Chemistry 301

FINAL EXAM REVIEW

Final Exam Study Tips

1. Study from the gchem, lecture notes, and review notes
    - Write out the complicated topics in your own words
    - If you study in a group, be the teacher not the student
2. Print the old exams and blank homeworks (white out the correct answers from the midterms)
    - Thoroughly review the questions you got wrong and why you missed them
3. Print the coversheet and write all the units associated with the terms on the equations
    - Identify any important equations that aren't provided on the coversheet that you might use
4. Take your time on the exam and read all the answer choices fully
    - Sometimes you can jog your memory or get closer to the last step of a problem if you review the answer choices before giving up on a tough question

Overview of the Exam

- 50 Multiple Choice Questions
- Five Units:
  1. Fundamentals
  2. Gas Laws (ideal, non-ideal, kinetic molecular theory)
  3. Atomic Theory (light, quantum mechanics, periodic trends)
  4. Bonding and IMF’s (Lewis Structures, VSEPR, VB, MO, IMF’s)
  5. Thermodynamics

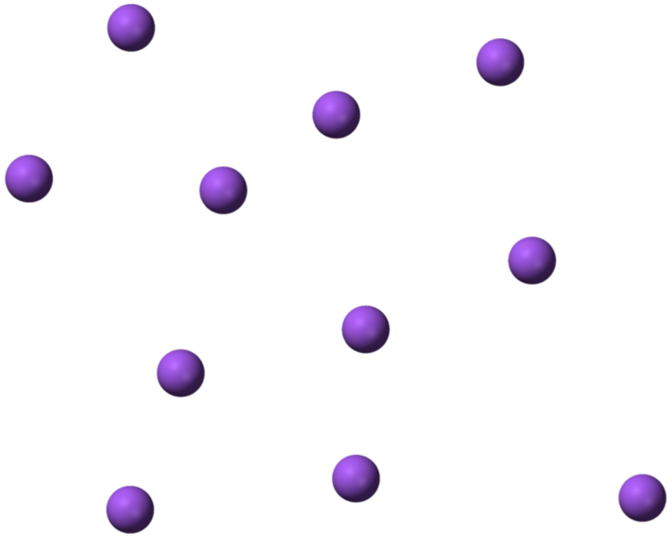
- **37 Conceptual questions, 13 calculations**

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, moles will look different (condensed phases vs. gas phase)
- Limiting reagent: the reactant that **runs out first**, thereby forcing the reaction to stop
- Excess: 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

Chemistry Fundamentals: Stoichiometry

- Given the following generic, balanced chemical reaction:

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

- **Simple ratio problems:** how many moles of B are required to make 7 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 10L of A are reacted with 10L 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**

Exam One Question

Calculate the mass of NH_3 that can be produced from 30.0g of N_2 and 5.0g H_2 in the following reaction:

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

1. 42.5 g
2. 18.2 g
3. 36.4 g
4. 28.3 g
5. 63.8 g

$1 \frac{mol}{rxn}$

rxn = **reaction**

$$\overset{36g}{1\,N_2} + \overset{5g}{3H_2} \longrightarrow 2NH_3$$

1) g → **moles**

Pressure, moles, V (gase)

$$30g\ N_2 \left(\frac{mol}{28g}\right) = \underline{1.07\text{ moles}}$$

$$5g\ H_2 \left(\frac{mol}{2g}\right) = \underline{2.5\text{ moles}}$$

2) # of reactions?

excess

$$1.07\text{ moles}\ \boxed{N_2} \left(\frac{rxn}{1mol}\right) = 1.07\ rxn$$

$$2.5\text{ mol}\ H_2 \left(\frac{rxn}{3mol}\right) \boxed{= 0.833\ rxn}$$

LR

3)

$$0.833\ rxns \left(\frac{2\text{ moles } NH_3}{rxn}\right)$$

$$= 1.67\text{ moles } NH_3$$

$\times 17\,g = 28.3g$

Exam 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 at 2.00 atm and 293K?

$$C_2H_4(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g)$$

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

$$\overset{6.0L}{C_2H_{4\,(g)}} + \overset{6.0L}{3O_{2\,(g)}} \rightarrow \overset{V=0L}{2H_2O_{(l)}} + 2CO_{2\,(g)}$$

$$6.0L\ C_2H_4 \times \frac{rxn}{1L} = \boxed{6\,rxn}\ \text{excess}$$

$$6.0L\ O_2 \times \frac{rxn}{3L} = \boxed{2\,rxn}\ LR$$

Produced

$$2\,rxn \times \frac{2L\ CO_2}{rxn} = 4L\ CO_2$$

Excess

$$\underset{\text{Initial amount}}{6L} - \underset{\text{amount consumed}}{\left(2\,rxn \times \frac{1L}{rxn}\right)} = \underset{\text{excess}}{4L\ C_2H_4}$$

$$\text{total } V = 4L\ CO_2 + 4L\ C_2H_4$$
$$= 8L$$

Gas Laws

IDEAL, MIXTURES, KMT, NON-IDEAL

The Ideal Gas Law

- This exam will test both your ability to **“plug-and-chug”** with the ideal gas law and your ability to apply the law to **conceptual** questions
- The relationship between these state functions is presented in the following equation:

$$PV = nRT$$

- Key points:
  - State functions on the same side have an **inverse** relationship
  - State functions on opposite sides have a **direct** relationship
  - R is a **constant**, not a state function
  - Temperature is always in Kelvin
    - Why? Kelvin can only be expressed as a value 0 or greater. If you used Celsius, you would get negative volumes, pressures, and numbers of moles at certain temperatures

Exam One Question

A chemist prepares a sample of helium gas at a certain pressure, temperature, and volume. She then removes all but a fourth of the gas molecules (only a fourth remain). How must the temperature be changed to keep the pressure and the volume the same?

1. $T_2 = 4T_1$
2. $T_2 = 0.25T_1$
3. $T_2 = .5T_1$
4. $T_2 = 2T_1$
5. $T_2 = 16T_1$

$$P_1V_1 = n_1RT_{\underline{\underline{\underline{1}}}}$$

$$\downarrow$$

$$P_1V_1 = \frac{1}{4}n_1R\,\underline{\underline{\underline{4}}}\,T_1 = n_1RT_1$$

cancel

$$\frac{1}{4}n_1 = n_2$$

$$4T_1 = T_2$$

$$mw\left(\frac{PV}{V}\right)=\left(\frac{nRT}{V}\right)mw$$

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

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

→ mass density

Partial Pressure

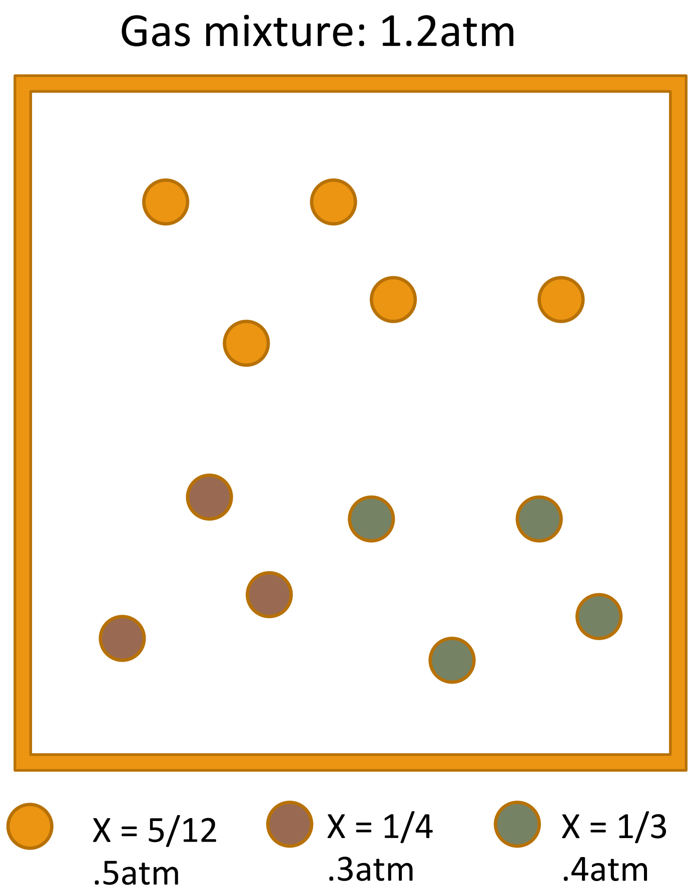
- Partial pressure is a method for quantifying the pressures exerted by individual species in a gas mixture.

