Chemistry 301

FINAL EXAM REVIEW

PLEASE LOOK OVER MIDTERM REVIEWS FOR COMPREHENSIVE TOPICS

Final Exam Preparation Checklist

Here is a suggested list of steps that can help you be successful on the final exam:

1. **Review your mistakes on the midterms (Quest).**
   - It is extremely valuable being able to look at questions you missed and gain confidence that you wouldn't miss them again if you took the exam again
2. **Do a broad conceptual review based on your notes, gchem, reviews**
   - Make an organized, colorful, annotated outline!
   - Print out your formula sheet and annotate it with missing equations, necessary conversions, etc.
3. **Work the homework problems with your notes**
4. **Work the midterms without your notes**
   - Based on your performance, you might want to go back to step 2 for a bit
5. **Work the practice final (in isolation) in under 3 hours**

Exam Study - The Final Exam

Downloaded

Surge
Above & Beyond • Surge

Gravity - Original Mix
Parker & Hanson • Gravity

Filmic
Above & Beyond • Group Therapy

+/- 2

Final Exam Breakdown

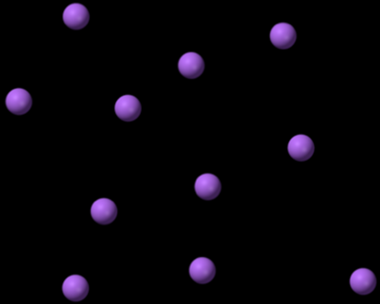
1. Fundamentals
2. Gas Laws

13

3. Atomic Theory, Ionic & Covalent Compounds 10
4. Bonding, IMFs, Liquid & Solid Properties 14
5. Thermodynamics 13

35 conceptual
15 calculation

PIB, RDF

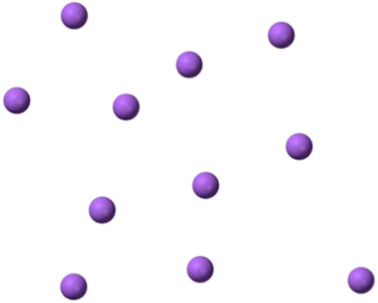


Fundamentals

STOICHIOMETRY, NOMENCLATURE, UNITS

Chemistry Fundamentals

- At this point you should really be able to approach problems like a true chemist. This means you should be able to analyze chemical systems and structures in a scientific way.
- Some of the basic chemistry knowledge you should bring to the test involves:
  - Nomenclature
    - Know how to name ionic compounds
    - Know the names and charges of the polyatomic ions
  - Stoichiometry
    - Apply stoichiometry to straightforward reactions
    - Apply stoichiometry to gas laws and thermodynamic problems
  - Unit analysis
    - Be able to easily convert between different units (conversions provided)
    - Know when to use certain units (g vs. kg ; R-values ; L atm vs. J ; etc.)



Basic Terminology in Reaction Stoichiometry

- **Mole:** a mole is basically a packet of atoms (6.02×10^{23} atoms to be exact)
  - We use the term "mole" because it is easier to work with in a lab.
  - The mass of each element is presented as its **molar mass** on the periodic table (g/mol)
  - Based on the phase of matter, a mixture will look different (condensed phases vs. gas phase)
    - **What is the difference? We now know that the condensed phases have potential energy in the form of IMF's**
- **Limiting reagent:** the reactant that **runs out first**, thereby forcing the reaction to stop
- **Excess reagent:** a reactant that is added in high quantities so that another reactant runs out first
  - You will have a certain amount of this "excess reagent" left over once the limiting reagent runs out
- Important: there is almost NO stoichiometry on the formula sheet. All stoichiometric formulas (composition, reaction, intensive vs. extensive) must be memorized

Molecules, Moles, and Mass

You are expected to know how to convert between molecules, moles, and molar mass.

Here's how you do it:

1. From Molecules to Moles
   - Remember: Avogadro's number ($N_A = 6.022 \times 10^{23}\ mol^{-1}$) represents the number of molecules in a mole.

$$\boxed{\frac{\#\ \text{molecules}}{N_A} = \#\ \text{moles}}$$

1 atom is one fundamental unit

2. From Moles to Molecules
   - On the exam, what if you forget if you multiply or divide by Avogadro's number? Remember, a mole is a "packet" of molecules. Converting from moles to molecules should always give you a **bigger number**

$$\boxed{\#\ \text{moles} \cdot \text{N}_A = \#\ \text{molecules}}$$

3. From Moles to Mass

$$\text{mol} \times \frac{g}{\text{mol}} = g$$

$$\boxed{\#\ \text{moles} \cdot \text{MW} = \text{mass}}$$

4. From Mass to Moles

$$g \times \frac{\text{mol}}{g} = \#\ \text{mol}$$

$$\boxed{\frac{\text{mass}}{\text{MW}} = \#\ \text{moles}}$$

5. Molecular Weight

$$\frac{g}{\text{mol}}$$

$$\boxed{\frac{\text{mass}}{\#\ \text{moles}} = \text{MW}}$$

1 mole is 6.022×10^{23} fundamental units

Chemistry Fundamentals: Stoichiometry

- Given the following generic, balanced chemical reaction:

$$A_{(g)} + 2B_{(g)} \text{ --> } 3C_{(g)} + 4D_{(l)}$$

$$\nearrow 9 \text{ mol C} \times \frac{2 \text{ mol B}}{3 \text{ mol C}} = 6 \text{ mol B}$$

- **Simple ratio problems:** how many moles of B are required to make 9 moles of C?
  - This problem can be solved by simply understanding the stoichiometric ratio
- **Limiting Reagent, Gas Law Problems:** what is the total volume of your system when 10 L of A are reacted with 10 L B at STP. Assume this reaction goes to completion.
  - This problem should be solved by working out the reaction

***Do not include condensed states (liquids, solids) in the volume or pressure of the final solution**

$$A: \quad 10 \text{ L A} \times \frac{\text{rxn}}{1 \text{ L A}} = 10 \text{ rxns}$$

$$B: \quad 10 \text{ L B} \times \frac{\text{rxn}}{2 \text{ L B}} = \boxed{5 \text{ rxns}} \rightarrow \text{L.R.}$$

Unit One Question

A 6.00L sample of C_2H_4 at 2.00 atm and 293K is burned in 6.00 L of oxygen gas at the same temperature and pressure to form carbon dioxide gas and liquid water. If the reaction goes to completion, what is the final volume of all gases?

$$1\ C_2H_4(g) + 3O_2(g) \rightarrow 2\cancel{H_2O}(l) + 2CO_2(g)$$

1. 2.66 L
2. 12.00 L
3. 2.00 L
4. [✓ 8.00 L]
5. 6.00 L

$$C_2H_4:\quad 6.00\,L \times \frac{rxn}{1\,L} = \boxed{6\ rxns} \rightarrow \text{excess}$$

$$O_2:\quad 6.00\,L \times \frac{rxn}{3\,L} = \boxed{2\ rxns} \rightarrow \text{L.R.}$$

$$CO_2\ \text{formed}\quad 2\ rxns \times \frac{2\,L}{rxn} = 4\,L\ CO_2$$

$$C_2H_4\ \text{excess}:\quad \text{Initial amount} - (\text{amount consumed})$$

$$6.00\,L - \left(2\ rxns \times \frac{1\,L}{rxn}\right) = 4\,L\ C_2H_4$$

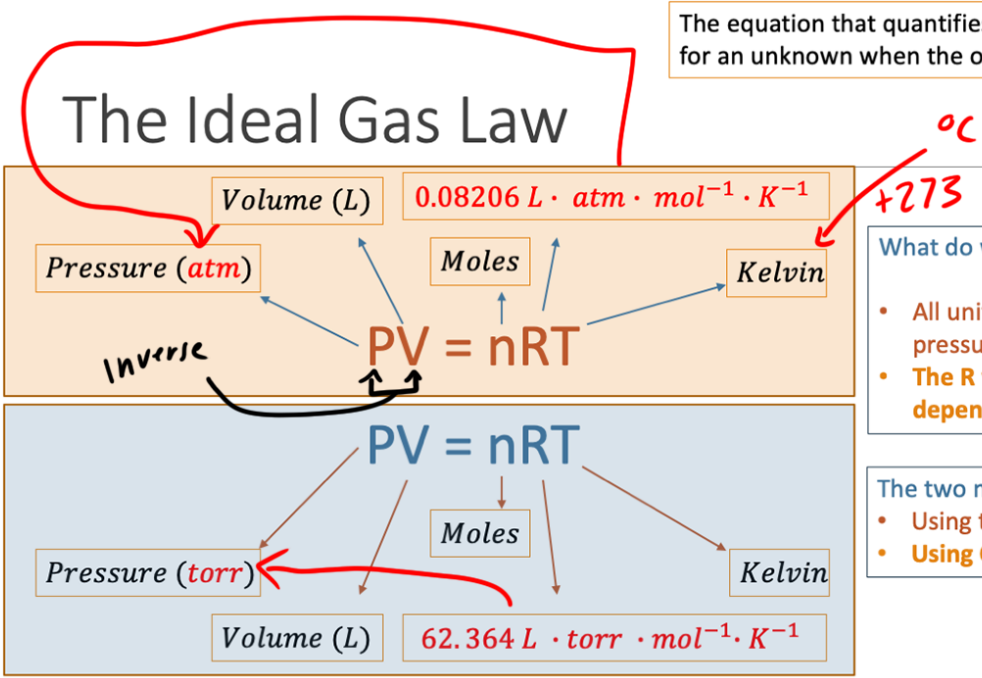
$$+\ \}\ 8\,L$$

Gas Laws

IDEAL, MIXTURES, KMT, NON-IDEAL

The Ideal Gas Law

The equation that quantifies the state of a gas; solves for an unknown when the other variables are given



PV = nRT

Pressure (atm)

Volume (L)

Moles

$0.08206\ L \cdot atm \cdot mol^{-1} \cdot K^{-1}$

Kelvin

°C

+273

Inverse

PV = nRT

Pressure (torr)

Volume (L)

Moles

$62.364\ L \cdot torr \cdot mol^{-1} \cdot K^{-1}$

Kelvin

What do we see here?

