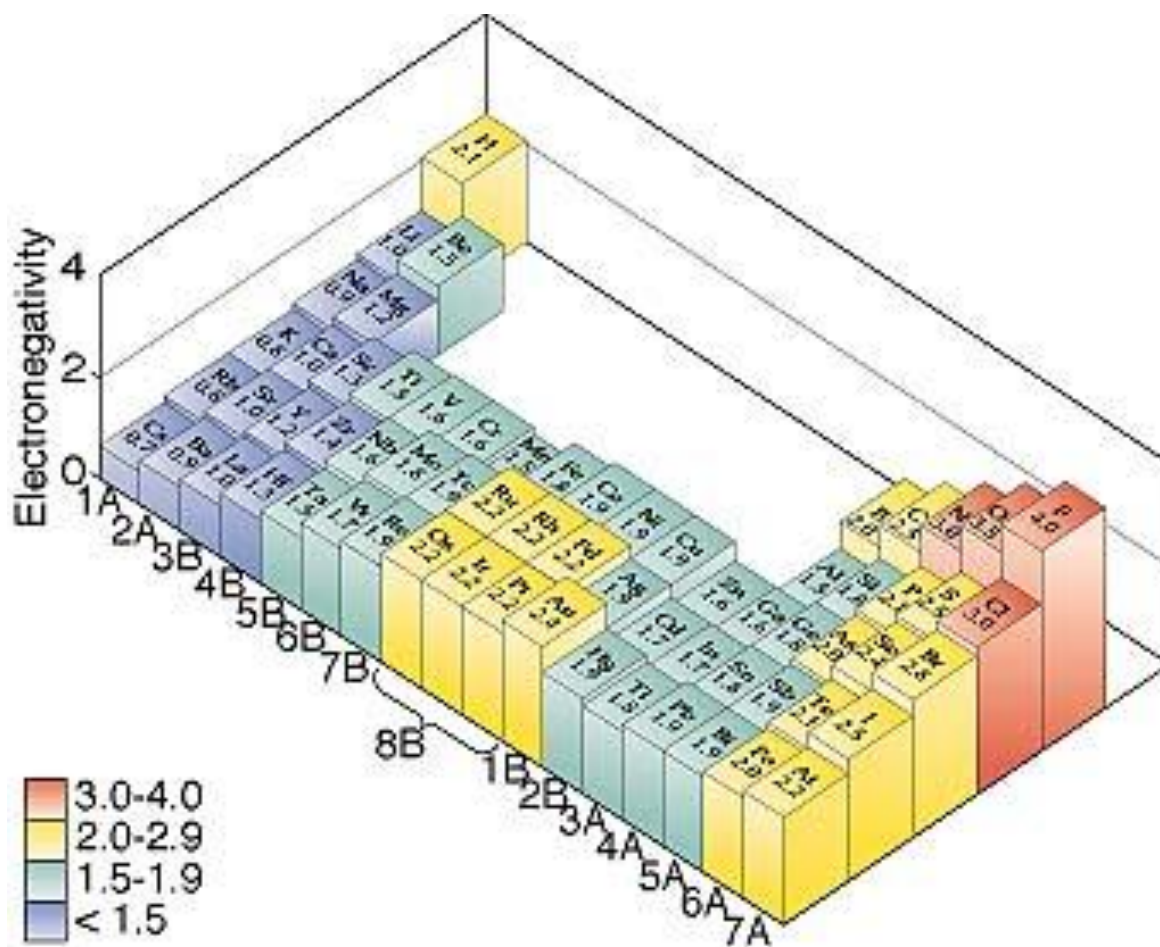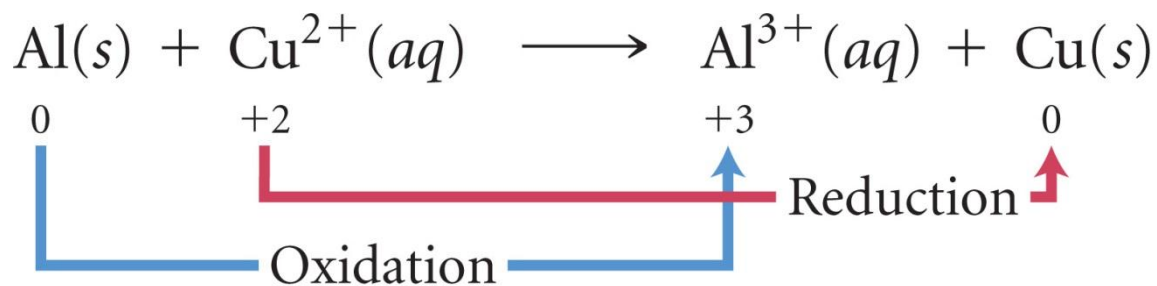
$$Fe \ (s) \ + \ Ni^{2+} \ (aq) \ \rightarrow \ Fe^{2+} \ (aq) \ + \ Ni \ (s)$$

$$Ca(s) \ + \ 2 \, H_2O(l) \ \longrightarrow \ Ca(OH)_2(aq) \ + \ H_2(g)$$

0   +1 −2   +2 −2 +1   0

Reduction

Oxidation

$$Al(s) + Cu^{2+}(aq) \longrightarrow Al^{3+}(aq) + Cu(s)$$

0   +2   +3   0

Reduction

Oxidation

$$Fe^{2+}(aq) + MnO_4^-(aq) \longrightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$$