$$x_A = \frac{P_A}{P_{total}}$$

- Three terms are necessary for understanding partial pressures:

1. Total pressure (P or 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

$$P_A = x_A P_{total}$$



$$\chi_A = \frac{P_A}{P_{total}}$$

→ mole fraction

% by pressure, volume or moles

→ NOT % by mass

↓

convert to moles

Standard Conditions (Memorize)

- STP is the default standard for gases
  - 0 degrees Celsius, 1atm (or 760 torr)
  - 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

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

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)

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**

KMT: Mass vs. Velocity; Velocity vs. Temperature

Based on the equation:

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

R = 8.314 J/mol K

Molecular Weight in Kg / mol

Note: these ratio derivations of the KMT formula are not provided

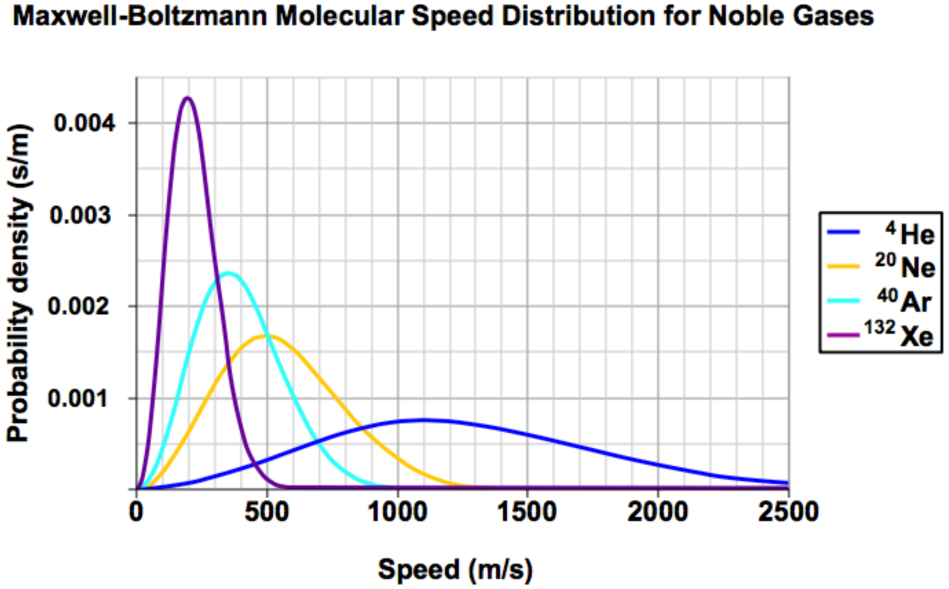
$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$$

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

We can determine that velocity is proportional to the **square root of temperature** and the **inverse square root** of mass.

1. **Mass vs. Velocity (V_{rms})**
   - Velocity is proportional to the inverse square root of mass.
   - When temperature is constant, lighter particles move faster
2. **Velocity (V_{rms}) vs. Temperature**
   - Velocity is proportional to the square of temperature
   - When dealing with the same species gas, particles move faster at higher temperatures

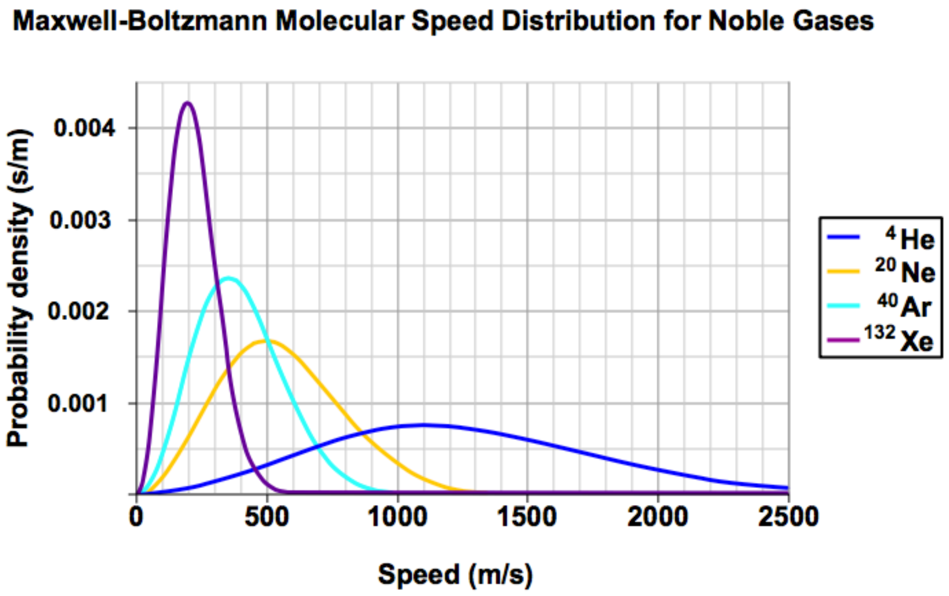
KMT: Mass vs. Velocity; Velocity vs. Temperature



- 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.

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:

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

- Key points:
  - Attractive forces decrease the pressure. **Stronger attractive forces give a larger “a” value**.
    - Think higher IMF’s ; especially higher dispersion forces/polarizability for gases
  - 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
  - More concisely, gases are modeled best **at high temperatures and low pressures**.
    - Attractions increase at lower temperatures (think of water at low temperatures vs. high temperatures)
    - Repulsions increase at high pressures

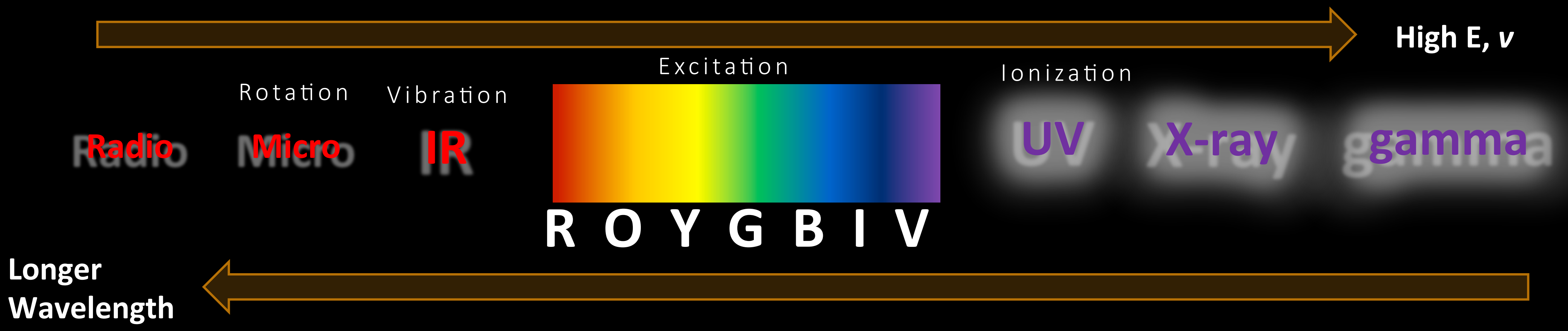
Favoring Non-Ideal Vs. Ideal Conditions

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

Atomic Theory

LIGHT, QUANTUM, ELECTRON CONFIGURATIONS, PERIODIC TRENDS

THE ELECTROMAGNETIC SPECTRUM



High E, *v*

Excitation

Ionization

Rotation

Vibration

Radio

Micro

IR

UV

X-ray

gamma

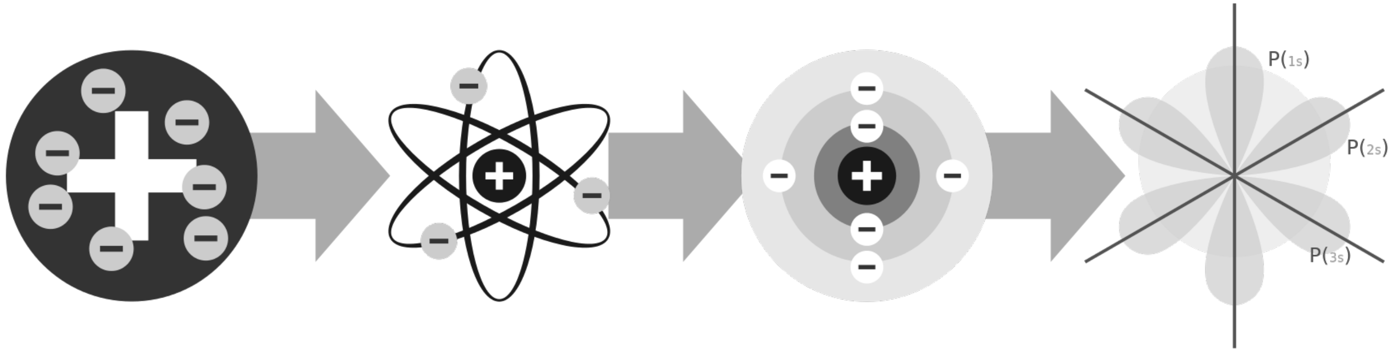
R O Y G B I V

Longer Wavelength

- Understand the relative energies, wavelengths, and frequencies of characteristic radiation types AND what this means for their interaction with matter.
- Microwaves: enough energy to begin rotating a molecule
- IR: enough energy to begin vibrating a molecule
- Visible (400-700nm): enough energy to begin exciting electrons
- UV and beyond: begins the full ionization (breaking) of electrons/bonds