- All units are the same except for pressure and R
- **The R you use for each problem depends on your pressure units**

The two mistakes students make:

- Using the wrong R-value
- **Using Celsius instead of Kelvin**

Note: P is pressure, ρ is mass density (m/V)

The Ideal Gas Law and Density

Choose one to memorize:

✓ $$\rho = \frac{MW \cdot P}{R \cdot T}$$

Solves directly for mass density (g/L)

$$\frac{m}{V}$$

$$MW = \frac{\rho \cdot R \cdot T}{P}$$

Solves directly for molecular weight (g/mol)

$$\frac{PV}{V} = \frac{nRT}{V}$$

$$MW \times P = \frac{n}{V} RT \times MW$$

$$MW \times P = \frac{m}{V} RT$$

Two take-away conceptual points:

- All other conditions being equal in the ideal gas law equation (P, V, & T), **all ideal gases have the same number density;** number density depends on P, V, & T but NOT molecular weight
- All other conditions being equal in the ideal gas law equation (P, V, & T), **a heavier gas will have a greater mass density;** mass density depends on the molecular weight of the gas

$$PV = nRT$$

$H_2 = 6.75$

Unit One Question

What is the final pressure of hydrogen gas (H_2) if 4.5 mol Al reacts to completion with excess HCl in the following reaction if the hydrogen gas occupies 14 L at 300K

$$2Al(s) + 6HCl(l) \rightarrow 2AlCl_3(s) + 3H_2(g)$$

1. [✓ 11.9 atm]
2. 0.233 atm
3. 1.07 atm
4. 0.0763 atm
5. 7.9 atm
6. 5.28 atm

$$\underset{\text{mol}}{4.5}\ Al \times \frac{3\ \text{mol}\ H_2}{2\ \text{mol Al}} = 6.75\ \text{mol}\ H_2$$

$$P = \frac{nRT}{V} = \frac{(6.75\ \cancel{\text{mol}})(0.08206\ \frac{\cancel{L}\cdot \text{atm}}{\cancel{\text{mol}}\ \cancel{K}})(300\ \cancel{K})}{14\ \cancel{L}}$$

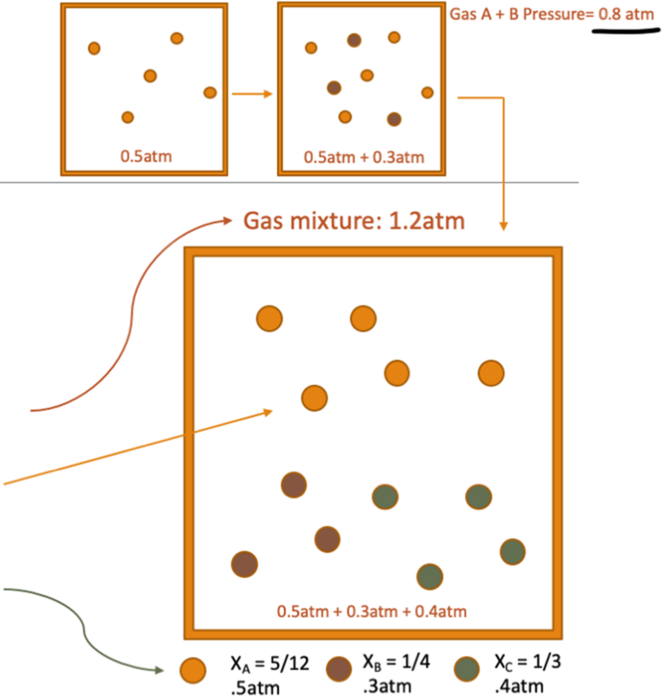
$$= 11.9\ \text{atm}$$

$$P_{total} = P_A + P_B + P_C \ldots$$

Partial Pressure

Partial pressure is a method for quantifying the pressures exerted by individual species in a gas mixture.

- Three terms are necessary for understanding partial pressures:
  1. **Total pressure** (P_{total}): the "actual" pressure of the system
  2. **Partial pressure** (P_i): the pressure exerted by a single species (i)
  3. **Mole fraction** (X_i): the ratio between the number of moles of a single species (i) and the total number of moles in the system



$$P_{N_2} = \chi_{N_2} \cdot P_{total}$$

Unit One Question

A 60:40 mixture (by mass) of nitrogen gas to carbon dioxide is made. What is the mole fraction of nitrogen in this mixture?

100g

1. 0.44
2. 0.39
3. [✓ 0.70]
4. 0.61
5. 0.27
6. 0.50
7. 0.56

$$60g\ N_2 \times \frac{mol}{28g} = 2.14 \text{ moles}$$

$$40g\ CO_2 \times \frac{mol}{44g} = 0.909\ldots \text{ moles}$$

$$\chi_{N_2} = \frac{\text{moles } N_2}{\text{moles}_{N_2} + \text{moles } CO_2} = \frac{2.14}{2.14 + 0.909}$$

Standard Conditions (Memorize)

- STP is the default standard for gases
  - 0 degrees Celsius, 1atm (or 760 torr) 273 K
  - **At STP, one mole of ideal gas occupies 22.4L** ✗
- STAP is a "modern" default for gases (less used)
  - 25 degrees Celsius (room temperature), 1 bar
- Thermodynamic room temperature, standard conditions
  - 25 degrees Celsius, 1 atm

↓ 298 K

↳ ΔH°, ΔG°

Kinetic Molecular Theory

1. **Gases are constantly moving in random directions**
2. **The distance between particles is large compared to the particle size**
   - True ideal gases have relatively **no volume**
3. **All particles have perfectly elastic collisions**
   - There is no energy loss in the system to collisions; energy cannot be created or destroyed based on Newtonian Physics
4. **No other forces act upon ideal gases**
   - There are no attractive or repulsive forces that act upon ideal gas particles
5. **The average kinetic energy of a gaseous system is dependent only on the average temperature of the system**

The ideal gas law fails us when these two assumptions do not hold true. Repulsions are caused by a low **available volume** (b); attractions are caused by significant **intermolecular forces** (a)

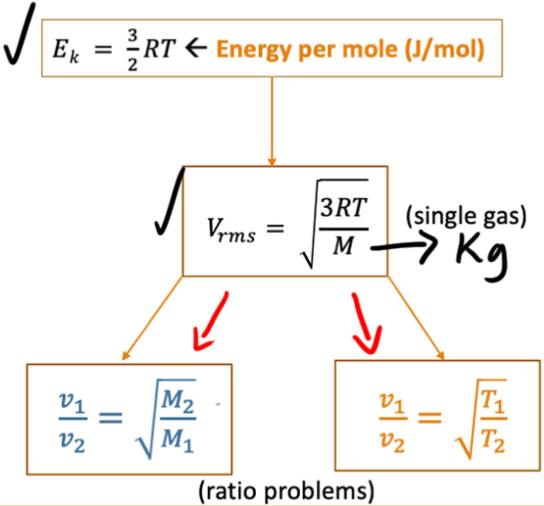
$$E_K = \frac{3}{2}RT = \frac{1}{2}mv^2$$

Main conclusions: the ideal gas law works because when these pillars of KMT hold true in a system. The ideal gas law is modeled best at **High Temperature** and **Low Pressure**

Kinetic Molecular Theory: Relationships

- Kinetic Molecules Theory gives us three key relationships that you should know as equations and by definition (in words)

1. **Kinetic Energy vs. Temperature**
    - Kinetic energy is dependent solely on the temperature of a gaseous system (direct relationship)
    - R = 8.314 J / mol K
    - Temperature in Kelvin
2. **Mass vs. Velocity**
3. **Temperature vs. Velocity**



✓ $E_k = \frac{3}{2}RT \leftarrow$ **Energy per mole (J/mol)**

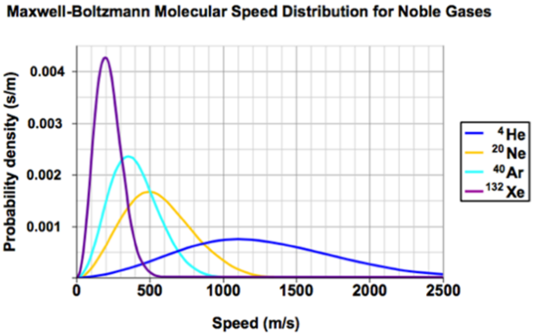
✓ $V_{rms} = \sqrt{\frac{3RT}{M}}$ (single gas) → Kg

$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$

$\frac{v_1}{v_2} = \sqrt{\frac{T_1}{T_2}}$

(ratio problems)

KMT: Mass vs. Velocity; Velocity vs. Temperature



Some key features of this graph include:

- Each curve looks like a unimodal distribution with a "tail" that approaches the limit infinite velocity (0 probability density)
- Molecules are traveling at a variety of speeds but there is a clear average
- The actual V_{rms} is slightly to the right of the peak

1. **Mass vs. Velocity (V_{rms})**
   - We can see that the heavier gases move slower and the lighter gases move faster
   - The faster the gas, the wider the distribution
2. **Velocity (V_{rms}) vs. Temperature**
   - If you were working with the same gas, a similar graph could be created by modifying temperature instead.
   - In this case, higher temperatures of the same gas result in faster speeds.

Pay very close attention to how the 1 and 2 match up in these relationships

KMT: Ratio Problems

When considering two gases, you can use the KMT equation to create a ratio:

1. **Mass vs. Velocity (V_{rms}) (same temperature, different molecule)**
    - Velocity is proportional to the inverse square root of mass.
    - **When temperature is constant, lighter particles move faster**

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$$

2. **Velocity (V_{rms}) vs. Temperature (same molecule, different T)**
    - Velocity is proportional to the square of temperature
    - **When dealing with the same species gas, particles move faster at higher temperatures**

$$\frac{v_1}{v_2} = \sqrt{\frac{T_1}{T_2}}$$

SO_2 to chlorine gas

Practice: What is the ratio of the effusion rates of SO_2 to Cl_2?