+2   +7 −2   +3   +2

Reduction

Oxidation

$$I^-(aq) + MnO_4^-(aq) \longrightarrow I_2(aq) + MnO_2(s)$$

−1   +7 −2   0   +4 −2

Reduction

Oxidation

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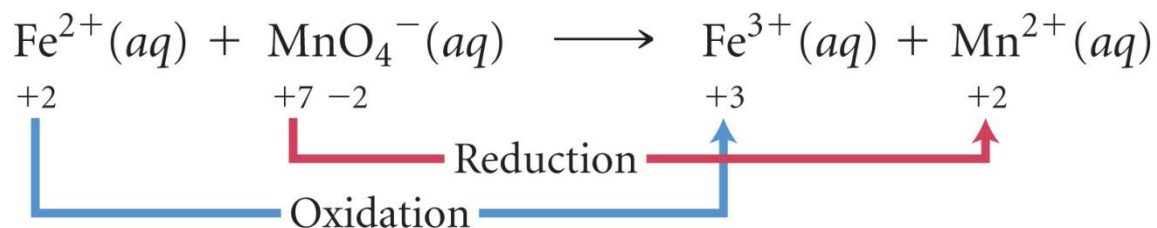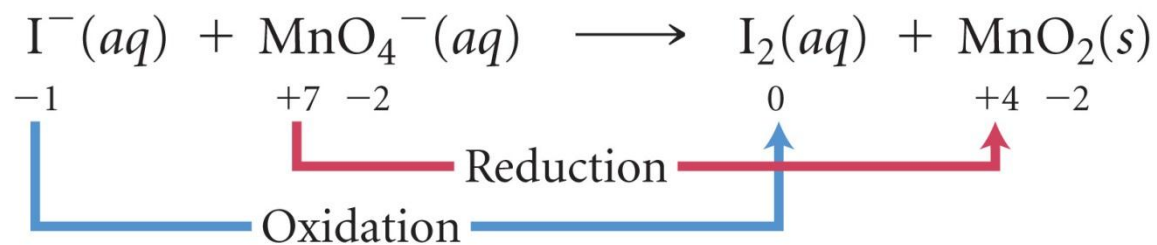
A Spontaneous Redox Reaction: Zn + Cu²⁺
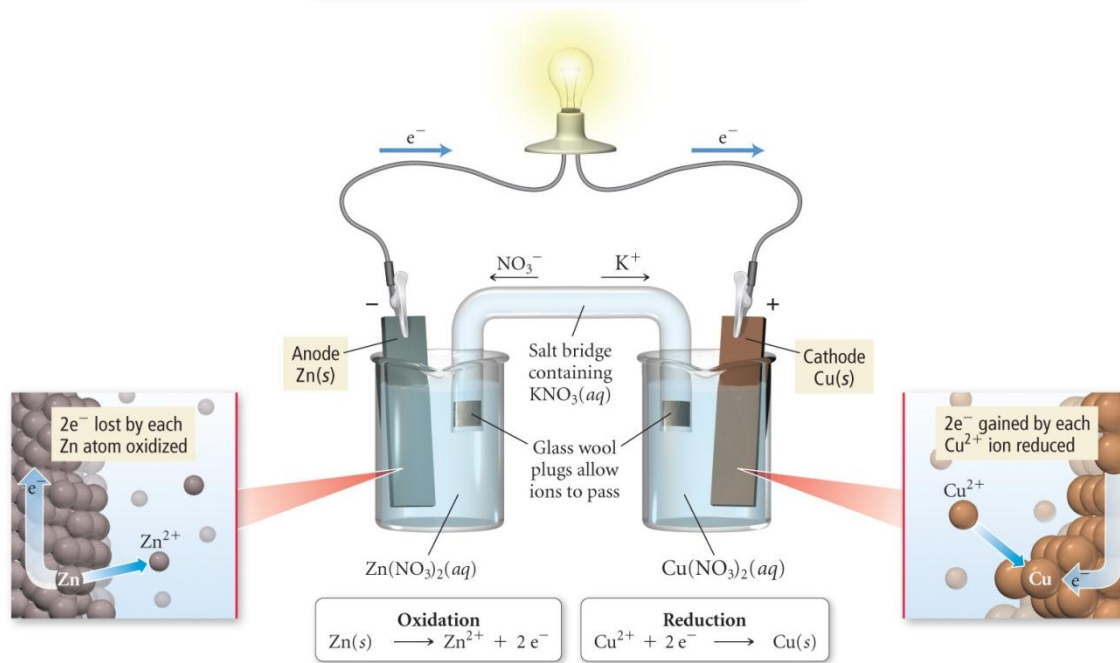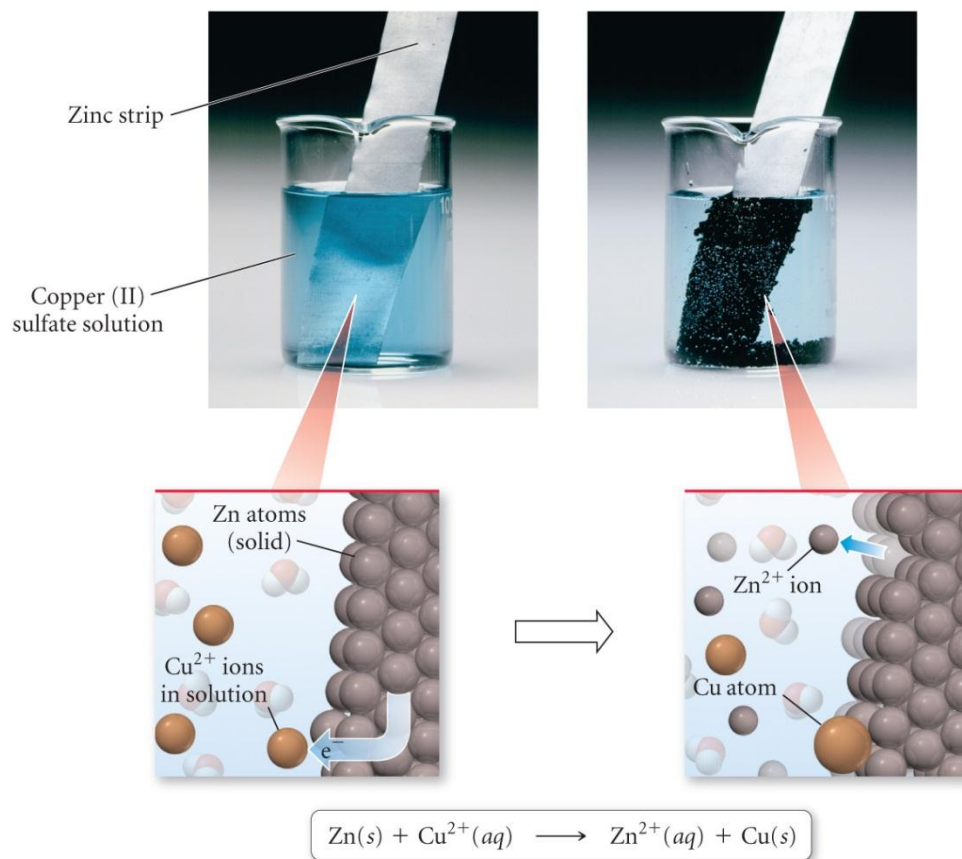
Zinc strip

Copper (II) sulfate solution

Zn atoms (solid)

Cu²⁺ ions in solution

e⁻

Zn²⁺ ion

Cu atom

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

e⁻   e⁻

NO_3^- K^+

Anode Zn(s)

Salt bridge containing $KNO_3(aq)$

Glass wool plugs allow ions to pass

Cathode Cu(s)

2e⁻ lost by each Zn atom oxidized

e⁻

Zn²⁺

Zn

$Zn(NO_3)_2(aq)$ $Cu(NO_3)_2(aq)$

2e⁻ gained by each Cu²⁺ ion reduced

Cu²⁺

Cu   e⁻

Oxidation
$$Zn(s) \longrightarrow Zn^{2+} + 2e^-$$

Reduction
$$Cu^{2+} + 2e^- \longrightarrow Cu(s)$$
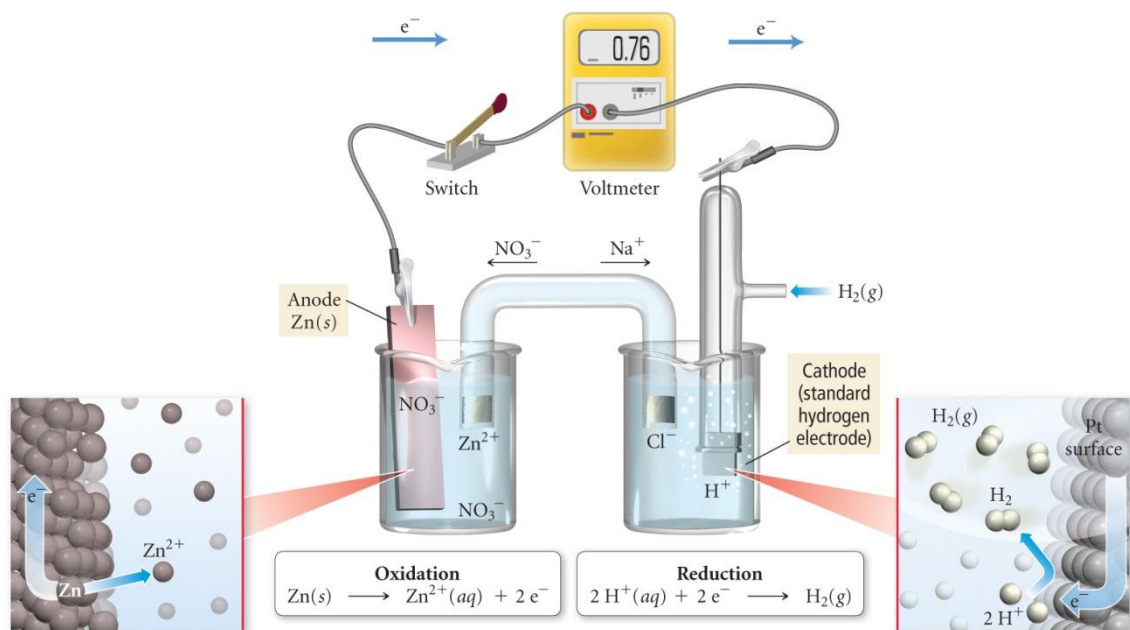
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$$E_{cell} = E_{cell}^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

$$= E_{cell}^\circ - \frac{0.0592 \text{ V}}{n} \log 1 \qquad \log 1 = 0$$

$$= E_{cell}^\circ$$

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$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q$$

E°_{cell}

$$= E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log K$$

$$= E^{\circ}_{\text{cell}} - E^{\circ}_{\text{cell}}$$

$$= 0$$

A Concentration Cell
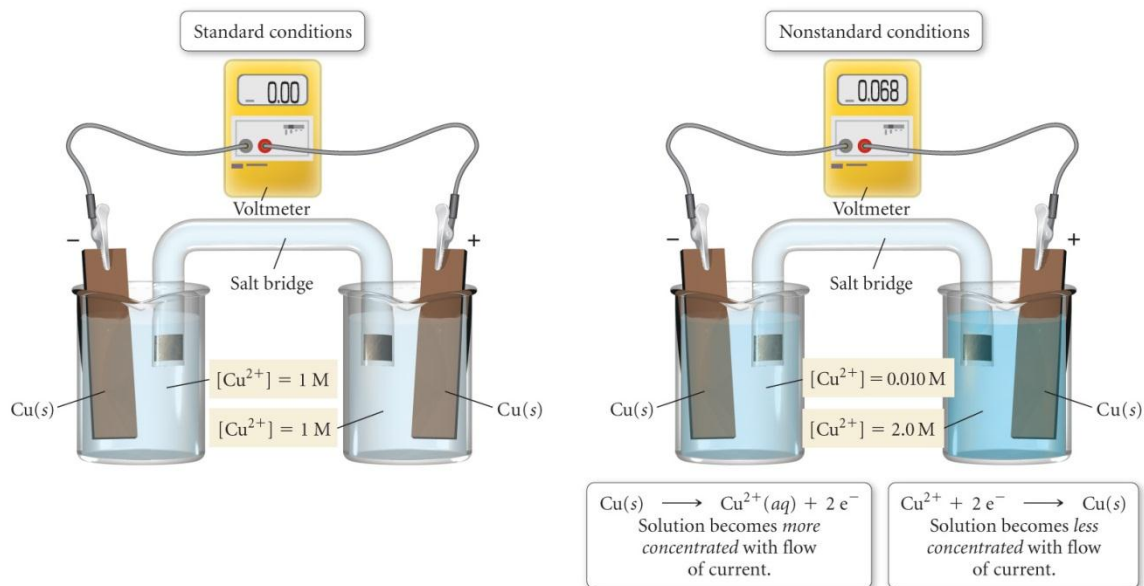
Standard conditions
0.00
Voltmeter
Salt bridge
−   +
$[Cu^{2+}] = 1 \text{ M}$
$Cu(s)$
$[Cu^{2+}] = 1 \text{ M}$
$Cu(s)$

Nonstandard conditions
_0.068
Voltmeter
Salt bridge
−   +
$[Cu^{2+}] = 0.010 \text{ M}$
$Cu(s)$
$[Cu^{2+}] = 2.0 \text{ M}$
$Cu(s)$

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2 e^{-}$
Solution becomes *more* concentrated with flow of current.