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:
  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 function, uncertainty principle)
     - Furthermore, this demonstrates that electrons exist in "clouds" and not circular orbits



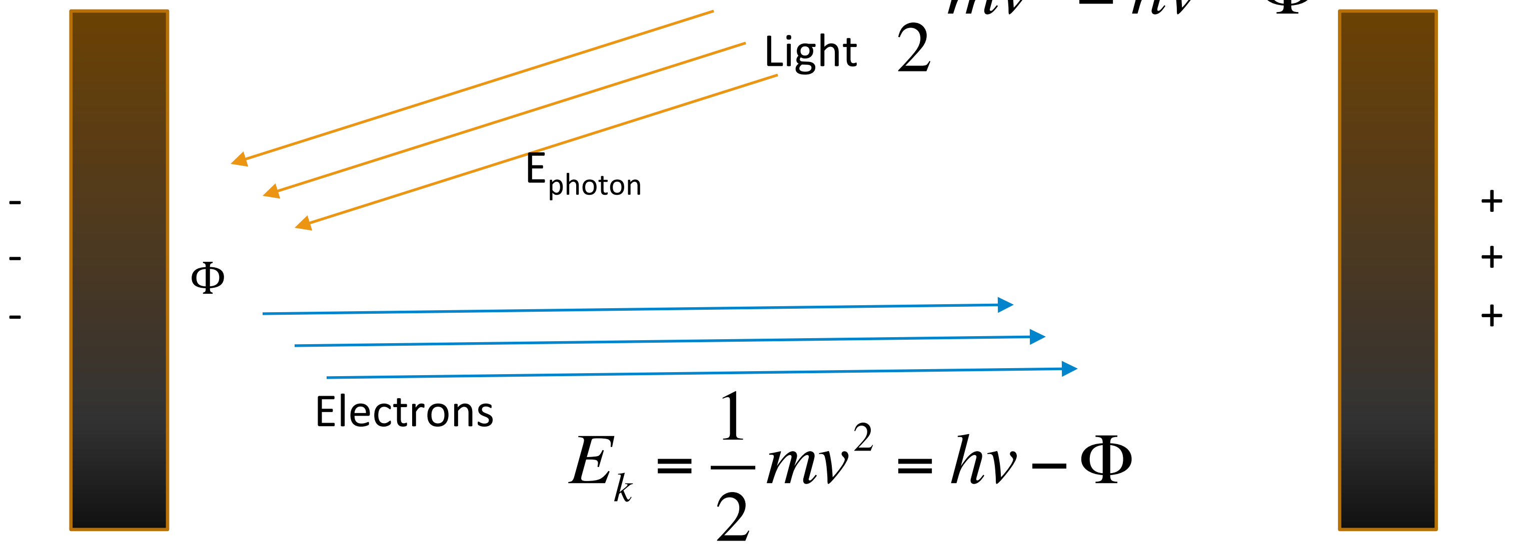
Classical Theory

Quantum Theory

Quantum Mechanics: Photoelectric Effect

- The postulates of quantum mechanics were demonstrated by a series of important experiments between 1885-1930’s.
- **Photoelectric Effect**: a metal will eject electrons if a beam of light reaches a threshold energy
  - Proves that matter (the electrons of a metal) can interact with light ; wave particle duality

$$\frac{1}{2}mv^2 = hv - \Phi$$



$$E_k = \frac{1}{2}mv^2 = hv - \Phi$$

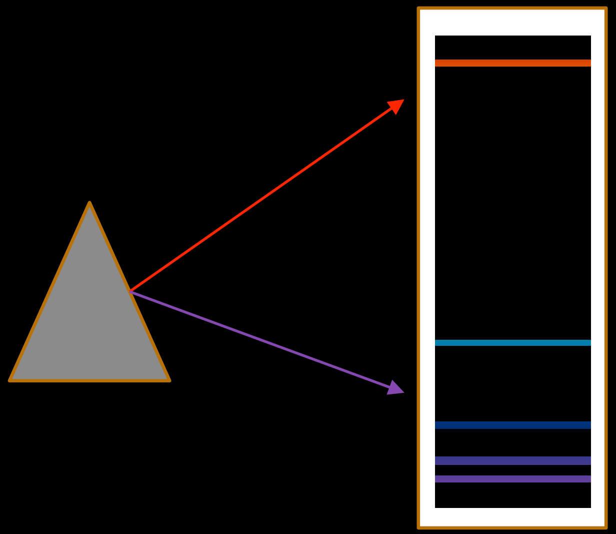
Key points:

- If an electron is not ejected, your light does not have sufficient energy (you must decrease wavelength / increase frequency)
- Increasing the intensity will result in more electrons ejected if the threshold is reached. If the threshold is not reached, increasing the intensity will do nothing

$$v = R(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

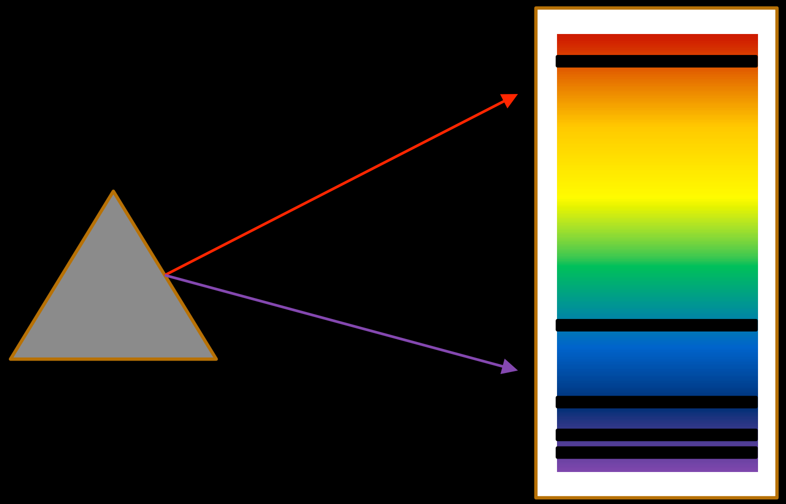
EMISSION:

- HIGH N TO LOW N



ABSORPTION

- LOW N TO HIGH N

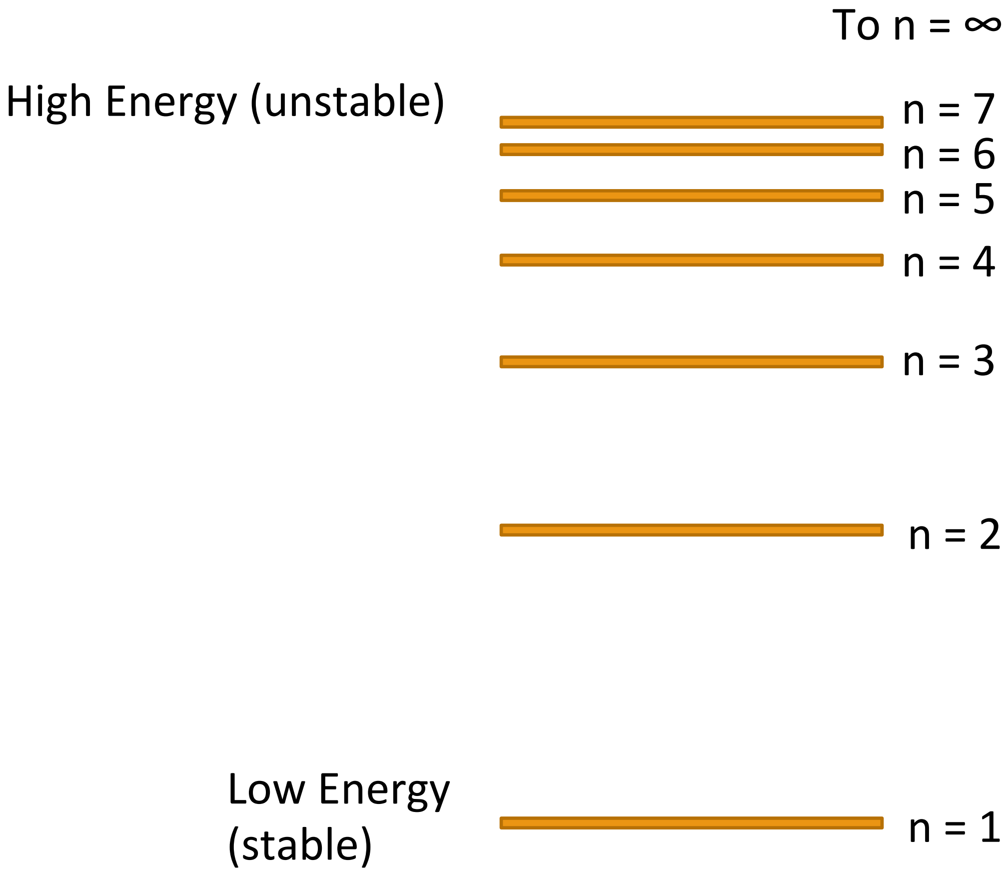


- The absorption and emission lines were an early experimental indicator that electrons emit characteristic frequencies
- Emission lines show a few colored lines on a black background.
- Absorptions lines show a few black lines on a rainbow background.
- The absorption and emission spectrums of a given element are the exact opposites
- Notice that you are given the Rydberg equation in terms of frequency (s^{-1}). Use the appropriate R-value.

Rydberg Energy Levels

- You can understand Rydberg n-values by adhering to the following rules:
  1. n values begin at 1 (closest to the nucleus) and go to infinity (completely out of the influence of the nucleus/ free in space)
  2. The potential energy of a given energy state is proportional to the inverse square of the whole number integer n
  3. The greatest energy difference between two consecutive numbers is 1 and 2.

$$v = R(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$



To n = ∞

High Energy (unstable)

n = 7

n = 6

n = 5

n = 4

n = 3

n = 2

Low Energy (stable)

n = 1

Exam Two Question

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

1. 2 to 3
2. 3 to 5
3. 5 to 6
4. 3 to 4
5. 2 to 5
6. 2 to 4

Exam Two Question

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

1. 2 to 3
2. 3 to 5
3. 5 to 6
4. 3 to 4
5. 2 to 5
6. 2 to 4

Exam Two Question

What is the wavelength of the photon corresponding to the change from n = 2 to n = 5? Is this photon emitted or absorbed?

1. 434nm absorbed
2. 434nm emitted
3. 276nm absorbed
4. 276nm emitted
5. 1875nm emitted

absorbed

$$\underline{\underline{\nu}} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$3.29\times10^{15}\left(\frac{1}{4} - \frac{1}{25}\right)$$

$$\nu = \underline{6.909\times10^{14}\,s^{-1}}$$

$$\underline{E=h}\nu \quad , \quad \underline{c=\lambda\nu}$$

$$\frac{c}{\nu} = \lambda = \frac{3\times10^{8}}{6.909\times10^{14}}$$

$$= 4.34\times10^{-7}\,m \xrightarrow{\times10^{9}} \boxed{\underline{434\,nm}}$$

Quantum Numbers

- The Schrödinger Wave Function gives us insight to the energy of an electron and the probability in finding that electron in a given range of three dimensional space.
- The Quantum Numbers (n, l, m_l, and m_s) stem from the solutions of the wave function 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
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

Quantum Numbers

- 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, …n

Angular Momentum (l) = 0,1,2,… to n-1

Magnetic (m_l) = -l to l

Spin Magnetic (m_s) = $\pm 1/2$

Example:

If n = 4

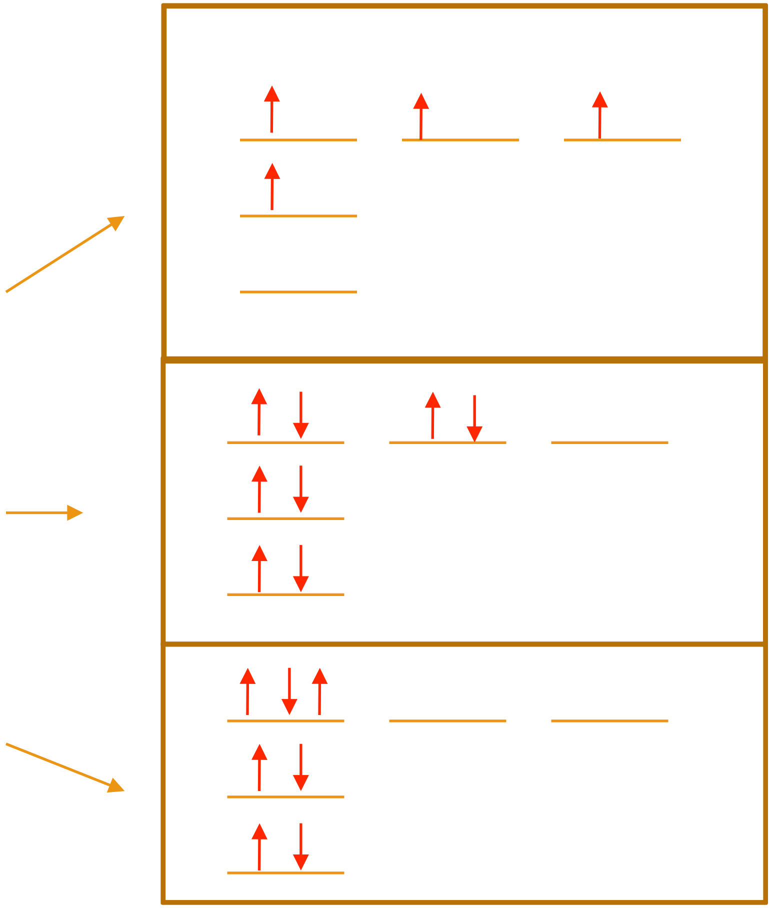
l can equal 0,1,2,3

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

m_s = +/- 1/2

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's rule:** 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 : $[He]2s^22p^4$

O^{2-} : $[He]2s^22p^6$ or $[Ne]$

- Difficult: Zr^{2+} (from exam 2)

Zr : $[Kr]5s^24d^2$

Zr^{2+} : $[Kr]4d^2$

Electron Configurations: Exceptions

- D-block and f-block elements prioritize filling their half-way or fully filled subshells if they are one electron away.
- The most common examples of this are chromium and copper. You would expect to write chromium with 4 electrons in 3d and copper with 9 electrons in 3d. Instead, you borrow one electron from the 4s to fill the subshell.