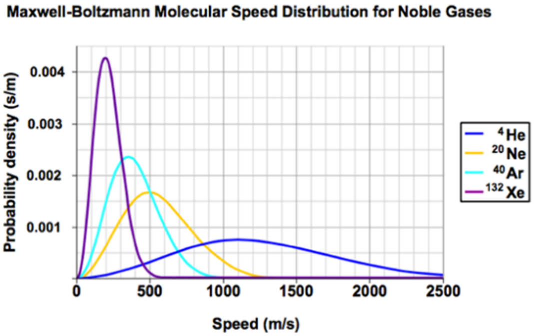
$\downarrow$ V_1 $\downarrow$ V_2

M_2 $\downarrow$

$$1.05 = \sqrt{\frac{M_{Cl_2}}{M_{SO_2}}} = \sqrt{\frac{70.9\ g/mol}{64\ g/mol}}$$

$M_1 \nearrow$

Maxwell-Boltzmann Distribution



- Given a Maxwell distribution, you should know:
  - Find the approximate V_{rms}
  - Be able to label **which gas is which** (or which temperature is which)
  - Understand the **relationships** between mass, velocity, and temperature
  - Understand how these relationships impact the **shape** of the curve

The Non-Ideal Gas Law

- **The Ideal Gas Law is adjusted for real gases in the following way:**

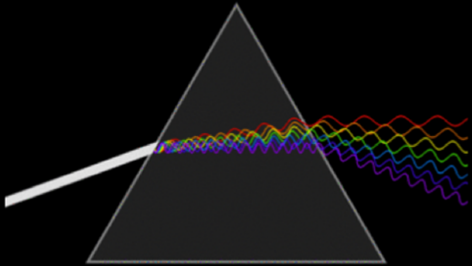
$$(P + \frac{an^2}{V^2})(V - nb) = nRT$$

- Important Notes:
  - The pressure expression $(P + \frac{an^2}{V^2})$ is equal to the **ideal pressure**. The P term is the **measured pressure**.
  - The volume expression $(V - nb)$ is equal to the **available volume**. The V term is the **volume of the container**.

- Key points:
  - Attractive forces decrease the pressure. **Stronger attractive forces give a larger "a" value**.
  - The size of the molecules decrease the available volume. **Larger molecules give a larger "b"**.
    - A larger b value correlates with more repulsions. Repulsions are an effect of the fact that two gas molecules can't take up the same space – therefore, they repel each other

Favoring Non-Ideal Vs. Ideal Conditions

Ideal Conditions	**Non-Ideal Conditions**
High Temperature	Low Temperature
Low Pressure	High Pressure
High Volume	Low Volume
Small Molecules (small b term)	Large Molecules
No attractive forces (small a term)	High Attractive Forces (Intermolecular forces)
Small number of molecules	Large number of molecules

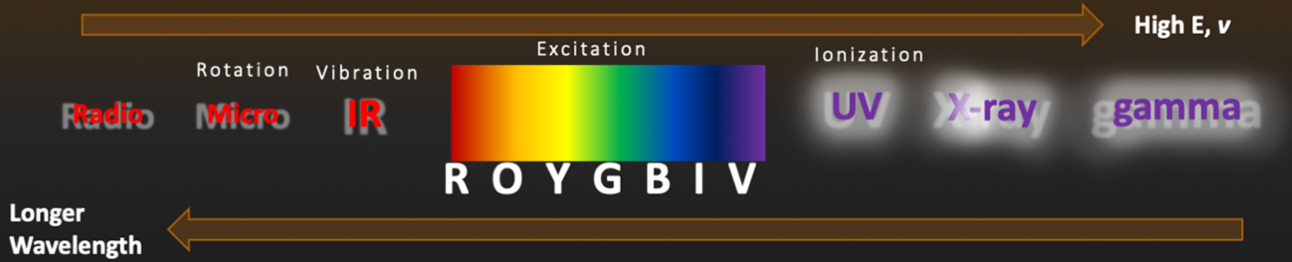


Atomic Theory

LIGHT, QUANTUM, ELECTRON CONFIGURATIONS, PERIODIC TRENDS

$$c = \lambda\nu \; ; \; E_{photon} = h\nu \; ; \; E_{photon} = \frac{hc}{\lambda}$$

THE ELECTROMAGNETIC SPECTRUM



High E, *v*

Rotation Vibration Excitation Ionization

Radio Micro IR UV X-ray gamma

R O Y G B I V

Longer Wavelength

- Microwaves: enough energy to begin rotating a molecule
- IR: enough energy to begin vibrating a molecule
- Visible (700nm to 400nm): enough energy to begin exciting electrons
- UV and beyond: begins the full ionization (breaking) of electrons/bonds

Quantifying Light

- Modern physics defines light as photon particles exhibiting wave-like properties:

$$\overset{m/s}{c} = \overset{nm}{\lambda}\nu$$

  - This equation states that the **speed of light** (c) is equal to the **frequency** (ν) times the **wavelength** (λ)
  - Remember this relationship: **wavelength and frequency are inversely proportional**

- You can also calculate the **energy per photon**:

$$E_{photon} = \mathrm{h}\nu \quad \text{or} \quad E_{photon} = \frac{hc}{\lambda}$$

  - This equation states that the **energy of a photon** (E) is equal to the **frequency** (ν) times the **Planck's constant** ($h = 6.626 \times 10^{-34}$ J s)
  - You get a tiny value here. Why?
  - **Energy and frequency are directly proportional**
  - **Energy and wavelength are inversely proportional**

evidence → conclusions

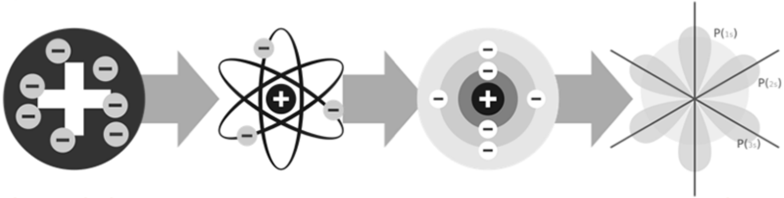
What is Quantum Mechanics?

- Quantum mechanics is the currently accepted model of the atom that describes the motion of subatomic particles and the interactions between them using the following empirically derived postulates:

evidence →

1. Electrons exist in **discrete, quantifiable energy states** (Rydberg, absorption/emission)
2. Electrons and light (photons) exhibit **wave-particle duality** (photoelectric effect, ~~deBroglie~~)
3. The motion of electrons can be described only with **probabilities**. That is, only the position or momentum can be known with certainty at any given time (wave functions, ~~uncertainty principle~~)
    - Furthermore, this demonstrates that electrons exist in “clouds” and not circular orbits

conclusion

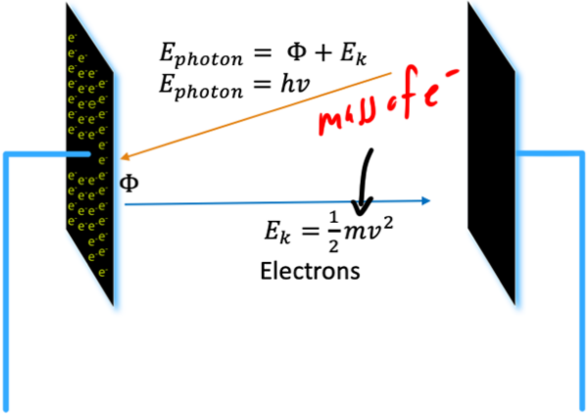


Classical Theory

Quantum Theory

Photoelectric Effect: Conceptual

- **Photoelectric Effect**: a metal will eject electrons if a beam of light reaches a threshold energy
  - Demonstrates how light can interact with matter (the electrons of a metal)



$E_{photon} = \Phi + E_k$

$E_{photon} = h\nu$

more of e^-

$E_k = \frac{1}{2}mv^2$

Electrons

Key points (If Φ is reached)

- Increasing photon energy:

v e^- ↑ , E_K ↑

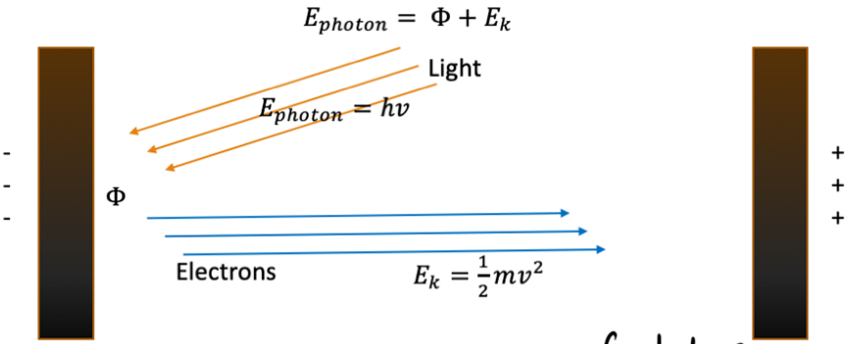
no effect on # of e^-

- Increasing intensity:

e^- ↑

no effect on v, E_K

Quantum Mechanics: Photoelectric Effect



$$E_{photon} = \Phi + E_k$$

$$E_{photon} = h\nu$$

$$E_k = \frac{1}{2}mv^2$$

Unit the work function is reached ($E_{photon} < \Phi$):

- **Increasing intensity has no effect** → # of photons, brightness
- Note: photon energy is **NOT additive in terms of reaching the work function**. See if you can understand the difference between *overall* energy and photon energy

IF THE WORK FUNCTION IS REACHED:

- **Increasing intensity:**
  - Increases the number of emitted electrons
  - Has NO EFFECT on the kinetic energy/ velocity of the emitted electrons
- **Increasing the energy of the photon** (or increasing the frequency/decreasing the wavelength):
  - Increases the kinetic energy of the emitted electrons
  - Increases the velocity of the emitted electrons
  - Has NO EFFECT on the number of electrons

ROYGBIV $\nu \uparrow$ # of e^- $\downarrow$

Exam Two Question

In a photoelectric effect experiment, a blue light forces the electrons of a metallic surface to eject at a velocity of about 380 m/s. The blue light is shut off and a dimmer (lower intensity) violet light is shined on the metal surface for the same amount of time. Which of the following best explains the results?