$Cu^{2+} + 2 e^{-} \longrightarrow Cu(s)$
Solution becomes *less* concentrated with flow of current.

+ terminal
Steel case
Graphite rod (cathode)
Zinc (anode)
MnO$_2$ in KOH paste
Absorbent/ separator
− terminal

Terminals

Anode (−): Lead grid packed with finely divided spongy lead

Electrolyte: 30% solution of H$_2$SO$_4$

Cathode (+): Lead grid packed with PbO$_2$
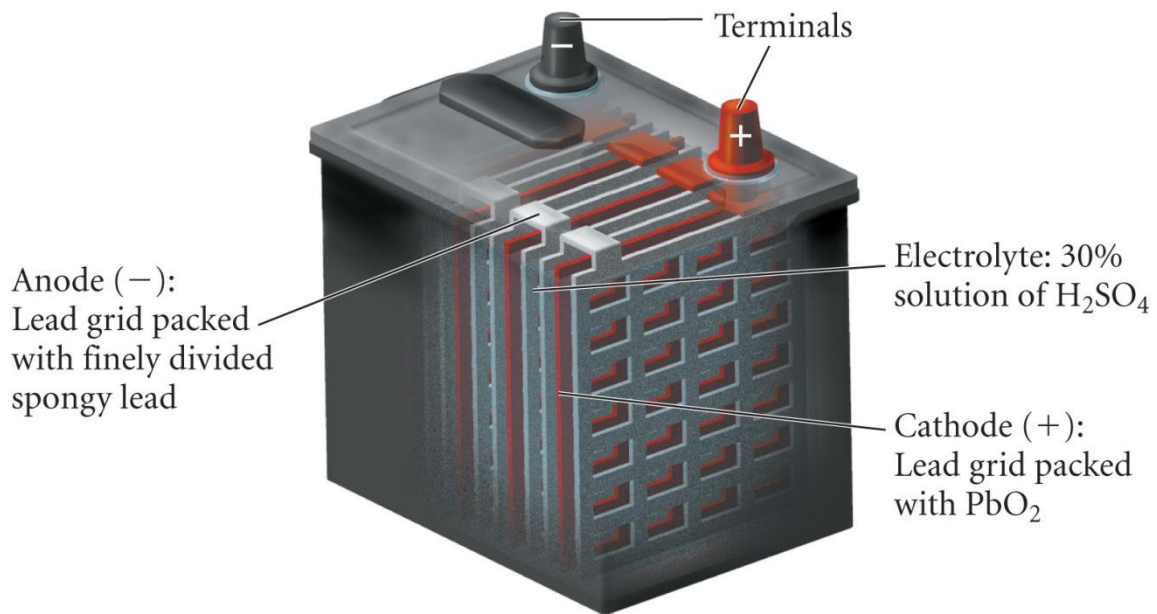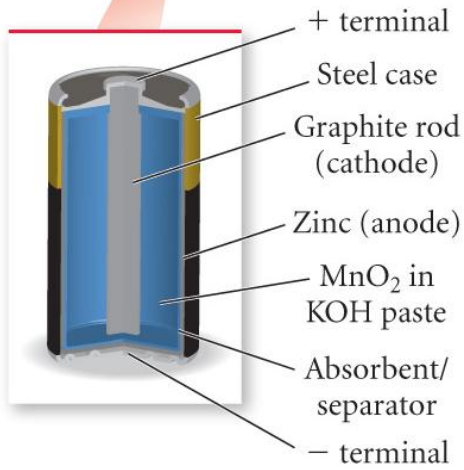
Nuclear Chemistry

* = 'important' homework question

Radioactivity

Discussion: What kinds of nuclear radiation are there? What are the origins of each type of radiation?

Types of radiation (see appendix)*
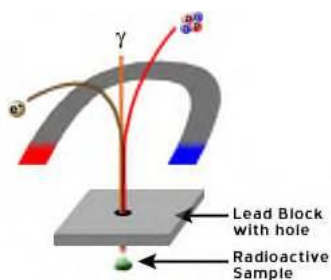
Alpha particles are helium nuclei (2 p, 2 n):

Beta particles are speedy electrons: *Yeeeeehaaaa!*

Gamma radiation is a high-energy photon:

Name	Symbol	Charge	Penetration Limit
alpha (α) particles	^4_2He or $^4_2\alpha$	+2	skin, thin metal foil
beta (β) particles	$^0_{-1}\beta$ or $^0_{-1}e$	-1	thicker foil, plastic
gamma (γ) rays	$^0_0\gamma$	0	lead, concrete

Overview
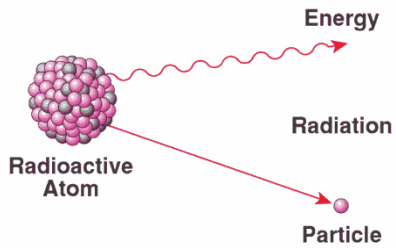
'Heavy' nuclei are unstable; they undergo nuclear decay via either alpha, beta and/or gamma emission to form lighter, more stable nuclei.

Iron has the most stable nucleus (ever wondered why the Earth and many other planets have iron cores?).

The Curve of Binding Energy
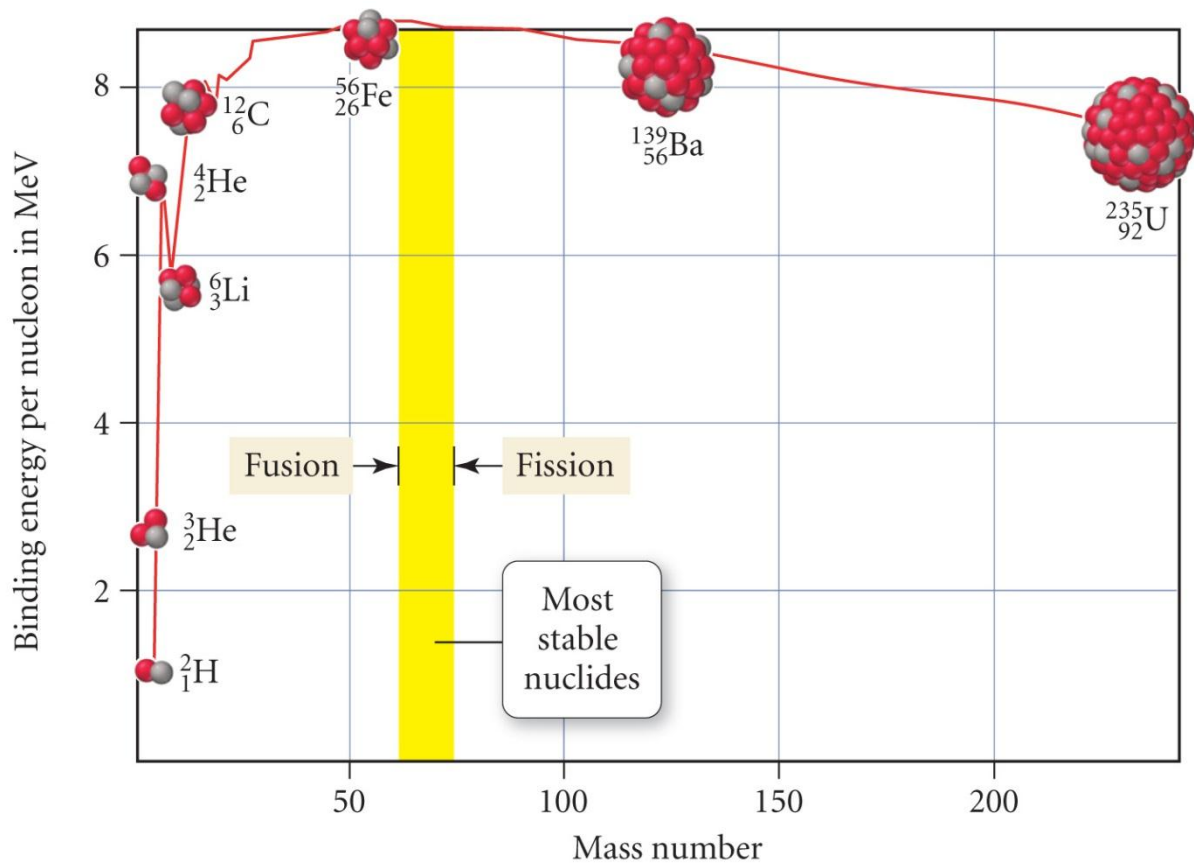
Strong v weak nuclear force - it's magnets with velcro (more later!)