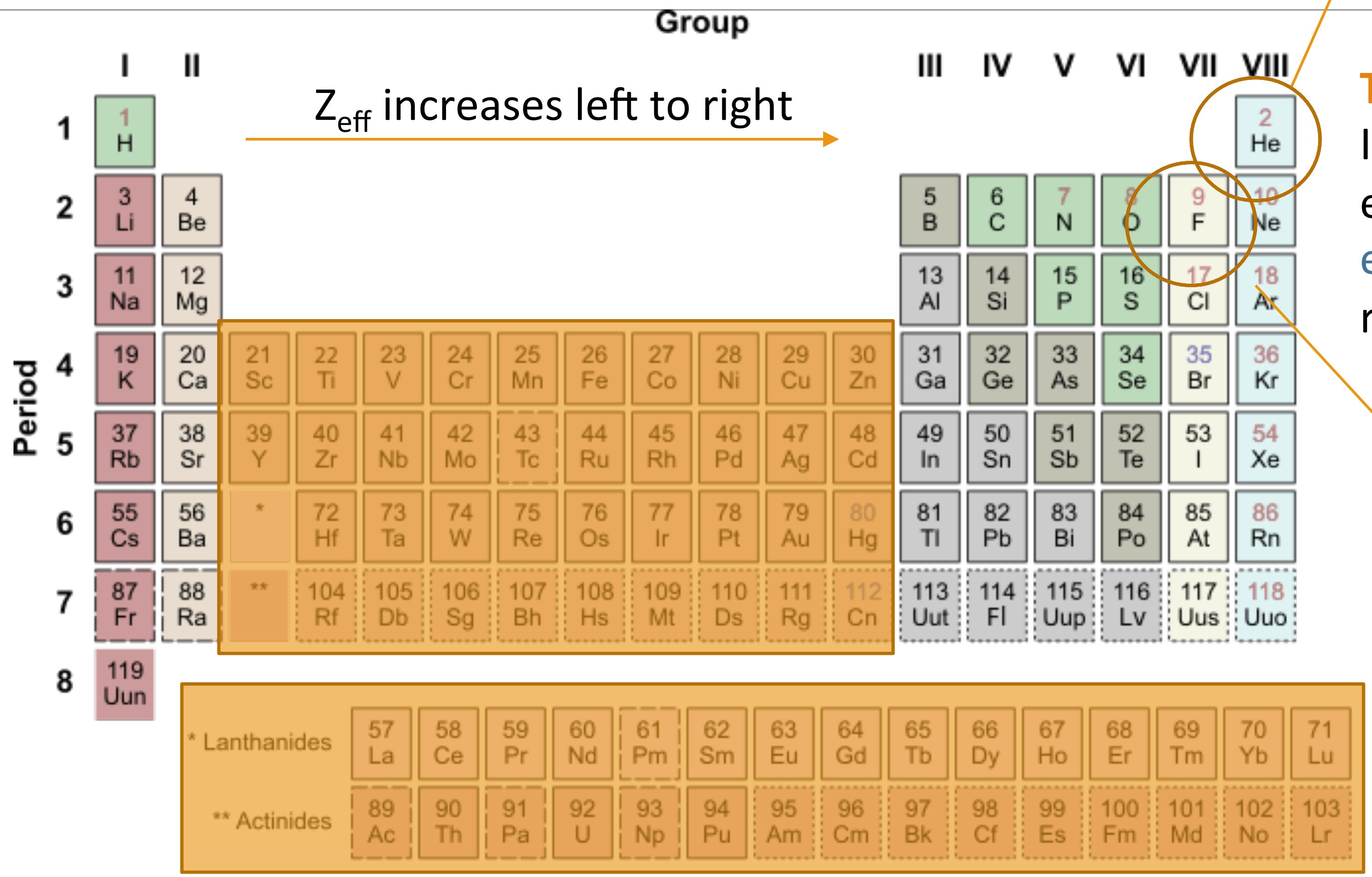
- The electron configurations are therefore:
- Cr = $[\text{Ar}]4s^1 3d^5$
- Cu = $[\text{Ar}]4s^1 3d^{10}$

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 the outer electrons by the nucleus**
  - Trend: increases as you go to the top right
  - Remember: Z_{eff} = Atomic Number – Core Electrons

Periodic Trends Visualized

Shielding Increases going down



Group

Period	I	II											III	IV	V	VI	VII	VIII
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
8	119 Uun																	

* Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Z_{eff} increases left to right

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

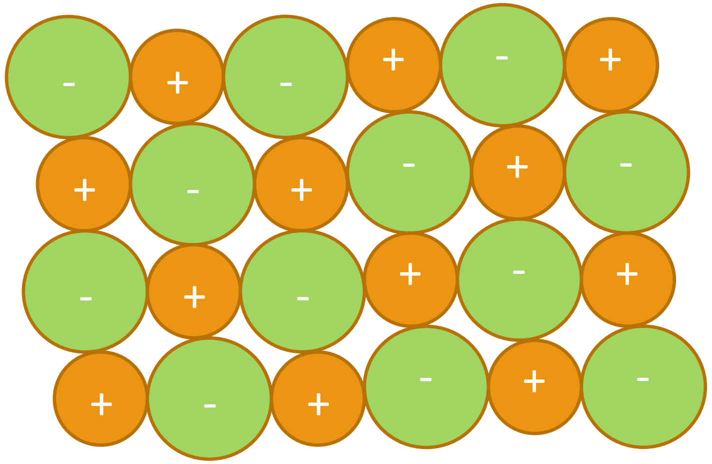
Helium has the maximum ionization energy

Fluorine has the maximum electron affinity and electronegativity

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

Visualizing Lattice Energy

$$E_{lattice} \propto \frac{q_1 q_2}{r}$$

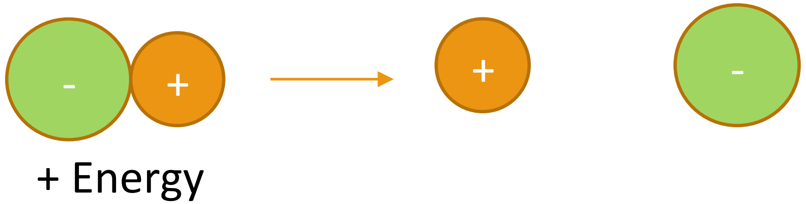


Lattice energies are big when:

1. Charges are high
2. The ions making up the lattice are small

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**

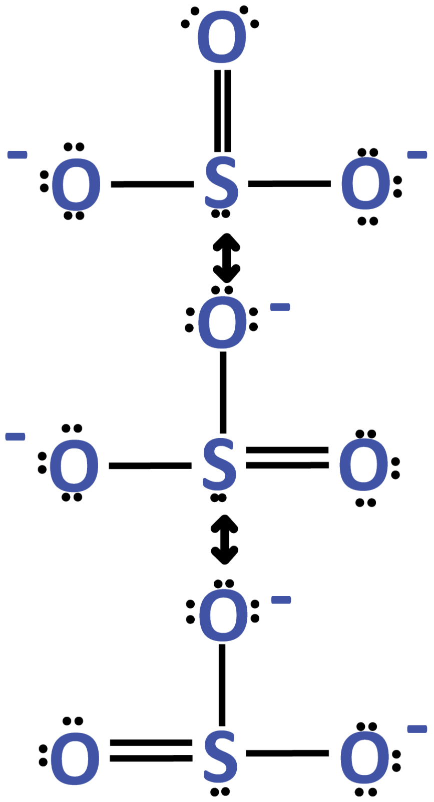


Bonding

LEWIS STRUCTURES, VSEPR, VB, MO, IMF'S

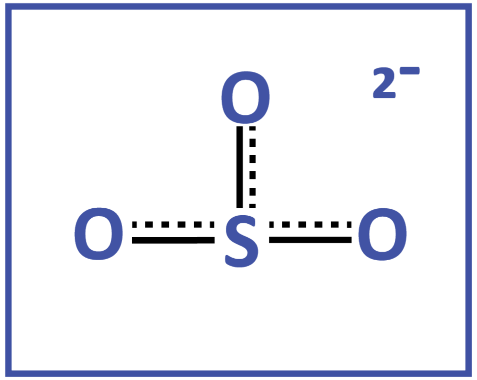
Bonding and Lewis Structures

- 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



General Formal Charge Rules

- Formal charge defines the distribution of charge throughout a molecule. More specifically, it is used to show the charge on each atom in a molecule.
- The formal charge of a molecule is the sum of the individual formal charges of the atoms in the molecule. Formal charges should be minimized in your Lewis Structures.

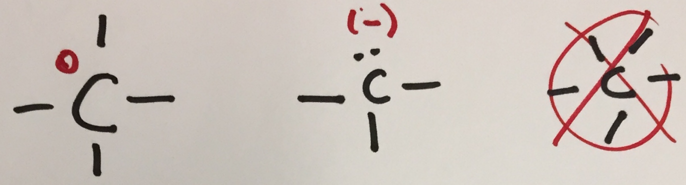
Element	-1 Charge	Neutral	+1 Charge
Carbon	3 bonds*	4 bonds	5 bonds*
Nitrogen	2 bonds	3 bonds	4 bonds
Oxygen	1 bond	2 bonds	3 bonds

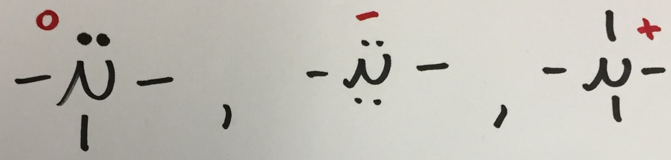
* In this class carbon is nearly always neutral (4 bonds). The main exception to this is Carbon monoxide.