[✓ **1.**] A fewer number of electrons are ejected, but the ejected electrons have a velocity greater than 380 m/s

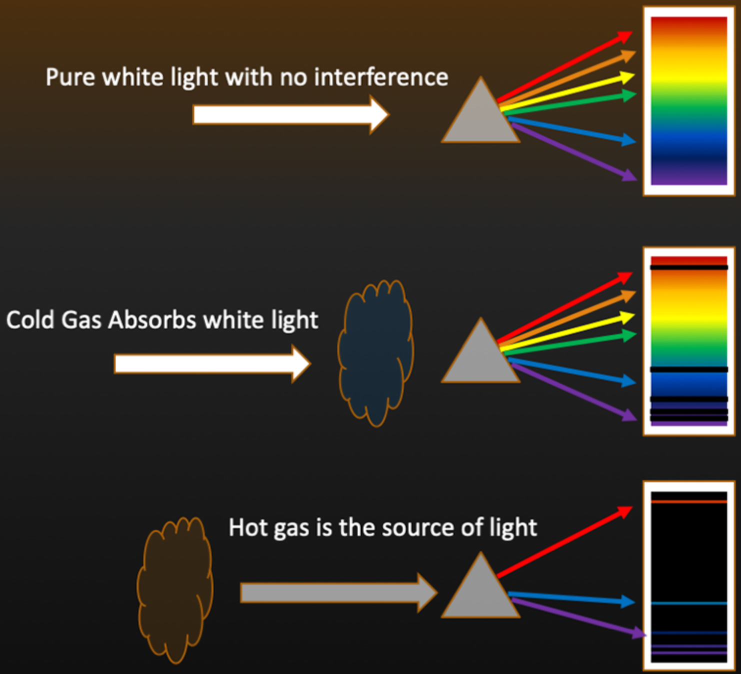
2. The same number of electrons are ejected with the same velocity

3. The same number of electrons are ejected, but the ejected electrons have a velocity greater than 380 m/s

4. A fewer number of electrons are ejected and the ejected electrons have a velocity less than 380 m/s

5. The same number of electrons are ejected and the ejected electrons have a velocity less than 380 m/s

Line spectra in various experiments



Pure white light with no interference

Cold Gas Absorbs white light

Hot gas is the source of light

CONTINUOUS

ABSORPTION

EMISSION

NOTICE HOW THESE ARE OPPOSITES FOR ANY GIVEN GAS. THIS IS EVIDENCE OF THE DISCRETE ENERGY LEVELS OF ELECTRONS

SPECIFIC GASES HAVE THEIR OWN DISCRETE ENERGY PATTERNS

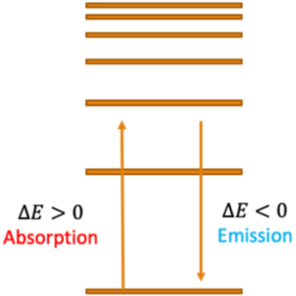
Rydberg Equation

$$\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

R = $2.18 \text{ X } 10^{-18}$J

$$\downarrow$$

$$|\Delta E| = E_{photon} = h\nu = \frac{hc}{\lambda}$$



$\Delta E > 0$
Absorption

$\Delta E < 0$
Emission

Electron energy level transition	**Sign of ΔE**	**Absorption/Emission ($\lvert\Delta E\rvert$)** **(Cause/Effect)**
Low n to high n	Positive (increasing energy)	Light absorbed
High n to low n	Negative (decreasing energy)	Light emitted

Unit Two Question

Which transition between energy levels in a hydrogen atom corresponds to the greatest frequency of light? Longest wavelength?

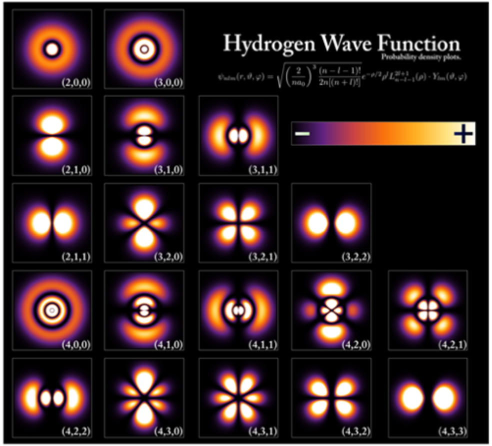
↳ highest E ↳ lowest E

1. 2 to 3
2. 5 to 6 → lowest E, longest λ
3. 3 to 4
4. 2 to 5 → highest E, ν

Conceptual look into the Schrödinger Equation

$$\underbrace{-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}}_{\text{kinetic energy}} + \underbrace{V(x)\psi}_{\text{potential energy}} = \underbrace{E\psi}_{\text{total energy}}$$

- The Schrödinger Equation gives us infinite wave functions (solutions) for the Hydrogen atom.
- The wave functions are classified by the quantum numbers:
  - Principle Quantum Number, n (Energy)
  - Angular Momentum Quantum Number, l (Shape)
  - Magnetic Quantum Number, m_l (Orientation)
- **This ultimately tells us the energy of an electron and the probable location of that electron in three dimensional space.**



Quantum Numbers

- The Quantum Numbers (n, l, m_l, and m_s) stem from the solutions of the Schrödinger Equation and represent the following:
  1. **Principle Quantum Number (n):** the size and energy of the shell; mostly corresponds to the row of the periodic table (exception: d, f block).
  2. **Angular Momentum (l):** the shape of the subshell; corresponds to the region on the periodic table.
     - 0= s subshell; 1 = p subshell; 2 = d subshell; 3 = f subshell
     - Depending on the question, l can signify the shape OR the shape can signify l
  3. **Magnetic (m_l):** the orbitals of the subshell; mathematically indicates the orientation of the subshell shape
     - The number of possible m_l values is equal to the number of orientations possible in space, which therefore represents the number of orbitals available
  4. **Spin Magnetic (m_s):** the spin of the electrons in a subshell
     - Can equal ½ or - ½, but all that really matters is that no two electrons in the same orbital have the same value

$l = 0, 1, 2, n-1$

$\downarrow \quad \downarrow \quad \downarrow$

s p d

Quantum Numbers: Rules

We are mostly interested in assigning possible quantum numbers to the electrons of a given species. To do this, we must understand the rules for assigning quantum numbers:

Principle Quantum Number (n) = 1,2,3, …to n = ∞

Angular Momentum (l) = 0,1,2,… to n-1

Magnetic (m_l) = -l to l

Spin Magnetic (m_s) = $\pm\frac{1}{2}$

Example:

If n = 4

l can equal 0,1,2,3

m_l can equal -3,-2,-1,0,1,2,3

m_s = +/- 1/2

for a 4s orbital, what is possible

$\rightarrow l = 0$

$n = 4$

$l = 0$

$m_l = 0$

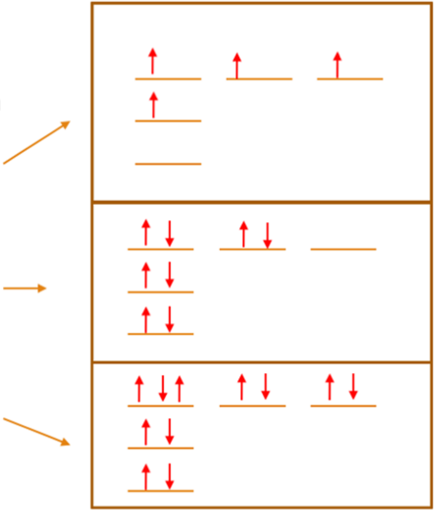
$m_s = +/- 1/2$

Ways to designate quantum numbers without saying it directly:

- "Highest energy electrons" = look at the last filled electrons. This will give you n and l.
- If we say 4s, we are giving you n (4) and l (s= 0)

Electron Configurations: Rules

- There are three main rules to abide by when filling out electron configurations. It is important to follow these rules when doing your own electron configurations and be able to identify the rule that an incorrect electron configuration breaks
- **Aufbau Principle:** fill electrons from the bottom (lowest energy) up
- **Hund's rule:** fill each orbital in a given subshell with a single electron before doubling up
  - Technically this refers to the idea that you should maximize the multiplicity of your configuration
- **Pauli's Exclusion Principle:** no electrons can occupy the same orbital with the same spin and a maximum of two electrons can exist in a single orbital



Note: these are all examples of these rules violated

Ion Electron Configurations

- If you want to write the electron configuration of an ion, start with the neutral atom and then add (- charge) or remove (+ charge) electrons accordingly.
- Easy: O^{2-}

$$O : [He]2s^2 2p^4$$

$$O^{2-} : [He]2s^2 2p^6 \text{ or just } [Ne]$$

- Difficult: Zr^{2+} OR Ti^{2+}

$$Zr : [Kr]5s^2 4d^2 \qquad Ti : [Ar]4s^2 3d^2$$

$$Zr^{2+} : [Kr]4d^2 \qquad Ti^{2+} : [Ar]3d^2$$

$$Ti^{3+} \ [Ar]3d^1$$

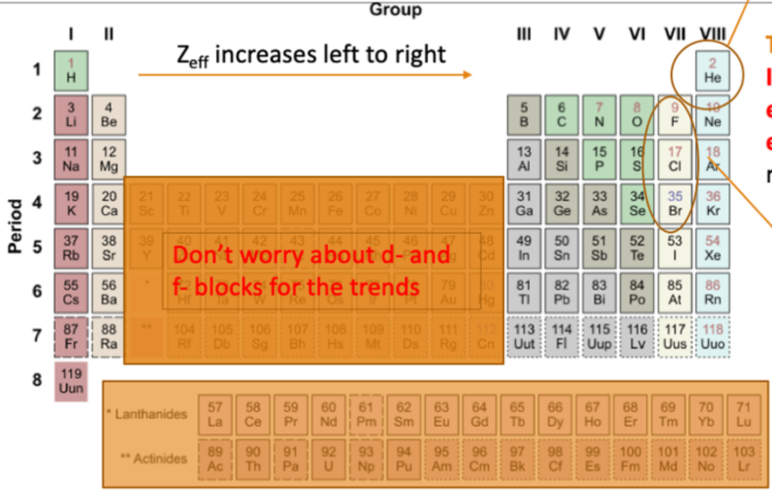
Basic Periodic Table Trends

- Ionization Energy: the energy required to **remove an electron** from an atom in the gas phase
  - Trend: generally increases going to the top right of the periodic table (*has notable exceptions)
  - Increases with each successive ionization (the second ionization energy is greater than the first, and so on)
- Electron Affinity: in much the opposite reaction, electron affinity is the energy released to **add an electron** to an atom in the gas phase
  - Trend: Electron affinity does not follow a stable trend; however, it generally trends toward the top right of the periodic table.
- Atomic Radius: size of the nucleus and its electrons (most of the size is in the space taken up by the electron clouds)
  - Trend: increases as you go to the bottom left where shielding is maximized and z_{eff} is minimized
- Z_{eff}: a measurement of the **pull of any given electrons (generally the valence) by the nucleus**
  - Trend: increases as you go from left to right
  - Remember: Z_{eff} = Atomic Number – Core Electrons
- **Electronegativity: how much an atom wants to pull the electron density in a covalent bond (leads to polarity)**
  - **Trend: increases as you go to the top right.**

Periodic Trends

Shielding Increases going down

Bottom Left: Low ionization energy, low electron affinity, low electronegativity, **large radius**