Writing radioactive decay equations

Recall writing complete atomic symbols from CHM 101. Writing nuclear decay equations is just accounting for changes in atomic number (Z) and atomic mass (A) in such symbols

Worked Example: Write reaction for the α-particle decay of Pu-240.

α-particle decay of Pu-240
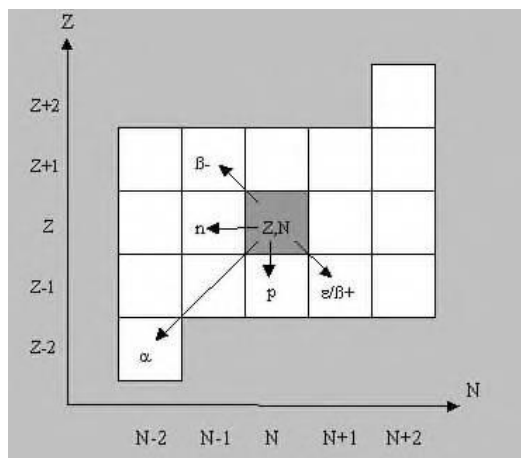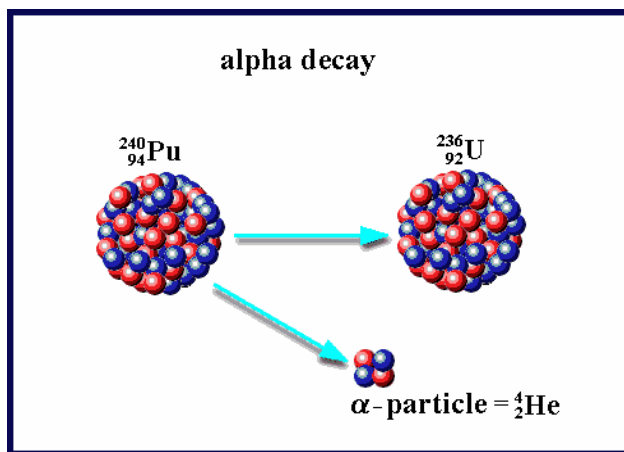
Variation in Z and #N for various types of nuclear decay

Task: Write nuclear decay equations for the following processes:

1. The β decay of I-131

2. The α decay of U-238 (see appendix)

Nuclear Transmutations

┌───┐
│ **Similar math (with regard to balancing mass and atomic numbers)** │
│ **can be used for writing nuclear transmutation equations**   │
└───┘

Worked example: Write an equation for the capture of a neutron (cosmic ray) by N-14

Task: Write nuclear transmutation equations for the following processes:

1. Fe-58 undergoing neutron capture

2. See Example question 19.2 (a – c), page 870, of your text

Radioactive Decay

> **All radioactive decay processes are 1st order in terms of their kinetics.** Thus, familiar relationships from the 'Kinetics' topic can be employed directly**. Remember the basic 'half-life trick' for simpler questions**

<u>Worked Example</u>: It takes 5.2 minutes for a 1.000 g sample of Fr-210 to decay to 0.250 g. What is the half-life of Fr-210?

<u>Task</u>: How much time is required for a 5.75 mg of Cr-51 to decay to 1.50 mg if its half-life is 27.8 days?

Nuclear Binding Energy

Discussion: What Holds a nucleus together? Shouldn't it fly apart – after all, protons must repel one another, right?

Remember: *Strong v weak nuclear force - it's magnets with velcro!*
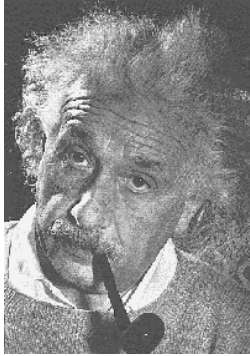
It's a little more complicated than that….

strong nuclear force
electrical force ∝ 1/r²
force
1 fm distance
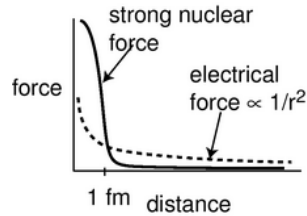
Einstein showed that mass and energy are *convertible*. The relationship is:

$$E = mc^2 \quad or \quad \Delta E = \Delta mc^2$$

The energy, or 'glue', that holds a nucleus' otherwise repulsive nuclear particles together appears as a *mass defect*

Where: mass proton = 1.00728 amu
             mass neutron = 1.00866 amu
             1 amu = 1.66053873 x10^{-24}g
             c = 3.0 x10^8 m/s

Mass Defect: the difference in mass between an atomic nucleus and the sum of its individual component particles.

To work out mass defect problems, the mass of the nucleus must be compared to the sum of the masses of its component neutrons and protons.

The mass difference, stated in the form of energy (from $E = mc^2$), is the binding energy of the nucleus.

Worked example: Calculate the binding energy per nucleon for C-12 (nuclear mass = 11.996708 amu)

Task: Calculate the binding energy per nucleon for Cl-37 (nuclear mass = 36.956576 amu)

Nuclear Fission and Fusion

Recall the graph of nuclear stability – Fe-56 has the most binding energy per nucleon, so is the most stable of all nuclei. Thus, ALL heavier nuclei may undergo *fission*, while all lighter nuclei may undergo *fusion* to form more stable products. *Hey, universe, there's a lot of iron in your distant future!?*
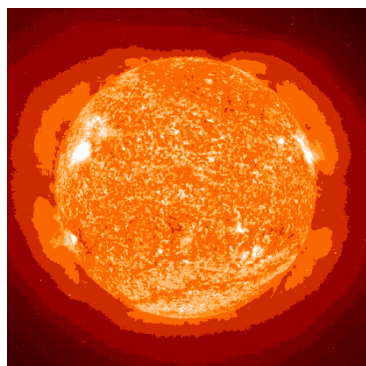
Vast amounts of energy are liberated during fission (nuclear weapons, U-235) or fusion (the sun, H → He) reactions. The origin of this energy is the mass deficit (Δm) between products and reactants in each respective process.

Fission and Fusion processes
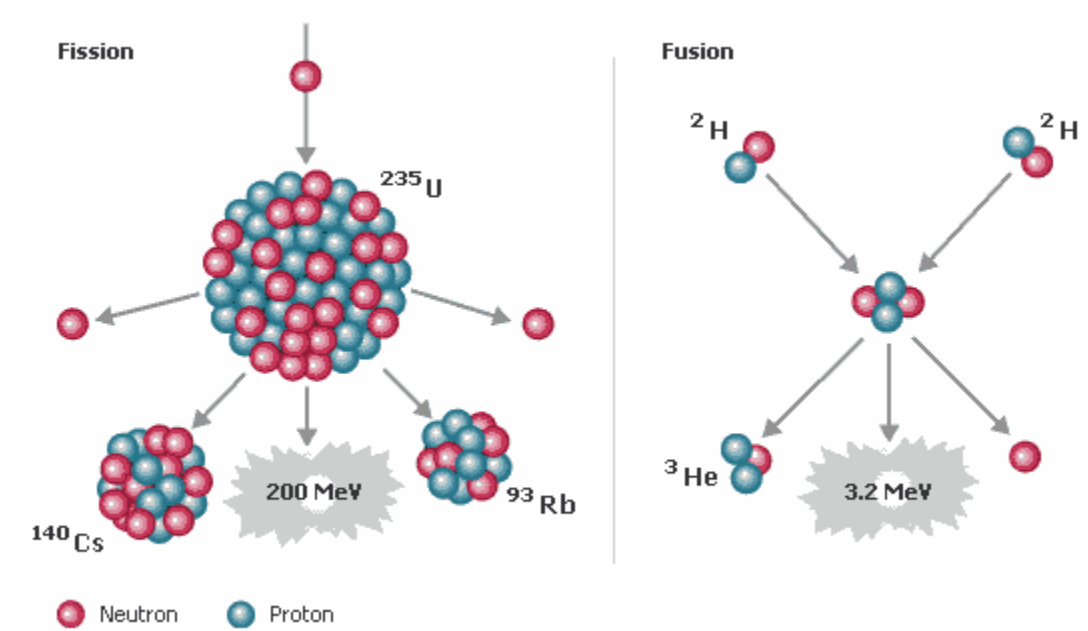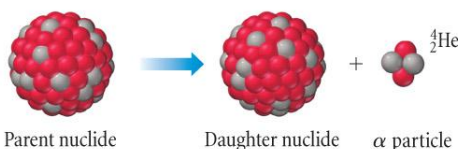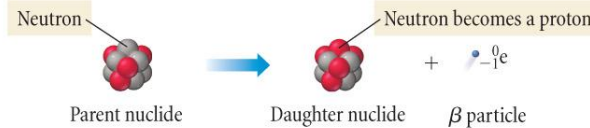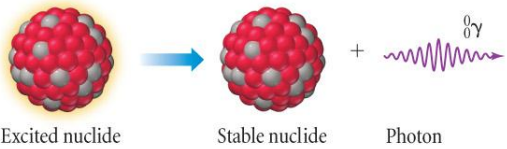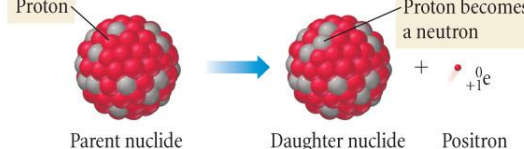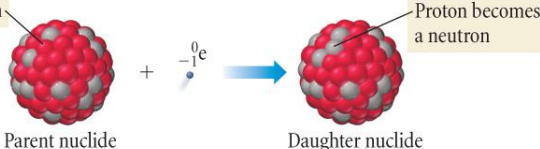
Group Wrap Up: Try question 19.7 from your text