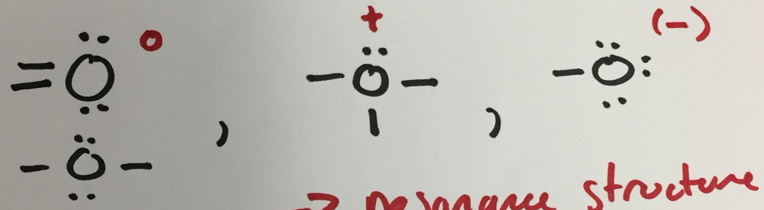
Exam Three Question

Which of the following compounds would be expected to have the longest N-O bonds? (hint: this question is really just asking which resonance structure has the lowest bond order because long bonds = weak bonds)

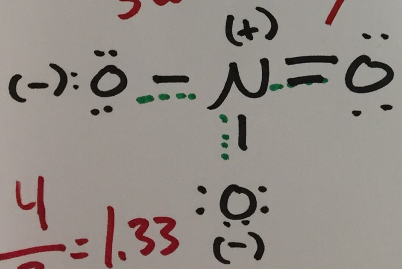
1. NO_3^{-1}
2. NO
3. NO_2^-





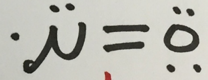


3 ways

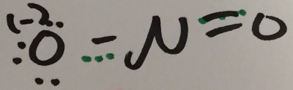


$\frac{4}{3} = 1.33$ bond order

resonance structure is a bonding extreme that is depicted better by the perfect average



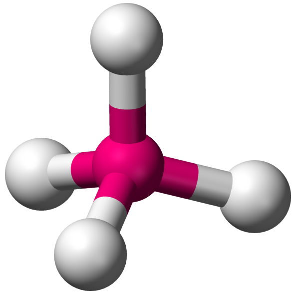
2 bond order



$\frac{3}{2} = 1.5$ bond order

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

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.

- **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

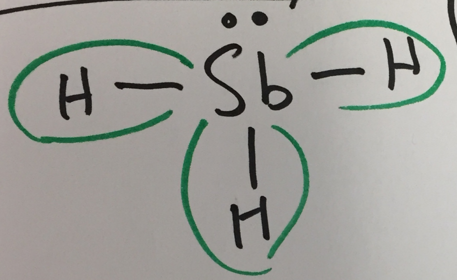
Exam Three Question

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

SbH_3

$\rightarrow sp^3$



electronic:
4 e^-, tetrahedral

Shape:
trigonal pyramid

Bond angles

→ Pure: 109.5°
Actual: 107°

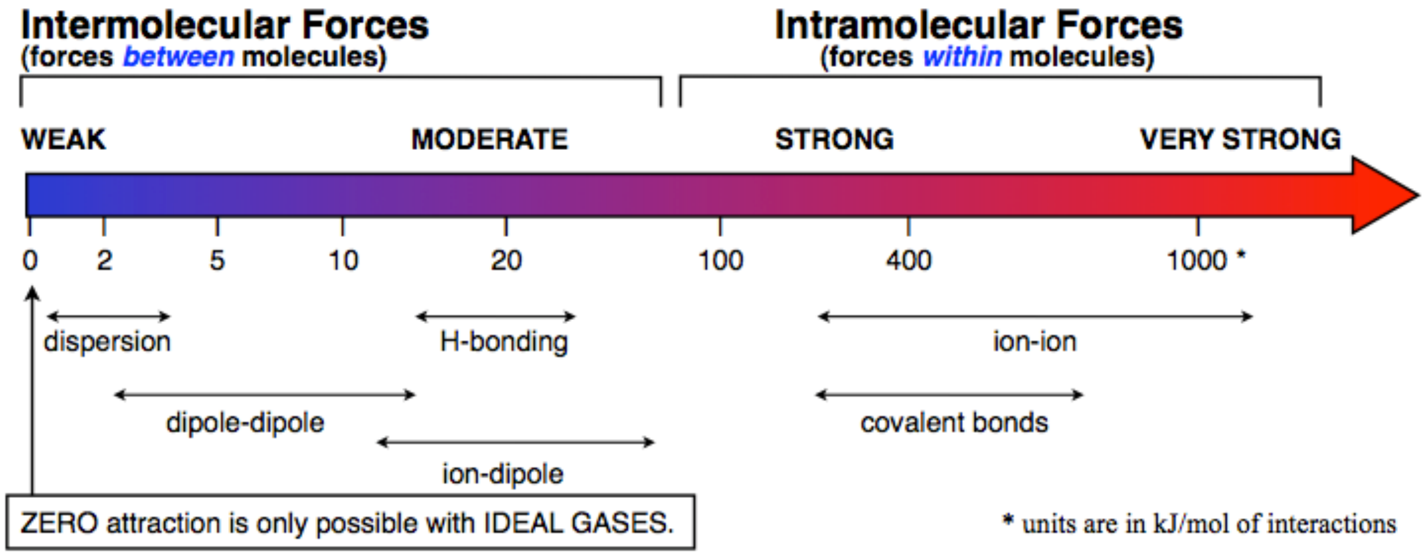
Intermolecular Forces

- 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



Liquid Properties Summary

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

Weak IMF -> High Vapor pressure

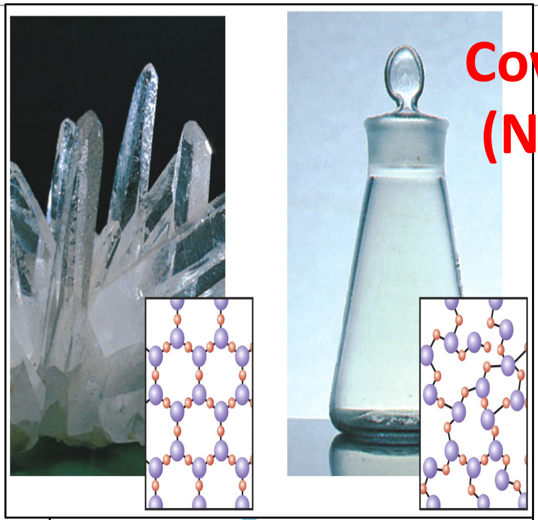
High Temperature - > Lowers IMF Strength, Viscosity, and Surface Tension

High Temperature -> Raises Vapor pressure

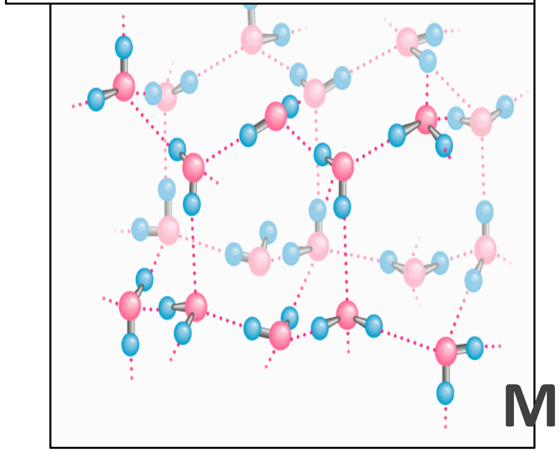
(no effect on intrinsic properties, like boiling point, melting point, etc.)