Z_{eff} increases left to right

Don't worry about d- and f- blocks for the trends

TOP RIGHT: **High Ionization energy, high electron affinity, high electronegativity,** small radius

Helium has the maximum ionization energy

The halogens have the highest electron affinity. Flourine has the highest En

Note: all Si atoms in these equations are in the gas state

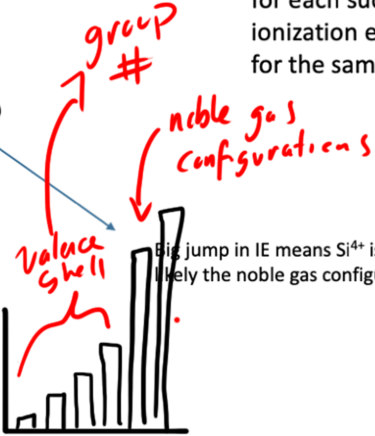
Successive Ionization Energies

The following table shows the first six ionization energies for an unknown element:

#	I.E. (kJ/mol)
1	7.89×10^2
2	1.58×10^3
3	3.23×10^3
4	4.36×10^3
5	1.61×10^4
6	1.98×10^4

The unknown element is:

1. Ne
2. O
3. As
4. B
5. Si correct



Big jump in IE means Si^{4+} is most likely the noble gas configuration

Energy increases for each successive ionization energy for the same atom

1. $Si \rightarrow Si^{+} + e^{-}$
2. $Si^{+} \rightarrow Si^{2+} + e^{-}$
3. $Si^{2+} \rightarrow Si^{3+} + e^{-}$
4. $Si^{3+} \rightarrow Si^{4+} + e^{-}$
5. $\underline{Si^{4+} \rightarrow Si^{5+} + e^{-}}$
6. $Si^{5+} \rightarrow Si^{6+} + e^{-}$

Ionic and Covalent Compounds

IONIC COMPOUNDS, LEWIS STRUCTURES, EXCEPTIONS, FORMAL CHARGE, RESONANCE

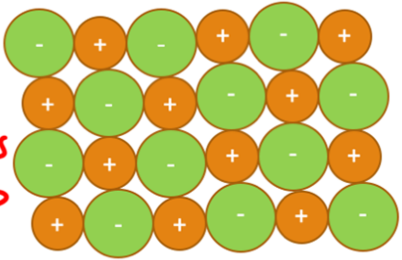
Lattice Energy

charge first

- Lattice Energy: is directly proportional to the charges of the ions (q_1 and q_2) and inversely proportional to the size of the ions (r)

$$\overset{E_p}{\Delta H_{lattice}} \propto \frac{q_1 q_2}{r}$$

big radius smaller E_p



- This describes the energy required for the following reaction:

$$NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)$$
$$NaOH\ (s) \rightarrow Na^{+}(g) + OH^{-}(g)$$

When Ranking Lattice Energies:

1. Prioritize **charge first**
2. If two ionic compounds have the same charge, the **smaller one will have a higher energy**
3. Polyatomic ions are **big**

Lattice Energy Problem

List the following in terms of increasing lattice energy:

1 -1 2 -2 1 -2 1 -1 2 -2 1 -1

LiF, MgO, Na_2SO_4, LiBr, $MgSO_4$, NH_4Br

1. Rank based on charge:

→ LiF

LiBr

→ NH_4Br)

Na_2SO_4 ,

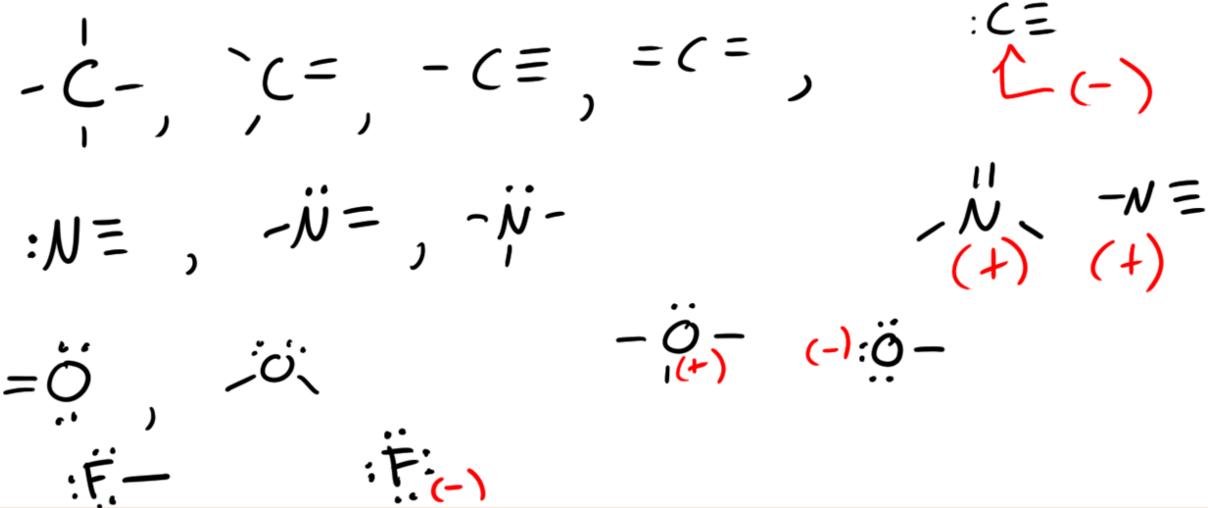
MgO

$MgSO_4$

2. Settle everything else based on size:

$NH_4Br < LiBr < LiF < Na_2SO_4 < MgSO_4 < MgO$

Lewis Structure Formal Charge Foundations



Lewis Structure Formal Charge Foundations

Element	-1 Charge	Neutral	+1 Charge
Hydrogen		1 bond	
Carbon*	3 bonds, 1 LP (rare)	4 bonds	
Nitrogen	2 bonds, 2 LP (rare)	3 bonds, 1 LP	4 bonds
Oxygen	1 bond, 3 LP	2 bonds, 2 LP	3 bonds, 1 LP
Halogens**	0 Bonds, 4 LP	1 bond, 3 LP	

FC = Valence – (lone electrons + bonds)

FC = Valence – ("things it's touching")

This chart represents a "best guess" to draw out simple Lewis Structures. The formal charges are calculated based on a full octet and no exceptions.

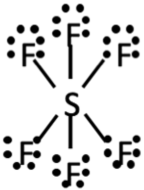
*Carbon almost always has four bonds. Some notable exceptions are CO, CN^-, CNO^-

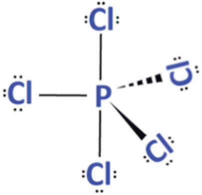
**Represents halogens as a peripheral atom, not a central atom. In other words, this applies to the fluorine in ClF_3 but not the chlorine.

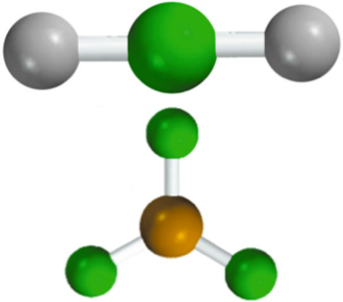
Solving For Lewis Structure Exceptions

Remember, the "octet" rule applies only to Carbon, Nitrogen, Oxygen, and Fluorine as central atoms.

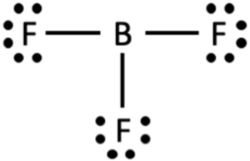
- Period 3 and beyond can exhibit "expanded valence"
- Be and B can exhibit "incomplete octet" as central atoms

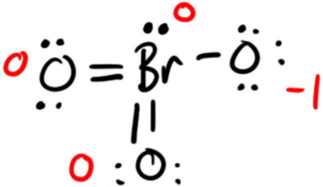






BrO_3^- $A = 7 + 18 + 1 = 26e^-$

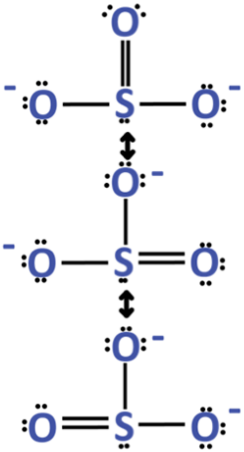




$$B.O. = \frac{total\ \#\ of\ bonds\ in\ resonance}{total\ \#\ of\ bonding\ regions\ in\ resonance}$$

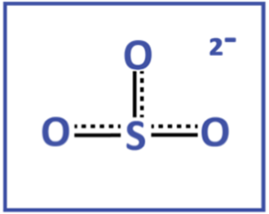
Bonding and Lewis Structures

- **Resonance**: multiple acceptable Lewis Structures are available for a given compound, meaning that the compound actually exists as the average of all acceptable structures
- **Delocalized electrons**: in the case of resonance, electrons are not confined to a single bond. Instead the electron charge is distributed over multiple bonds. We call this delocalization.
- **If you have multiple acceptable Lewis Structures in resonance, your actual structure will have the bonding character of the average. Example: Sulfite (SO_3^{2-})**



"Acceptable" Structures: double and single bonds

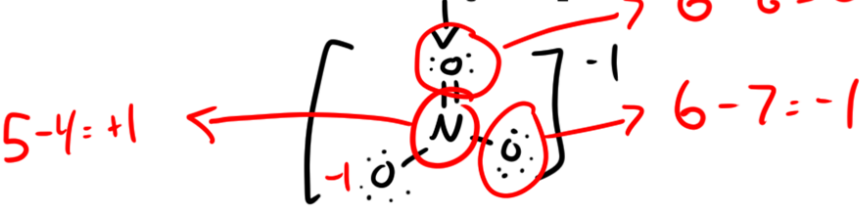
Correct Structure: three 1.33 bonds



Unit Three Question

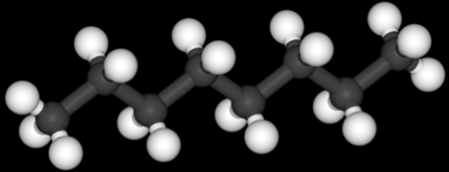
What is the formal charge on the central atom(s) for the following molecules:

CN^-, NO_3^-, NO_2^-



FC = Valence – (lone electrons + bonds)

FC = Valence – (“things it’s touching”)

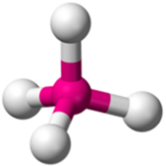


Bonding Theories

VSEPR, VB, MO

Bonding Theories Compared

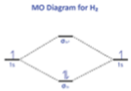
- **VSEPR Theory:**
  - Shapes: molecular and electronic geometries
  - Explains bond angles
  - Focuses on the electron "regions"
  - Depends on the number of electron-dense regions (bonding and lone-pair regions)