Appendix:

TABLE 19.1   Modes of Radioactive Decay

Decay Mode	Process	A	Z	N/Z*	Example
α	Parent nuclide → Daughter nuclide + $^{4}_{2}\text{He}$ (α particle)	−4	−2	Increase	$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$
β	Neutron → Parent nuclide → Neutron becomes a proton, Daughter nuclide + $^{0}_{-1}\text{e}$ (β particle)	0	+1	Decrease	$^{228}_{88}\text{Ra} \longrightarrow {}^{228}_{89}\text{Ac} + {}^{0}_{-1}\text{e}$
γ	Excited nuclide → Stable nuclide + $^{0}_{0}\gamma$ (Photon)	0	0	None	$^{234}_{90}\text{Th} \longrightarrow {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma$
Positron emission	Proton → Parent nuclide → Proton becomes a neutron, Daughter nuclide + $^{0}_{+1}\text{e}$ (Positron)	0	−1	Increase	$^{30}_{15}\text{P} \longrightarrow {}^{30}_{14}\text{Si} + {}^{0}_{+1}\text{e}$
Electron capture	Proton → Parent nuclide + $^{0}_{-1}\text{e}$ → Proton becomes a neutron, Daughter nuclide	0	−1	Increase	$^{92}_{44}\text{Ru} + {}^{0}_{-1}\text{e} \longrightarrow {}^{92}_{43}\text{Tc}$

*Neutron-to-proton ratio

Alpha Decay

α particle $= {}^{4}_{2}\text{He}$

Beta Decay

Electron (β particle) is emitted from nucleus

Neutron becomes a proton

${}^{0}_{-1}\text{e}$

Neutron

${}^{14}_{6}\text{C}$ nucleus

${}^{14}_{7}\text{N}$ nucleus

Positron Emission

Positron is emitted from nucleus

Proton becomes a neutron

Proton

$^{10}_{6}C$ nucleus $\longrightarrow$ $^{10}_{5}B$ nucleus

$^{0}_{+1}e$
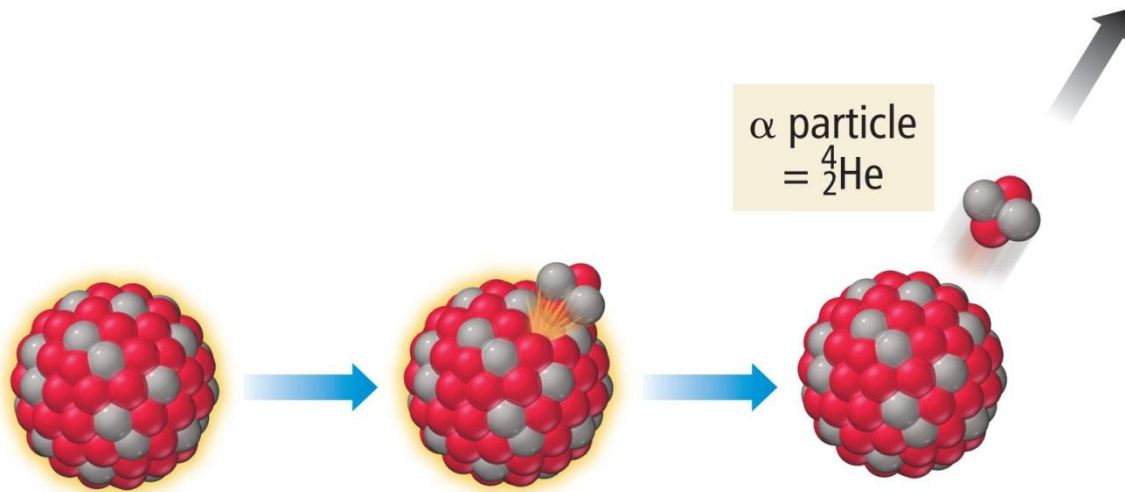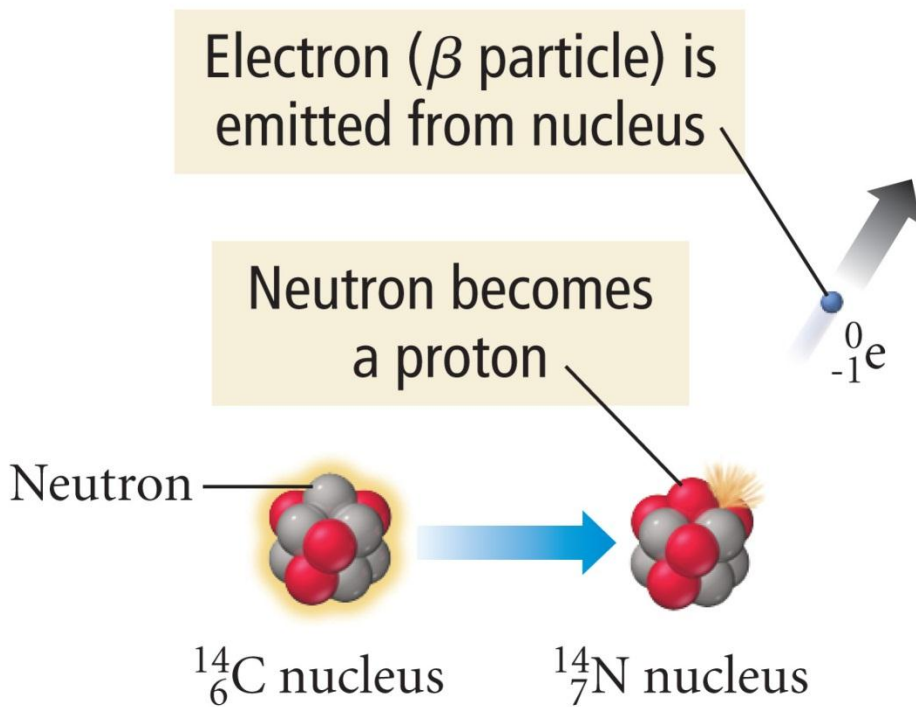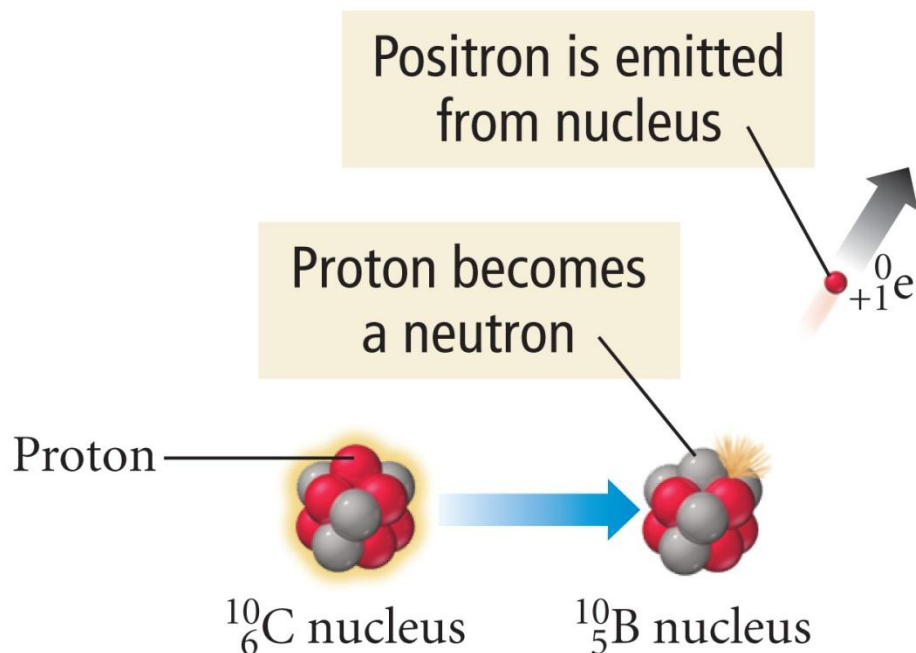
PET Scan
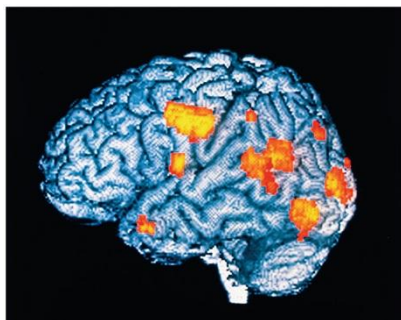
TABLE 19.6	Common Radiotracers		
Nuclide	Type of Emission	Half-Life	Part of Body Studied
Technetium-99m	Gamma (primarily)	6.01 hours	Various organs, bones
Iodine-131	Beta	8.0 days	Thyroid
Iron-59	Beta	44.5 days	Blood, spleen
Thallium-201	Electron capture	3.05 days	Heart
Fluorine-18	Positron emission	1.83 hours	PET studies of heart, brain
Phosphorus-32	Beta	14.3 days	Tumors in various organs