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 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 600K, but more often between 200-300K).
- **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 (exception: graphene contains delocalized p_z orbitals, resulting in delocalization)**



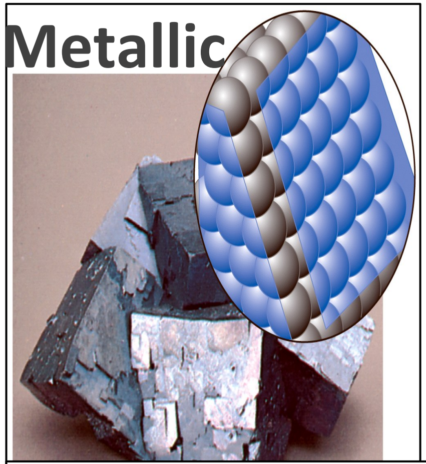
Covalent or (Network)

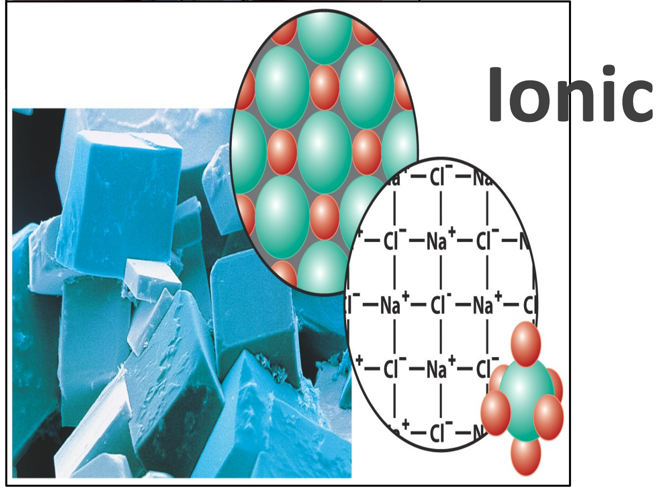


Molecular

Ionic vs. Metallic Solids

- Ionic and metallic solids have similar melting points (about 1000K) 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 the reason why metallic solids are used for wires and ionic solids are more like grains (think table salt)





Comparing Solids

Class	**Examples**	**Characteristics**
Ionic	NaCl, KNO_3, $CuSO_4 \bullet H_2O$	Hard, rigid, brittle; high melting/ boiling points; those soluble in water give conducting solutions
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

Comparing Solids

Class	**Electrons**	**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

Thermodynamics

EXAM 4 TROUBLES

Exam Four Question

Consider a system where 2.50 L of ideal gas expands to 6.25 L against a constant external pressure of 330 torr. Calculate work (w) for this system.

1. +165 J
2. -165 J
3. +1238 J
4. -1238 J
5. -1.63J
6. +1.63 J

$2.5\,L \rightarrow 6.25\,L$

expanding $(w = (-))$

$$w = -P\Delta V$$

↑

$$-\left(\frac{330\ \text{torr}}{760\ \frac{\text{atm}}{\text{torr}}}\right)(3.75\,L)$$

$$= -1.63\ L\,\text{atm} \neq J$$

$$\times\ 101.35\ \frac{J}{L\,\text{atm}}$$

$$\boxed{= -165\ J}$$

65% got right

Exam Four Question

2.26 g or liquid water at 23.5 °C was completely converted to ice at 0 °C. How much heat was (absorbed/released) by the system during this process?

1. 755 ; released
2. 1478 ; released
3. 977 ; absorbed
4. 977 ; released

2 events

cooling

$$q = mC\Delta T \; \Big] \longrightarrow \Delta S = m\underbrace{C}_{\frac{J}{gK}}\ln\left(\underbrace{\frac{T_f}{T_i}}_{K}\right)$$

$$2.26\,g\left(4.184\,\frac{J}{g\,^\circ C}\right)\left(-23.5\,^\circ C\right)$$

$$\boxed{= -222.2\,J}$$

phase change

$$q = m\Delta H_{freezing} \; \Big] \longrightarrow \Delta S = \frac{m\Delta H}{\underbrace{T_{freezing}}_{K}}$$

$$\Delta H_{freezing} = -\Delta H_{fus}$$

$$\left(-334\,\frac{J}{g}\right)\left(2.26\,g\right)$$

$$\boxed{= -755\,J}$$

released $\longrightarrow$ $\boxed{-977\,J}$

Exam Four Question

What is the change in entropy for the heating of 20.0 g of methanol liquid from 34 °C to 62 °C?

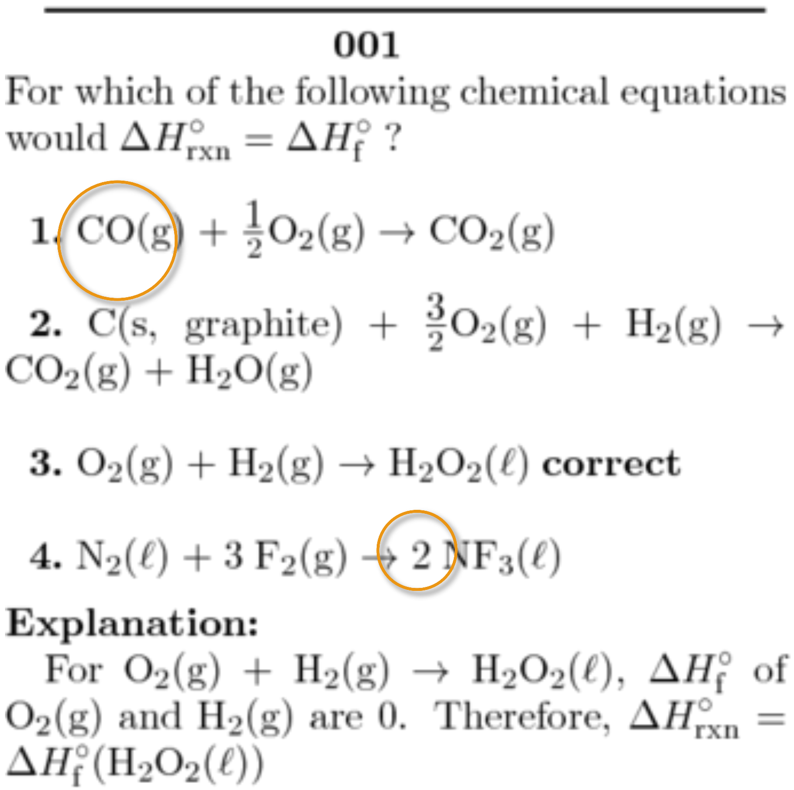
1. 30.42 J / K
2. 168.81 J / K
3. 0 J / K
4. 4.42 J / K
5. 0.22 J / K

$$\Delta S = m C_s \ln\left(\frac{T_f}{T_i}\right)$$

$$\Delta S = 20.0\,g\left(2.53\,\frac{J}{\underbrace{g\,{}^\circ C}_{K}}\right)\ln\left(\frac{62+273}{34+273}\right)$$

$$\boxed{\Delta S = 4.42\ \frac{J}{K}}$$

Formation Reactions



001

For which of the following chemical equations would $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{f}}$?

1. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

2. $C(s,\ \text{graphite}) + \frac{3}{2}O_2(g) + H_2(g) \rightarrow CO_2(g) + H_2O(g)$

3. $O_2(g) + H_2(g) \rightarrow H_2O_2(\ell)$ **correct**

4. $N_2(\ell) + 3\ F_2(g) \rightarrow 2\ NF_3(\ell)$

Explanation:

For $O_2(g) + H_2(g) \rightarrow H_2O_2(\ell)$, $\Delta H^\circ_{\text{f}}$ of $O_2(g)$ and $H_2(g)$ are 0. Therefore, $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{f}}(H_2O_2(\ell))$

This question is asking: which of the following is a formation reaction.

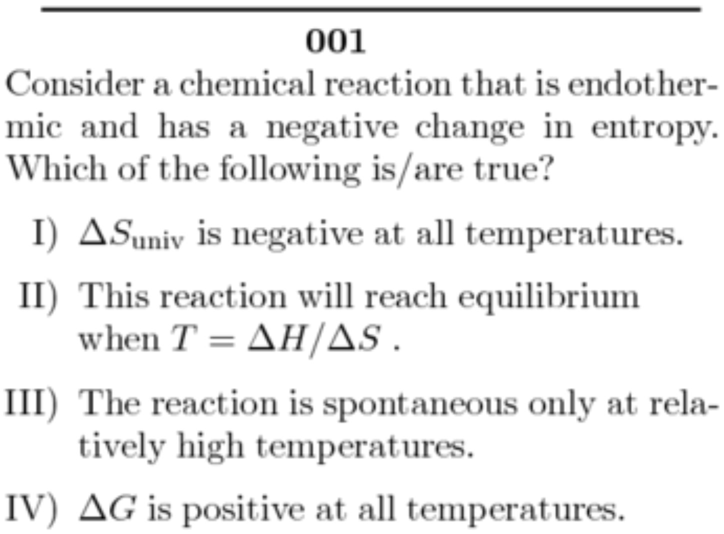
Students miss these types of questions because they forget what constitutes a formation reaction:

- The reactants are elements and must be in their standard state
- There should only be 1 product
- There should only be 1 mole of that 1 product
- Fractional coefficients of reactants are OK
- The value for the enthalpy of formation for elements (including diatomics) in their standard state is zero.
  - This is also true for free energy but NOT for absolute entropy

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$$C_{(graphite)} + \frac{1}{2}O_{2(g)} + H_{2(g)} \rightarrow C_2H_5OH_{(l)}$$