- **Valence Bond Theory**
  - Hybrid Orbitals: sp, sp^2, sp^3, sp^3d, sp^3d^2
  - Sigma and pi bonds
  - Identifies the overlapping orbitals to "name" the bonds
  - Focuses on the electron "clouds"
  - Depends on the number of electron-dense regions

sp^3

- **Molecular Orbital Theory**
  - Diagrams
  - Answers three fundamental questions regarding your molecule: bond order, magnetism, HOMO-LUMO gap
  - Sigma and pi bonds and anti-bonds
  - Focuses on the electrons as "waves"
  - Depends on the number of electrons



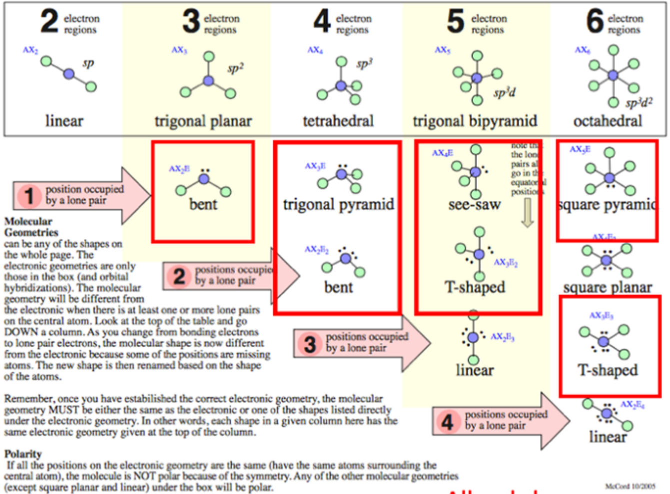
These theories might seem like a lot of information, but if you tie them together and simplify their conclusions, they actually make a lot of sense and don't require too much memorization.

Note: none of this means anything if your Lewis Structure is drawn incorrectly!

Valence Shell Electron Pair Repulsion

- **The basis of VSEPR is that electron-rich regions will achieve the lowest possible energy state by minimizing repulsions (maximizing the angles to spread out)**
- VSEPR gives us two different 3D geometries: **electronic geometry and molecular geometry**.
  - **Electronic geometry**: the shape of all electron-rich regions around a central atom, determined by counting the bonding AND lone pair regions
  - **Molecular geometry**: the shape of only the bonding regions around a central atom, determined by the electronic geometry and the (only) bonding regions
- The VSEPR shape is essential for the "actual" shape of the molecule, which gives us insight into the molecule's bond angles and polarity.

VSEPR Geometries: Molecular Polarity



Molecular Geometries can be any of the shapes on the whole page. The electronic geometries are only those in the box (and orbital hybridizations). The molecular geometry will be different from the electronic when there is at least one or more lone pairs on the central atom. Look at the top of the table and go DOWN a column. As you change from bonding electrons to lone pair electrons, the molecular shape is now different from the electronic because some of the positions are missing atoms. The new shape is then renamed based on the shape of the atoms.

Remember, once you have estabilished the correct electronic geometry, the molecular geometry MUST be either the same as the electronic or one of the shapes listed directly under the electronic geometry. In other words, each shape in a given column here has the same electronic geometry given at the top of the column.

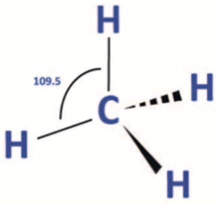
Polarity
If all the positions on the electronic geometry are the same (have the same atoms surrounding the central atom), the molecule is NOT polar because of the symmetry. Any of the other molecular geometries (except square planar and linear) under the box will be polar.

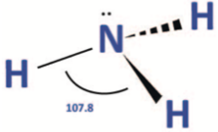
All red shapes are polar

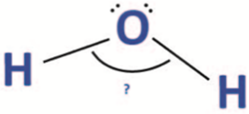
- Polarity in a molecule occurs when there is a permanent dipole moment on the molecule. This can be identified by a few rules:
  - **A perfectly symmetrical molecule will always be nonpolar if its bonds are to the same atom.**
    - Examples: CO_2, SO_3, SF_6, PCl_5, CCl_4 are non-polar molecules even though they have polar bonds
  - **A central atom bound to different peripheral atoms will always be polar, as long as there is at least one polar bond.**
    - Examples: CH_3Cl, CHF_3, PCl_4F
  - **Molecular geometries with lone pairs are polar (even if the bonds are non-polar), except in linear and square planar geometries**
    - Examples: H_2O, NH_3, H_2S, O_3

VSEPR: The Effect of Lone Pairs

- Lone pairs occupy more space on the central atom than a bonding pair of electrons, meaning they end up being more repulsive than bonding regions
- The electron density of lone pairs **is ALL on the one central atom** – not shared between two– as in a conventional bond
- **The extra repulsive strength of the lone pair tweaks the bond angles of the central atom, making them smaller than expected for a pure geometry**







Unit Three Question

The best predicted shape and bond angle of SbH_3 is:

1. Trigonal pyramidal, 109.5
2. Tetrahedral, 109.5
[✓ 3.] Trigonal pyramidal, 107
4. Trigonal planar, 120

Follow-up: What are the IMF’s present in this molecule?

Valence Bond Summary

Hybrids

# of Electron-Dense Regions	Hybridization
2	sp
3	sp^2
4	sp^3
5	sp^3d
6	sp^3d^2

Types of Bonds

Single Bonds: 1 sigma bond

Double Bonds: 1 pi bond and 1 sigma bond

Triple Bonds: 2 pi bonds and 1 sigma bond

Bonding Names Overview

Name bonds by identifying the “overlapping” orbitals:

1. Identify the bond(s) present
2. Identify the hybridization of each bonding atom
3. Name the bond based on the type of bond and overlapping orbitals

Sigma bonds are the **end-on-end (on axis)** overlap between hybrid orbitals (or pure 1s in the case of hydrogen because hydrogen doesn’t hybridize)

- Sigma bonds form on the inter-nuclear axis (one region of overlap)

Pi bonds are the **side-by-side (off axis)** overlap between p orbitals

- Pi bonds form above and below the inter-nuclear axis (two regions of overlap)

$\sigma_{\text{hybrid-hybrid}}$

$\sigma_{\text{hybrid-1s}}$

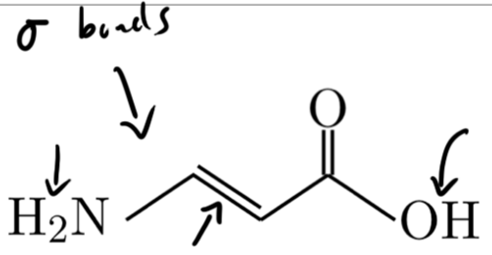
$\pi_{\text{valence p-valence p}}$

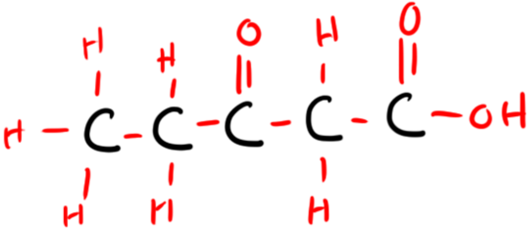
$CH_3CH_2\underbrace{COC}H_2COOH$

Organic Molecules

A few rules go a long way when drawing organic molecules:

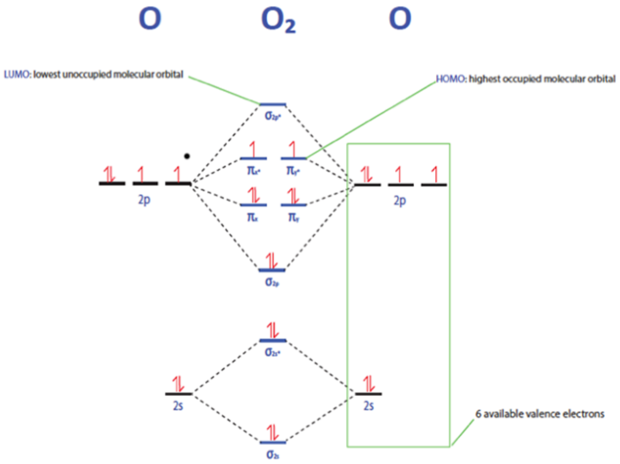
1. Each turn and terminal on a line structure is an implied carbon
2. All neutral carbons make 4 bonds, so you should add hydrogens until each carbon has a filled octet
3. If there is an electronegative atom (such as O, N, F, Cl, etc.), add lone pairs until they have a full octet





MO Theory: The one with the “Diagrams”

- MO Theory is a quantum mechanical model for bonding that merges pure atomic orbitals into molecular orbitals
  - Stability can be described by bond order
    - **BO = bonding electrons – antibonding electrons / 2**
    - Bonding electrons aid in stability
    - Antibonding electrons lead to instability
  - Magnetism can be identified by the presence of paired or unpaired electrons in the highest occupied orbital
    - Diamagnetic: paired electrons, repelled from magnetic field
    - Paramagnetic: unpaired electrons, attracted to magnetic field
  - Identify the HOMO-LUMO gap and what it means



LUMO: lowest unoccupied molecular orbital

HOMO: highest occupied molecular orbital

6 available valence electrons

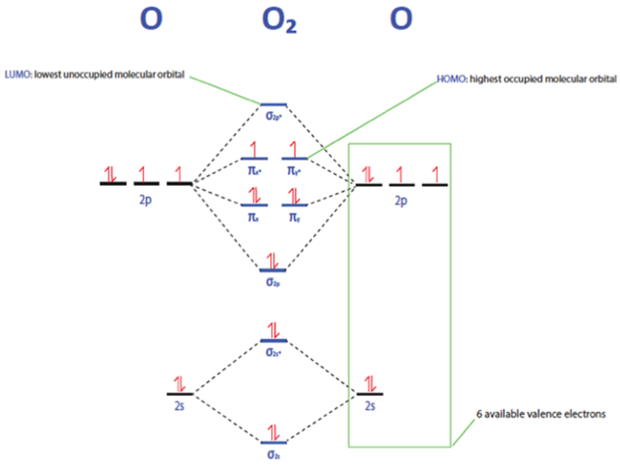
Molecular Orbital Theory: HOMO-LUMO

- One of the most important conclusions in molecular orbital theory is the energy difference between the **Highest Occupied Molecular Orbital (HOMO)** and the **Lowest Unoccupied Molecular Orbital (LUMO)**.
- This energy gap is important because it corresponds to energy of the photon emitted when an excited electron falls back down to ground state. **This can be applied to far more complicated molecules/materials**
- Because light is important here:

Remember:

IR....R.O.Y.G.B.I.V. ...UV

(---increasing energy, decreasing wavelength-->)

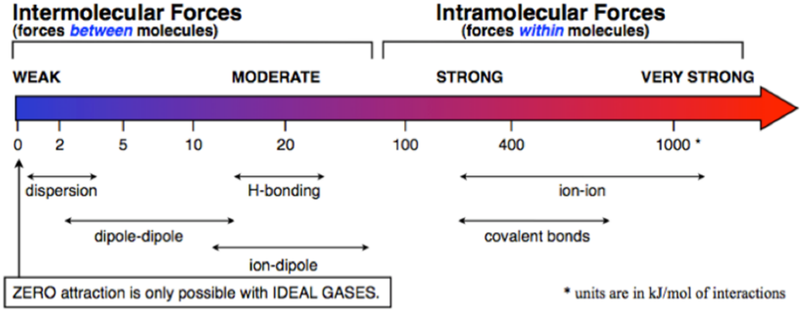


Intermolecular Forces

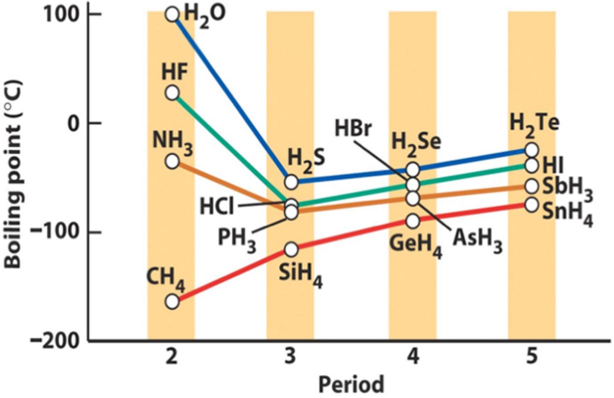
IMF’S, LIQUID AND SOLID PROPERTIES

Intermolecular Forces

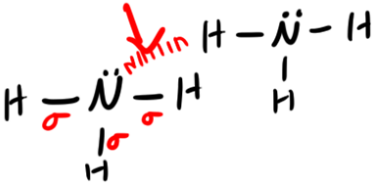
- Intermolecular forces (IMF's) are **electrostatic** interactions between molecules.
  - IMF's vary in strength, but are weaker than **intramolecular** forces (bonds)
  - Intermolecular forces are the electrostatic "glue" that hold molecules in condensed phases
- The three types of IMF's (in decreasing strength) are:
  1. Hydrogen bonding
  2. Dipole-dipole
  3. Dispersion forces
- And they depend on:
  1. Shape
  2. Polarizability (size)
  3. Temperature



IMF Comparisons

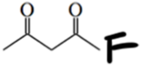


$NH_3(l) \rightarrow NH_3(g)$



Exam Three Question

What types of intermolecular forces are present in a homogenous mixture of the molecule shown below?



1. dispersion forces only

2. dispersion forces, dipole-dipole, hydrogen bonding

3. dispersion forces, dipole-dipole, ion-dipole

4. dispersion forces, hydrogen bonding

[✓ **5.**] dispersion forces, dipole-dipole

6. hydrogen bonding only

For H-bonding:

H–O

H–N

H–F

~~$NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$~~

Liquid Properties Summary

Strong IMF - > High *Viscosity, High BP, High *Surface Tension

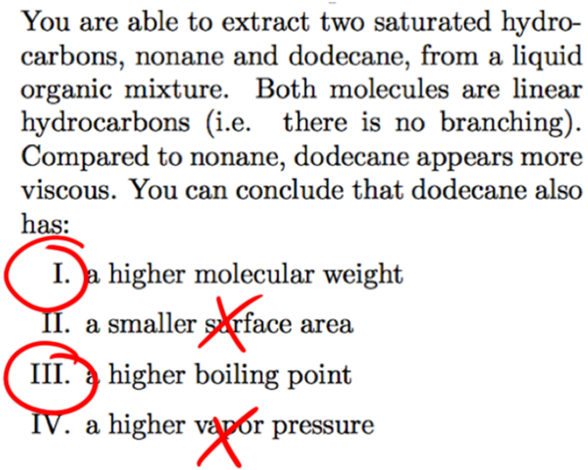
Weak IMF -> High Vapor pressure

High Temperature - > Lowers IMF Strength, Viscosity, and Surface Tension

High Temperature -> Raises Vapor pressure

(no effect on intrinsic properties, like boiling point, melting point, etc.)

Unit Three Question



You are able to extract two saturated hydrocarbons, nonane and dodecane, from a liquid organic mixture. Both molecules are linear hydrocarbons (i.e. there is no branching). Compared to nonane, dodecane appears more viscous. You can conclude that dodecane also has:

[✓ I.] a higher molecular weight
II. a smaller surface area
[✓ III.] a higher boiling point
IV. a higher vapor pressure

In-Depth Explanations

Dispersion forces scale with the size of a molecule, which correlates directly to polarizability

- **The larger the electron cloud, the larger the polarizability**
- **The larger the surface area (overlap), the larger the polarizability**
- When in doubt, a higher molar mass will likely be a higher polarizability, but beware of other forces that could be present!

Lowest Polarizability, Lowest IMF's

Gas: Cl_2

Liquid: Br_2

Solid: I_2

Highest Polarizability, Highest IMF's

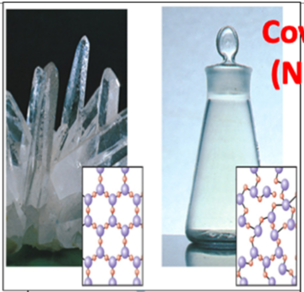
Comparing Solids

Class	**Examples**	**Characteristics**
Ionic	NaCl, KNO_3, $CuSO_4$	Hard, rigid, brittle; high melting/boiling points; those soluble in water give conducting solutions
Covalent Network	B, C, black P, BN, SiO_2	Hard, rigid, brittle; very high melting points; insoluble in water
Metallic	*s*- and *d*-elements	Malleable, ductile, lustrous; electrically and thermally conducting
Molecular	$BeCl_2$, S_8, P_4, I_2, ice, glucose	Relatively low melting/boiling points; brittle if pure

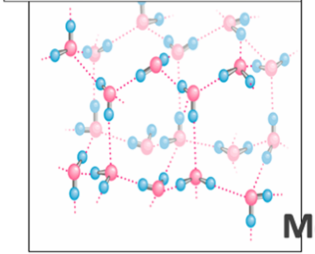
Class	**Electrons**	**Electrical Conductivity**
Ionic	Localized	Not a good conductor (only conducts electricity in aqueous solutions or when molten)
Network	Localized	Not a good conductor
Metallic	Delocalized	Good conductor
Molecular	Localized	Not a good conductor

Molecular vs. Covalent Network Solids

- Molecular and Covalent Network solids are often confused because they can appear very similar on paper (CO_2 is molecular, while SiO_2 is a covalent network)
- Covalent network solids are atoms held together by **intramolecular forces** (covalent bonds in this case), resulting in extremely high (over 1000K) melting points.
- Molecular solids are molecules held together by **intermolecular forces**, resulting in low melting points (usually maxed out around 500-600K).
- **Covalent solids have small molecular weights** (think of diamond, MW = 12.01g/mol). **Molecular solids can be small or very large** (sucrose = 342 g/mol; oxytocin = 1009 g/mol)
- **Both are negligible conductors of electricity**



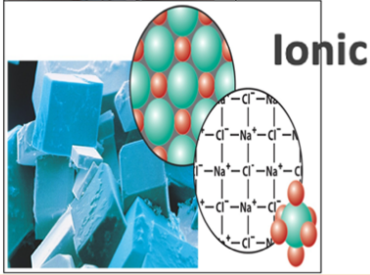
Covalent or (Network)



Molecular

Ionic vs. Metallic Solids

- Ionic and metallic solids have similar melting points (about 1000 K) and both have interactions with electricity.
- **The delocalized electrons of metallic bonds allow metallic solids to conduct electricity**
- **Ionic solids only conduct electricity when liquid or dissolved in water**
- We say that ionic solids are hard and brittle, while metallic solids are malleable and ductile.
  - This is one reason why metallic solids are used for wires and ionic solids are more like grains (think table salt)



Unit 3 Question

Select the option that correctly lists the substances in order of INCREASING boiling points.

1. O_2, NH_3, C_2H_6, C_3H_8, H_2O, CaO, $NaCl$

2. None of these places the substances in correct order of increasing boiling points

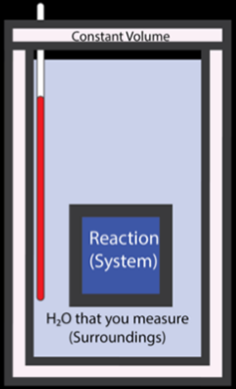
[✓ **3.**] O_2, C_2H_6, C_3H_8, NH_3, H_2O, $NaCl$, CaO

4. O_2, C_3H_8, C_2H_6, NH_3, H_2O, $NaCl$, CaO

5. O_2, NH_3, C_3H_8, C_2H_6, $NaCl$, CaO, H_2O

dispersion → O_2, C_2H_6, C_3H_8 } molecular
H-bond → NH_3, H_2O

$NaCl$, CaO } ionic



Thermodynamics

EXAM 4 TROUBLES, HEADS-UP
PLEASE LOOK OVER YOUR EXAM 4 AND MY EXAM 4 REVIEW FOR COMPREHENSIVE TOPICS

Big Picture Exam Question

Hydrogen spontaneously combusts with oxygen to form liquid water at standard conditions.

$$2C_3H_8O(\ell) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(\ell)$$

What are the signs of:

1. ΔH = (−)
2. w = (+)
3. ΔS_{sys} = (−)
4. ΔS_{surr} = (+)
5. ΔS_{total} = (+)
6. q = (−)
7. ΔG° = (−)

What are the conclusions you can make about…

ΔU vs ΔH? → $\Delta U > \Delta H$ because $w > 0$

ΔS_{surr} vs ΔS_{sys}?

When is this reaction spontaneous / non-spontaneous?