$$^{238}_{92}\text{U} \longrightarrow ^{234}_{90}\text{Th} + ^{4}_{2}\text{He}$$

$$^{235}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{140}_{56}\text{Ba} + ^{93}_{36}\text{Kr} + 3\,^{1}_{0}\text{n} + \text{energy}$$

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \longrightarrow ^{239}_{93}\text{X} + ^{0}_{-1}\text{e}$$

Neutron   Newly synthesized element

$^{235}_{92}$U

$^{93}_{36}$Kr

$^{1}_{0}$n

$^{1}_{0}$n

$^{1}_{0}$n

$^{140}_{56}$Ba

$^{93}_{36}$Kr

$^{1}_{0}$n

$^{235}_{92}$U

$^{1}_{0}$n

$^{1}_{0}$n

$^{235}_{92}$U

$^{1}_{0}$n

$^{93}_{36}$Kr

$^{1}_{0}$n

$^{235}_{92}$U

$^{1}_{0}$n

$^{1}_{0}$n

$^{140}_{56}$Ba

Neutron (n)

$^{140}_{56}$Ba

$^{93}_{36}$Kr

$^{1}_{0}$n

$^{235}_{92}$U

$^{1}_{0}$n

$^{1}_{0}$n

$^{140}_{56}$Ba
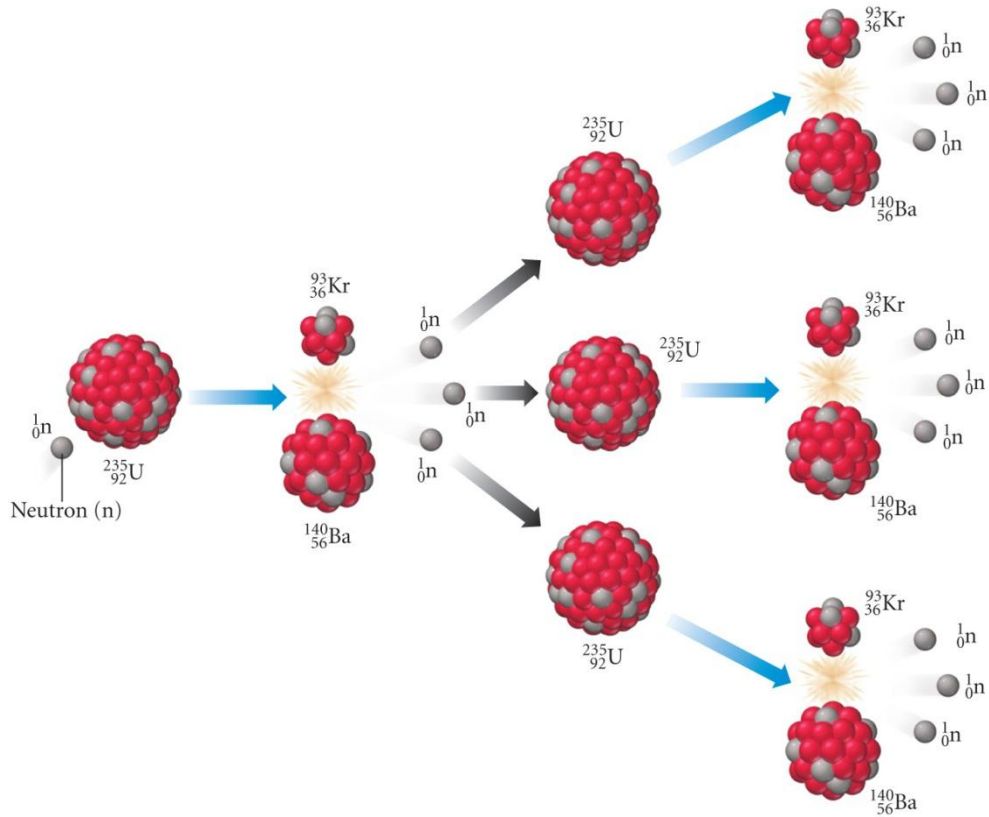
Deuterium-Tritium Fusion Reaction

Deuterium ($^{2}_{1}$H)

Tritium ($^{3}_{1}$H)

Helium-4 ($^{4}_{2}$He)

Neutron ($^{1}_{0}$n)
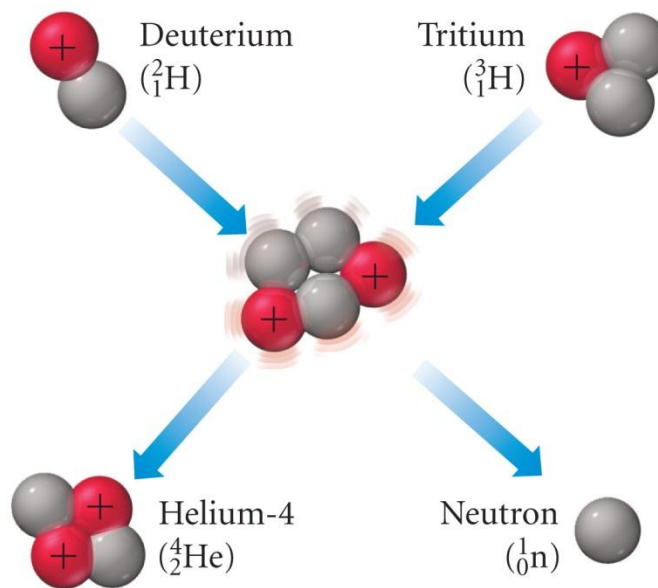
TABLE 19.3	Selected Nuclides and Their Half-Lives	
Nuclide	Half-life	Type of Decay
$^{232}_{90}Th$	1.4×10^{10} yr	Alpha
$^{238}_{92}U$	4.5×10^{9} yr	Alpha
$^{14}_{6}C$	5730 yr	Beta
$^{220}_{86}Rn$	55.6 s	Alpha
$^{219}_{90}Th$	1.05×10^{-6} s	Alpha

Final Exam Review

Your ACS standardized final exam is a *comprehensive*, 70 question multiple choice (a – d) test featuring material from BOTH the CHM 101 and 102 syllabi. Questions are graded as either correct or incorrect. No points are subtracted for wrong guesses. There are two versions of the test, so your neighbors will have a different version of the test.

I normalize your final exam score out of 70 to a score out of 150. This score out of 150 is included in your final course total.

Tips

A great way to ensure a good grade on your final exam is to practice ACS style questions*. To help you with this, a pair of ACS study guides has been put on reserve in the library. Additionally, if you are going to take the MCAT or PCAT etc., the ACS guide is makes for an excellent resource for these tests' respective chemistry sections. If you wish to purchase a copy ($12 ea.) log on to:
http://www3.uwm.edu/dept/chemexams/guides/details_guides.cfm?ID=162

*Ask me to remind you of the 'BB' story

Due to the number of questions set and the time allowed, most of the multiple choice questions you will meet on the final may be considered to be 'lite' versions of my midterm and quiz questions. The following tips will help you record a better score on your final:

1. The test is *cumulative*, so review everything we have covered since the beginning for the course, *as well as the CHM 101 materials*.

2. Review *all the topics*, but concentrate on topics you have had *difficulty* with. Since the questions are not 'super hard', this will increase your number of correct answers. Do not fall in to the trap of studying what you are good at (you'll get those questions right regardless, most likely), so preferentially study what you are 'bad' at.

3. Try to answer the questions *in order* when using a scantron sheet. It is better to guess a wrong answer (and then come back to it) than risk systematically filling out ovals 'a line out'.