Free Energy: Equilibrium Question



001

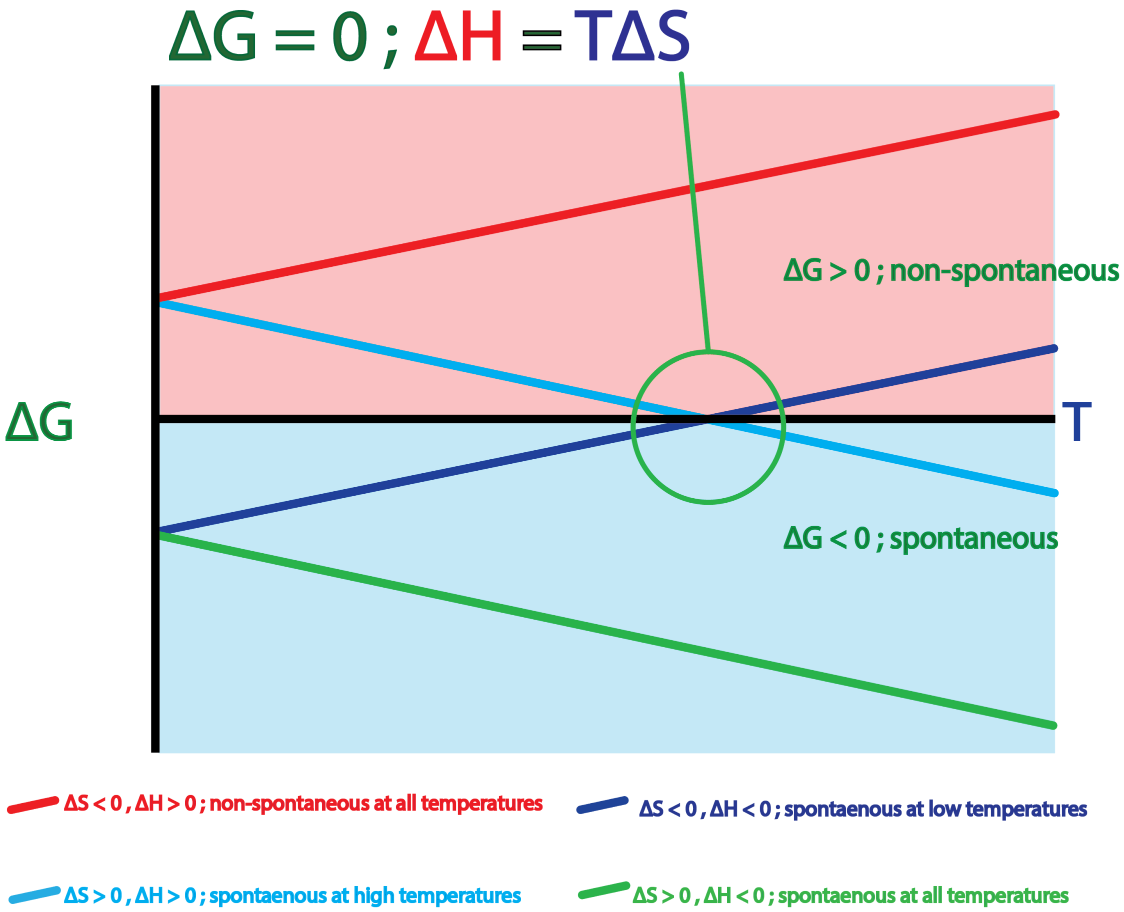
Consider a chemical reaction that is endothermic and has a negative change in entropy. Which of the following is/are true?

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

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

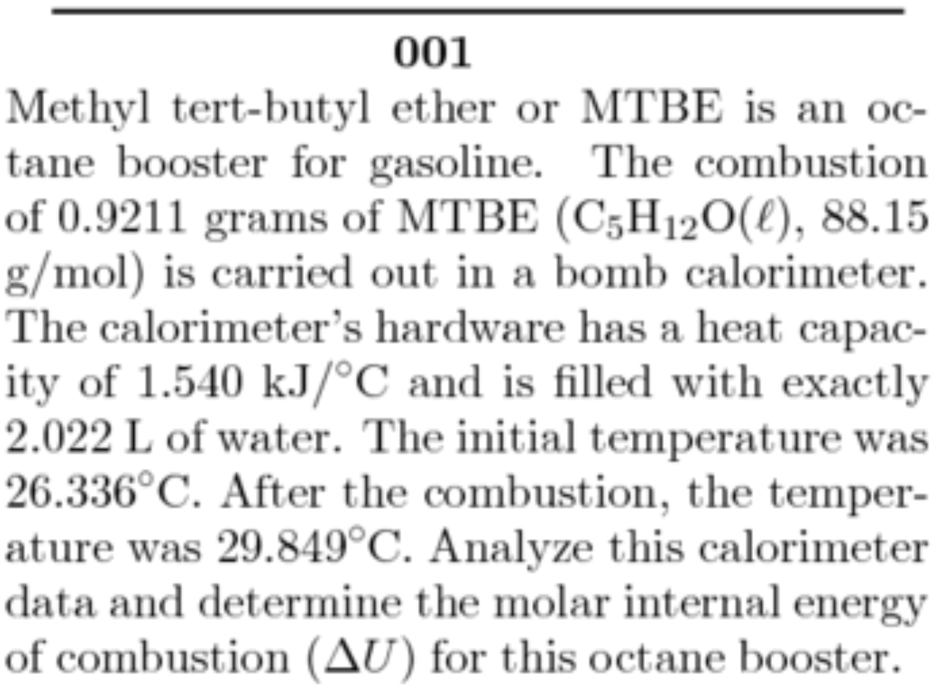
III) The reaction is spontaneous only at relatively high temperatures.

IV) ΔG is positive at all temperatures.



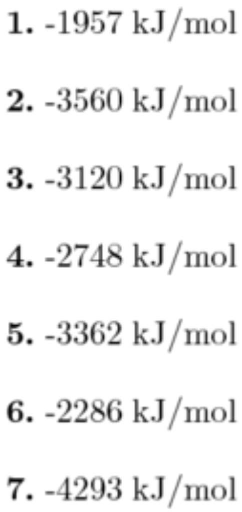
I and IV are correct

Free Energy: Equilibrium Question



001

Methyl tert-butyl ether or MTBE is an octane booster for gasoline. The combustion of 0.9211 grams of MTBE ($C_5H_{12}O(\ell)$, 88.15 g/mol) is carried out in a bomb calorimeter. The calorimeter's hardware has a heat capacity of 1.540 kJ/°C and is filled with exactly 2.022 L of water. The initial temperature was 26.336°C. After the combustion, the temperature was 29.849°C. Analyze this calorimeter data and determine the molar internal energy of combustion (ΔU) for this octane booster.



1. -1957 kJ/mol

2. -3560 kJ/mol

3. -3120 kJ/mol

4. -2748 kJ/mol

5. -3362 kJ/mol

6. -2286 kJ/mol

7. -4293 kJ/mol

Note: the units in the answer choices are all kJ / mol. It is very important that your final answer matches the units of the answer choices!

$$q_{cal} = C_{hardware}\Delta T + m_{water}C_{water}\Delta T = -q_{v,sys}$$

$$q_{v,sys} = \Delta U_{sys}$$

$$\boxed{\begin{array}{l} C_{cal} = 1.54\ \frac{kJ}{°C} \\ C_w = 4.184\ \frac{J}{g°C} \\ \Delta T = 3.513°C \\ \text{mass MTBE} = 0.9211\ g \\ MW = 88.15\ g/mol \\ H_2O\ L = \underline{2.022\ L} \end{array}}$$

$$q = \underbrace{C\Delta T}_{cal} + \underbrace{mC\Delta T}_{H_2O} \qquad \approx 30{,}000\ J$$

H_2O ↓ $2{,}022\ g\ (4.184)(3.513)$ ↗ $\approx 30{,}000\ J$

cal ↓

$$1.54\ \frac{kJ}{°C} \times 3.513 = 5.4\ kJ$$

$$= 5400\ J$$

$$\boxed{q_{cal} = 35{,}400\ J} \rightarrow \underline{35.4\ kJ}$$

sur

$$-35.4\ \frac{kJ}{0.9211\ g}\left(\frac{88.15\ g}{mol}\right) \approx \boxed{-3362\ \frac{kJ}{mol}}$$