First Law of Thermodynamics

$$\Delta U_{sys} = q + w$$

Work is the energy derived from **organized molecular motion**

w > 0 ; work energy in, work is done on the system (+), compression

w < 0 ; work energy out, work is done by the system (-), expansion

Heat is the energy derived from **random molecular motion** (always travels from high T to low T)

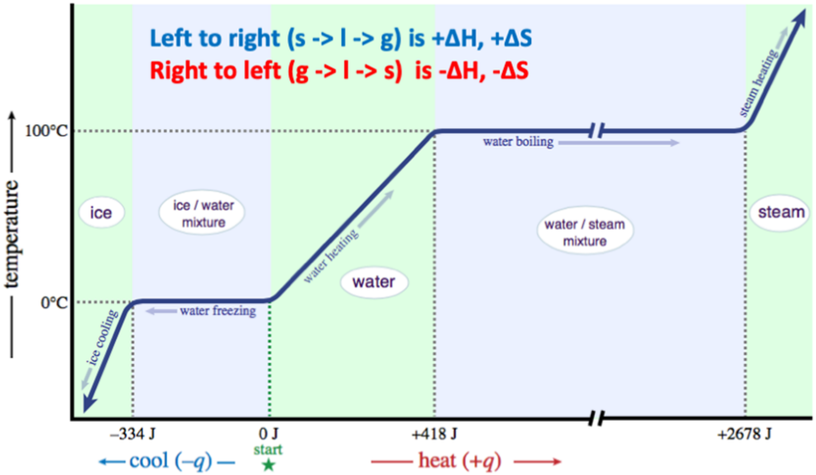
q > 0 ; endothermic (+), heat is absorbed

q < 0 ; exothermic (-), heat is released

At constant pressure…

$$\Delta U_{sys} = \Delta H - \Delta nRT$$

Heat Flow: Heating Curves



Left to right (s -> l -> g) is +ΔH, +ΔS

Right to left (g -> l -> s) is -ΔH, -ΔS

Heat of a Temperature Change

$q = mC_s\Delta T$

Heat of a Phase Change

$q = m\Delta H_{trans}$

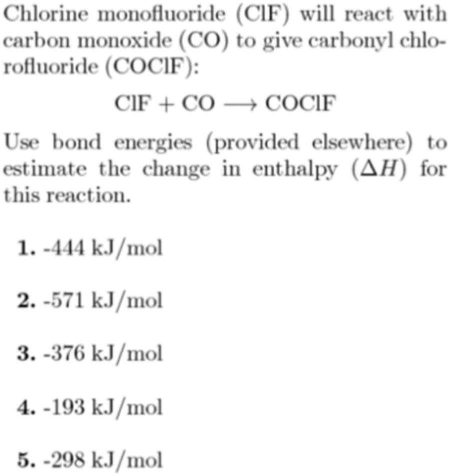
Entropy of a temperature change

$\Delta S = mC_s \ln(T_f/T_i)$

Entropy of a phase change

$\Delta S = m\Delta H_{trans}/T$

Hess' Law: Bonds

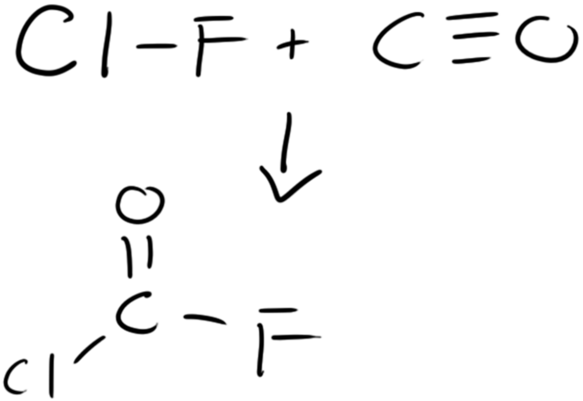


Chlorine monofluoride (ClF) will react with carbon monoxide (CO) to give carbonyl chlorofluoride (COClF):

$$\text{ClF} + \text{CO} \longrightarrow \text{COClF}$$

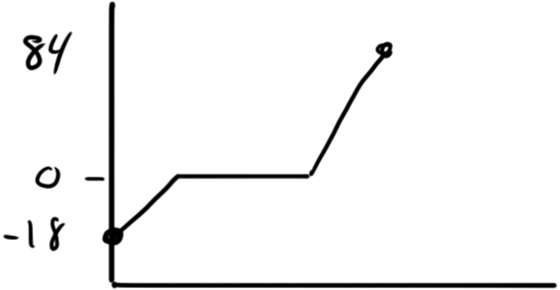
Use bond energies (provided elsewhere) to estimate the change in enthalpy (ΔH) for this reaction.

1. -444 kJ/mol
2. -571 kJ/mol
3. -376 kJ/mol
4. -193 kJ/mol
5. -298 kJ/mol



Exam Four Question + Entropy

On Exam 4, we heated 14 g of ice at -18.0˚C to water at 84˚C, and determined it took 10.1 kJ. Now let's calculate the entropy for this full process of both the system and surroundings. Assume the room is at standard conditions.



1) $\Delta S = mC_{s,ice} \ln\left(\frac{0+273}{-18+273}\right)$

2) $\Delta S = \frac{m\Delta H_{fus}}{T_{melting}}$

3) $\Delta S = mC_{s,H_2O} \ln\left(\frac{84+273}{273}\right)$

$\Delta S_{surr} = \frac{-10.1 \times 10^{-3} J}{298.15 K}$

Spontaneity: Entropy and Free Energy

- **The second law of thermodynamics states that the entropy of the universe is always increasing.**

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

- This law gives us three conditions for **ΔS_{total}**:
  1. $\Delta S < 0$ (negative) ; your reaction is nonspontaneous
  2. $\Delta S = 0$ (zero) ; your reaction is at equilibrium / reversible
  3. $\Delta S > 0$ (positive) ; your reaction is spontaneous

- **The equation for the second law can be rewritten for free energy**

$$\Delta G = \Delta H - T\Delta S$$

- This law gives us three conditions for **ΔG_{rxn}**:
  1. $\Delta G < 0$ (negative) ; your reaction is spontaneous
  2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium
  3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous

Free Energy: Equilibrium Question

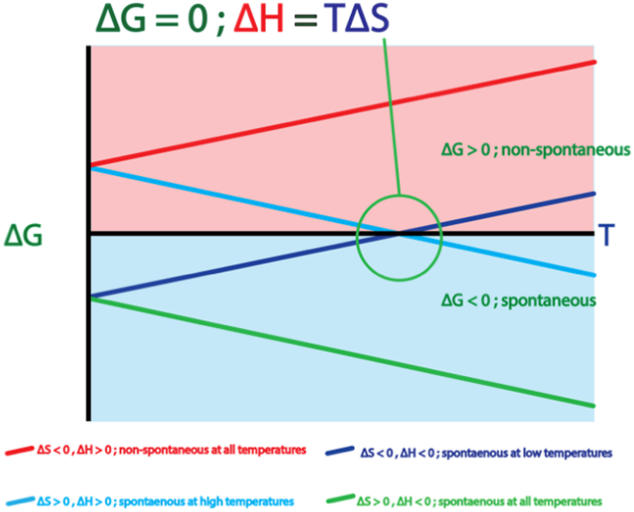
Consider a chemical reaction that is endothermic and has a negative change in entropy. Which of the following is/are true?

[✓ I)] ΔS_{univ} is negative at all temperatures.

II) This reaction will reach equilibrium when $T = \Delta H/\Delta S$.

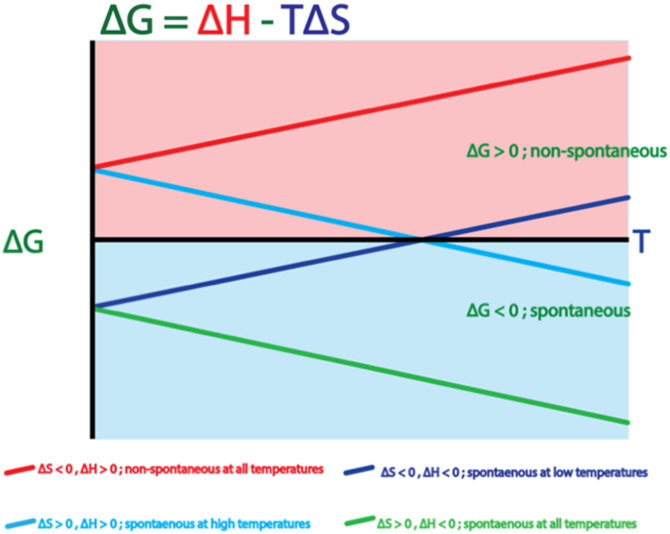
III) The reaction is spontaneous only at relatively high temperatures.

[✓ IV)] ΔG is positive at all temperatures.



Free Energy: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T



Free Energy and Equilibrium Questions

What is the ΔG°_f of Fe_2O_3? $2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$

At what temperature (if any) is this reaction first spontaneous?

300 K & below

What's the *sign* of work for this reaction? (+)

What's the change in internal energy?

$-820.48 \frac{kJ}{mol}$

formula	ΔH_f° kJ/mol	S° J/mol K
Fe_3O_4 (s)	-1118.4	146.4
Fe_2O_3 (s)	-824.2	87.40
O (g)	249.2	161.1
O_2 (g)	0 ✓	205 ✓
Fe (s)	0 ✓	27.28 ✓

$$\Delta G = \Delta H - T\Delta S \longrightarrow \left(87.40 - \left(\tfrac{3}{2}(205) + 2(27.28)\right)\right)$$

$$\uparrow$$

$$\underset{(-)}{-824.2}\ \frac{kJ}{mol} - 298.15K\left(\underset{(-)}{-0.27466}\ \frac{kJ}{mol\,K}\right)$$

$$= -742.35\ \frac{kJ}{mol}$$

$$\Delta G = 0 \quad , \quad 0 = \Delta H - T\Delta S$$

$$T\Delta S = \Delta H \qquad T = \frac{\Delta H}{\Delta S}$$

$$\Delta U = \Delta H - \Delta nRT$$

$$= -824.2\frac{kJ}{mol} - \left(-\frac{3}{2}\ mol\right)\left(.008314\frac{kJ}{mol\,K}\right)(298.15\ K)$$

$$\boxed{3001K} = \frac{-824.2\ \frac{kJ}{mol}}{-0.27466\ \frac{kJ}{mol\,K}}$$