4. *Work out the answers on the scratch paper provided*, then check the possible answers provided. This will cut down on 'red herring' type errors (see below)

5. Watch out for obvious 'red herrings', as illustrated by the following example. MOST questions DO NOT have a red herring, but a reasonable fraction do:

Example: CO is the formula for:

a.	copper	c.	cobalt
b.	carbon monoxide	d.	Monocarbon monoxide

Sample Final Exam Questions (CHM 101 syllabus)

1. In all neutral atoms, there are equal numbers of:

a.	electrons and protons	c.	electrons and neutrons
b.	protons and neutrons	d.	electrons and positrons

2. Which pair of particles has the same number of electrons?

a.	F^-, Mg^{2+}	c.	P^{3-}, Al^{3+}
b.	Ne, Ar	d.	Br^-, Se

3. What is the mass percent of oxygen in $Ca(NO_3)_2$?

a.	29.3 %	c.	58.5 %
b.	47.1 %	d.	94.1%

4. A 24.0 g sample of carbon contains how many atoms:

a. 6.02×10^{23} c. 3.01×10^{23}
b. 1.20×10^{24} d. 2.04×10^{24}

5. When 1.187 g of a metallic oxide is reduced with excess hydrogen, 1.054 g of the metal is produced. What is the metallic oxide?

a. Ag_2O c. K_2O
b. Cu_2O d. Tl_2O

6. A single molecule of a certain compound has a mass of 3.4×10^{-22} g. Which value comes closest to the mass of a mole of this compound?

a.   50 g   c.   150 g
b.   100 g   d.   200 g

7. The electronic configuration for the Ca atom is:

a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
b. $1s^2 2s^2 2p^6 3s^2$ d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

8. Two moles of any gas will occupy what volume at STP?

a.   22.4 L   c.   4.48 L
b.   11.2 L   d.   44.8 L

Answers:

1.   a.   5.   b.
2.   a.   6.   d.
3.   c.   7.   c.
4.   b.   8.   d.

Sample Final Exam Questions (CHM 102 syllabus)

1. When a material in the liquid state is vaporized and then condensed to a liquid, the steps in the process are, respectively:

a. $\Delta T_2 = 4 \ \Delta T_1$ c. $\Delta T_2 = 0.5 \ \Delta T_1$
b. $\Delta T_2 = 2 \ \Delta T_1$ d. $\Delta T_2 = \Delta T_1$

2. Calculate ΔH^o for the chemical reaction:

$$Cl_2 \ (g) \ + \ F_2 \ (g) \ \rightarrow \ 2ClF \ (g)$$
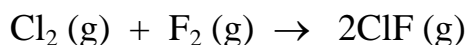
Given the bond enthalpies: F-F = 159 kJ/mol
                               Cl-Cl = 243 kJ/mol
                               Cl-F = 255 kJ/mol

a.   -147 kJ   c.   +171 kJ
b.   -108 kJ   d.   +912 kJ

3. The standard enthalpy of formation ΔH^o_f for NO_2 is the enthalpy change for which reaction?

a. $N \ (g) + 2O \ (g) \rightarrow NO_2 \ (g)$ c. $\frac{1}{2} N_2 \ (g) + O_2 \ (g) \rightarrow NO_2 \ (g)$
b. $\frac{1}{2} N_2O_4 \ (g) \rightarrow NO_2 \ (g)$ d. $NO \ (g) + \frac{1}{2}O_2 \ (g) \rightarrow NO_2 \ (g)$

4. In a bomb calorimeter, reactions are carried out at:

a.   constant pressure   c.   constant volume
b.   1 atm and 25^oC d.   1 atm and 0^oC

5. Calculate ΔH^o for the chemical reaction:

$$3H_2 \text{ (g)} + O_3 \text{ (g)} \rightarrow 3H_2O \text{ (l)}$$
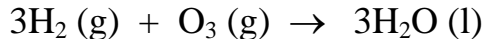
Given the ΔH^o_{rxn} enthalpies: $H_2 \text{ (g)} + \frac{1}{2}O_2 \text{ (g)} \rightarrow H_2O \text{ (l)} = -286$ kJ/mol
$3O_2 \text{ (g)} \rightarrow 2O_3 \text{ (g)} = +271$ kJ/mol

a.   -15 kJ   c.   -722 kJ
b.   -558 kJ   d.   -994 kJ

6. The gas phase reaction $A_2 + B_2 \rightarrow 2$ AB proceeds by bimolecular collisions between A_2 and B_2 molecules. If the concentrations of both A_2 and B_2 are doubled, the reaction rate will change by a factor of:

a.   ½   c.   2
b. $\sqrt{2}$ d.   4

7. Under certain conditions, the average rate of *appearance* of ozone gas in the reaction

$$3O_2 \text{ (g)} \rightarrow 2O_3 \text{ (g)}$$
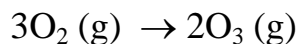
is 1.2×10^{-3} atm.s^{-1}. What is the average rate for the *disappearance* of O_2 (g)?

a. 8.0×10^{-4} atm.s^{-1} c. 1.8×10^{-3} atm.s^{-1}
b. 1.2×10^{-3} atm.s^{-1} d. 5.3×10^{-3} atm.s^{-1}

8. A plot of reactant concentration as a function of time gives a straight line. What is the order of reaction for this reactant?

a.   zero   c.   second
b.   first   d.   third

9. Carbon monoxide gas reacts with hydrogen gas at elevated temperatures to form methanol, according to the equation:

$$CO \text{ (g)} + 2H_2 \text{ (g)} \Leftrightarrow CH_3OH \text{ (g)}$$
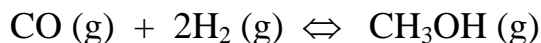
When 0.40 mol of CO and 0.30 mol of H_2 are allowed to reach equilibrium in a 1.0 L container, 0.060 mol of CH_3OH (g) is formed. What is the value of K_c?

a.   0.50   c.   1.7
b.   0.98   d.   5.4

10. Which factors will affect both the position of the equilibrium and the value of the equilibrium constant for this reaction:

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \Leftrightarrow 2NH_3 \text{ (g); } \Delta H = -92 \text{ kJ}$$
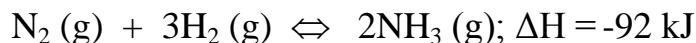
a.   Increasing the volume   c.   Removing ammonia gas
      of the container
b.   Adding more N_2 gas   d.   Lowering the temperature

11. In a 0.050 M solution of weak monoprotic acid, $[H^+] = 1.8 \times 10^{-3}$ M. What is K_a?

a. 3.6×10^{-2} c. 6.7×10^{-5}
b. 9.0×10^{-5} d. 1.6×10^{-7}

12. What is the value of the equilibrium constant K, for a reaction in which $\Delta G^\circ = -5.20$ kJ at 50 °C?

a.   0.144   c.   6.93
b.   0.287   d.   86.4

Answers:

1.	d.	7.	c.
2.	b.	8.	a.
3.	c.	9.	d.
4.	c.	10.	d.
5.	d.	11.	c.
6.	d.	12.	c.

Post-Final Wrap Up

General chemistry final exams are graded immediately after they have been completed by the students. The final exam scores (out of 150), as well as overall course scores and letter grades, will be available from 10:00 am on Thursday of exam week. **Students can check their scores by sending Dr. Mills an e-mail request at any time before noon on Thursday of exam week**. In order to ensure confidentiality, students requesting such feedback must include the following code word(s) within their e-mail requests:

So Close, Yet so Far?

Unfortunately, it is sometimes the case that students find themselves just a few points below the C/D (50%) cut-off line after the completion of all course materials. In order for such students to achieve a passing 'C' grades, an optional 25 pt. extra credit assignment may be completed. ***Students may only complete this assignment if they are in good academic standing (no more than one missed quiz, exam or lab) and contact Dr. Mills, via e-mail with a grade request, no later than noon on Thursday of exam week*****. Such students' final scores must have fallen no more than 25 points below the C/D cut-off in order for them to be eligible to take the assignment.**

Dr. Mills will supply qualifying students with a copy of the extra credit assignment, as an e-mail attachment, via return e-mail. **The hard deadline for completing this assignment is 10:00 am on Friday of exam week – no exceptions.**

Instructor: Mills

Chemistry 102: 1st Practice Examination

Answer all five questions. Each question is worth 30 points. Please ensure you have all *five* pages of questions, as well as a formula sheet and a copy of the periodic table, *before* starting.

SHOW ALL WORK

Question	Score
1	
2	
3	
4	
5	
Total	

"Expressing reaction rates"

The reaction between hydrogen and nitrogen to form ammonia is known as the Haber process:

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightarrow 2NH_3 \text{ (g)}$$
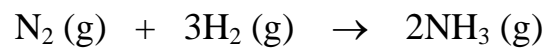
Question 1a (5 points each): Express the rate of the above reaction in terms of changes in $[N_2]$ with time, $[H_2]$ with time, and $[NH_3]$ with time.

Question 1b (15 points): When $[H_2]$ is decreasing at 0.175 $molL^{-1}s^{-1}$, at what rate is $[NH_3]$ increasing?

"Initial rates"

Question 2 (30 points): Consider the generic reaction:

$$A + B + C \rightarrow D$$

Assuming the above reaction was analyzed using the initial rate method at 25°C, use the data below to determine:

5. The order of reaction with respect to each reactant and the overall order of the reaction. **Summarize your findings in the form of a complete rate equation**.
6. The value of k at this temperature.
7. What is the rate of reaction when the concentrations of *each* reactant is 0.50 M,

Experiment	Initial concentrations (molL^{-1})			Initial rate (molL^{-1}s^{-1})
	A	B	C	
1	0.10	0.10	0.50	1.5 x 10^{-6}
2	0.20	0.10	0.50	3.0 x 10^{-6}
3	0.10	0.20	0.50	6.0 x 10^{-6}
4	0.10	0.10	1.00	1.5 x 10^{-6}

"Half - life"

<u>Question 3a</u> (15 points): The decomposition of N_2O_5 (g) is a first order process:

$$2N_2O_5 \text{ (g)} \quad \rightarrow \quad 4NO_2 \text{ (g)} + O_2 \text{ (g)}$$

The concentration of N_2O_5 (g) may be monitored with time using a simple diode colorimeter. If, during such an experiment, k is determined to be 5.2 x 10^{-4} s^{-1}, then what is the half-life of the reaction measured in minutes?

<u>Question 3b</u> (15 points): If, in the above experiment, an absorbance of 0.84 is recorded immediately prior to the commencement of N_2O_5 (g) decomposition (i.e. at t = 0), then what absorbance value will be recorded record after exactly one half-life has passed? Recall that Abs $\propto [N_2O_5]$

For the above reaction, what Abs value would be detected by the colorimeter after exactly three half-lives had passed?

"Arrhenius"

<u>Question 4</u> (30 points): The activation energy for a certain reaction is 65.7 kJ/mol. How many times faster will the reaction occur at 50°C than 0°C?

"Bloody Solution"

<u>Question 5</u> (30 points): Calculate the osmotic pressure of a solution containing 20.5 mg of hemoglobin in 15.0 mL of solution at 25°C. The molar mass of hemoglobin is 6.5 x10^{4} g/mol.

Data sheet

Molar volume: $V_m = 22.41$ L.mol^{-1} at STP (0.00°C, 1.00 atm)

Daltons law of partial pressures:
$$P_{Tot} = P_a + P_b + P_c \ldots.$$

Ideal gas law: $PV = nRT$

Beer's law
$$A = \log(I_o/I) = \varepsilon bc$$

Combined gas law: $P_1V_1/T_1 = P_2V_2/T_2$

$R = 0.0821$ L atm mol^{-1} K^{-1}
$\quad = 8.315$ Jmol^{-1}K^{-1}

Boyle's Law: $P \propto 1/V$ (at fixed T and n)

$d = m/v$

Charles's Law: $P \propto T$ (at fixed V and n)

1.00 atm = 760 mmHg = 101.5 kPa

Avagadro's Law: $V = nV_m$

$\rho H_2O = 1.00$ gmL^{-1}

1st order rate equations
$\ln([A]_t/[A]_o) = -kt$
$t_{1/2} = 0.693/k$

2nd order rate equations
$1/[A]_t = kt + 1/[A]_o$
$t_{1/2} = 1/k[A]_o$

Osmotic pressure: $\Pi = MRT$

Arrhenius equation

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Substance	Specific heat (Jg^{-1}°C^{-1})
Water, H$_2$O (l)	4.18
Iron, Fe	0.450
steel	0.455
Graphite, C	0.711

Substance	ΔH^o_f (kJmol^{-1})
H$_2$O (g)	-241.8
H$_2$O (l)	-285.8
CH$_4$ (g)	-74.9
NH$_3$ (g)	-45.9
HCN (g)	135

Instructor: Mills

Chemistry 102: 2nd Practice Examination

Answer all five questions. Each question is worth 30 points. Please ensure you have all *five* pages of questions, as well as a formula sheet and a copy of the periodic table, *before* starting.

SHOW ALL WORK

Question	Score
1	
2	
3	
4	
5	
Total	

"Gibbs"

Question 1 (30 points): Using the thermodynamic information given in the data sheet, calculate ΔG° for the following reaction:

$$Fe_2O_{3\ (s)} + 6\ HCl_{\ (g)} \rightarrow 2\ FeCl_{3\ (s)} + 3\ H_2O_{\ (g)}$$
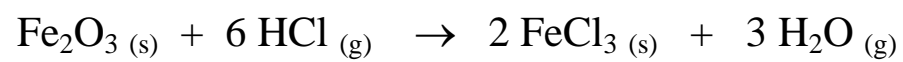
"What's the pH?"

Question 2 (30 points): Calculate the pH of each of the following solutions:

8.   0.015 M HCl (aq) (assume complete dissociation)

9.   0.015 M H_2SO_4 (aq) (assume complete dissociation)

10. 0.015 M NaOH (aq) (assume complete dissociation)

11. 0.015 M $HC_2H_3O_2$ (aq), $K_a = 1.8 \times 10^{-5}$

"Weak Acid"

<u>Question 3</u> (30 points): A 0.200 M solution of a weak acid HA (aq) is 9.4 % ionized (dissociated) at equilibrium. Use this information to calculate $[H^+]$, $[HA]$ and K_a for HA.

"Weak Base"

Codeine ($C_{18}H_{21}NO_3$) is a weak organic base. A 5.0 x 10^{-3} M solution of codeine has a pH of 9.95.

<u>Question 4a</u> (30 points): Calculate K_b for codeine.

<u>Question 4b</u> (5 points): Calculate pK_b for codeine.

"Common Ion"

Question 5 (30 points): A solution contains 2.5×10^{-4} M Ag^+(aq) and 1.7×10^{-3} M Pb^{2+}(aq).

   C. If NaI (aq) is added, will AgI ($K_{sp} = 8.3 \times 10^{-17}$) or PbI_2 ($K_{sp} = 7.9 \times 10^{-9}$) precipitate first?

   D. Specify the concentration of I^- (aq) needed to begin precipitation of the material you determined would precipitate first in part A.
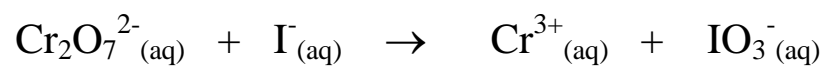
"REDOX"

Question 5a (10 points): State the oxidation state of the specified atom in each of the chemical species listed below:

Cr in $Cr_2O_7^{2-}$ I in IO_3^-

Question5b (20 points): Balance the following REDOX reaction. Assume acidic conditions.

$$Cr_2O_7^{2-}{}_{(aq)} \;+\; I^-{}_{(aq)} \;\rightarrow\; Cr^{3+}{}_{(aq)} \;+\; IO_3^-{}_{(aq)}$$

Data sheet

Molar volume: V_m = 22.41 L.mol^{-1} at STP (0.00°C, 1.00 atm)

Daltons law of partial pressures:
$P_{Tot} = P_a + P_b + P_c$ ....

Ideal gas law: $PV = nRT$

Beer's law
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1st order rate equations
$\ln([A]_t/[A]_o) = -kt$
$t_{1/2} = 0.693/k$

2nd order rate equations
$1/[A]_t = kt + 1/[A]_o$
$t_{1/2} = 1/k[A]_o$

Arrhenius equation
$\ln(k_2/k_1) = E_a(1/T_1 - 1/T_2)/R$

Equilibrium constants: $K_p = K_c(RT)^{\Delta n}$

$K_w = [H^+][^-OH] = 1 \times 10^{-14}$
$pH + pOH = 14$
$\Delta G = \Delta H - T\Delta S$

$pH = -\log[H^+]$
$K_aK_b = K_w$
$\Delta H_{rxn} = \Delta H_f \text{(products)} - \Delta H_f \text{(reactants)}$

Substance	S^o (Jmol^{-1}K^{-1})
H_2O (g)	188.83
Fe_2O_3 (s)	89.96
$FeCl_3$ (s)	142.3
HCl (g)	186.69

Substance	ΔH^o_f (kJmol^{-1})
H_2O (g)	- 241.8
Fe_2O_3 (s)	- 822.16
$FeCl_3$ (s)	- 400.0
HCl (g)	- 92.30

Notes

Periodic Table of the Elements

(Mass Numbers in Parentheses are from the most stable of common isotopes.)

Non-Metals

Metals

Transition Metals

Rare Earth Elements

Atomic #
Symbol
Atomic Mass

New Designation
Original Designation

Group	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 H 1.0094																	2 He 4.00260
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
3	11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 to 71	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.03	89 to 103	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)	110 Uun (267)								

d-block / Lanthanide Series

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97

Actinide Series

89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

s-block   p-block   d-block   f-block

300