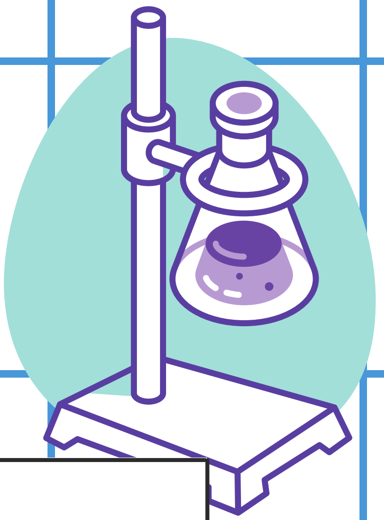


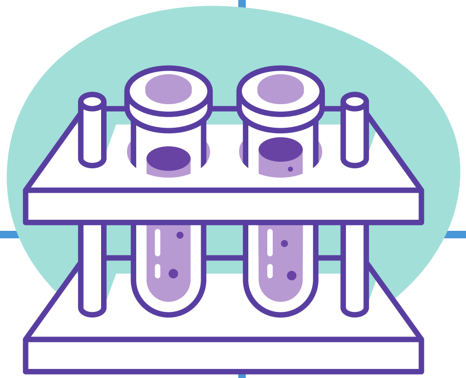
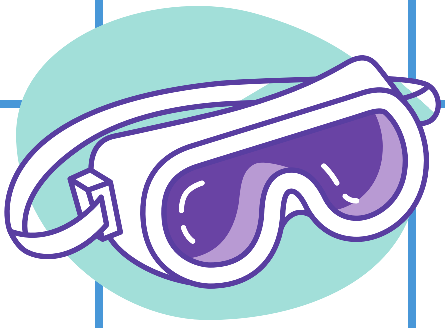
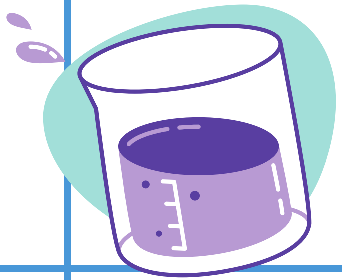


2022

Mr. Nackers

# AP CHEMISTRY REVIEW

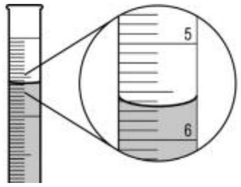
Belongs to


# AP Test Tips from AP Chem Teachers…

## General Test Tips:

- Spend more time on the problems you know rather than the problems you don't know
- Do the MC in three passes - ones you know that are quick, then ones you know that take time, then try the ones you didn't know (on first pass through, answer quick MC, circle MC you know that take time, circle MC you don't know)
- Pay attention to you MC pacing → answer 10 MCQs in the first 15 min., 20 MCQs in 30 min., etc. (90 sec/question) …If you start to spend too long on an MC question, remember that 10 of the 60 MC questions don't even contribute to your score. Efficiency is key
- In multiple choice math questions round, approximate. You NEVER need long division et al.
- Do the easy FR question first. Only the suckers/losers go in order.
- If part (a) looks too confusing to you, then skip it and come back to it later. You can answer part (b) before part (a). Label your answers clearly.
- "RTQ - ATQ" (read the question – answer the question) …After you have finished your FRQ answer, read it back to yourself. Did you actually answer the question that was being asked?
- Don't write too much, just answer the question! Be brief… be brilliant
- If they ask you to make a choice (higher, lower, increase, decrease, etc.) make the choice and write this part down FIRST...BEFORE you start justifying your answer.
- If the question asks you to compare 2 substances make sure you refer to TWO substances
- When in doubt, find moles.
- MV =moles, but millimoles works just fine a lot of the time.
- Get a good night's sleep
- Lab error normally looks for an increase or decrease in experimental values.
- Burets measure liquids more precisely than beakers or graduated cylinders. STOP TRYING TO USE A BEAKER TO MEASURE TENTHS OF A MILLILITER!!!!!!!
- You would read the volume on this buret as 5.65 mL...NOT 6.35 mL



- If you are clueless about rounding off your answer, 3 sig figs is plenty most of the time.

- % error does not mean the same thing as % yield

- How about this..."The AP test writers are lazy and boring. I highly doubt that they will come up with anything original. You have seen these questions before!!"

- Avoid the use of the word "it" ...refer to substances by name, so we know exactly what you meant to say.

- "Just remember this, if I get your exam back next fall and I see that you answered, YES/NO when asked if something will increase, decrease, or stay the same, I will hunt you down like a bloodhound and taser you in your face! Now, good luck on your test!" ;)

- Don't forget units! (and pay attention to the units you're given!)

## Big Idea 1 – Atoms & Elements

- **Horizontal trends**: they both have the same energy level (subshell), but one of them has more protons (greater nuclear charge).

- **Vertical trends**: one of them has valence electrons in an orbital with a higher value of n; this orbital is higher in energy (and farther away from the nucleus).

- Atoms/elements/ions/molecules/compounds don't "like" or "want" anything (ex. Justification for a trend cannot it "it wants to have a full shell) …also, stating a trend is NOT a justification. Give the scientific reason why things happen. Trends are usually about nuclear charge & distance (coulomb's law!)

- When explaining trends, don't talk about placement on the table or the atom having a full shell. Period... Talk about things in the atoms like $Z_{eff}$ (nuclear charge), nuclear pull, distance between nucleus and valence electrons, etc.

- Mass Spectroscopy is all about isotopes! Proton Electron Spectroscopy (PES) is all about coulomb's law & electron configurations!

- Ions have a charge… Na and $Na^+$ are not the same!

## Big Idea 2 – Structure & Properties of Matter

- If the question says, "Draw ALL resonance structures," chances are there's more than one Lewis Structure.

- Never trust printed structures for bond angles! Count the electron domains.

- For heaven's sake, carbon will make 4 bonds total and hydrogen will only have one bond in a Lewis structure!!!!!!!!!!!!!

- Use electron domains to help with determining shapes (and double bonds represent a single domain)

- "Tetrahedral" is not a bond angle.

- Non-polar molecules can contain polar bonds.

- The greater the difference in electronegativity between two atoms, the more polar the bond is.

- Breaking attractions (bonds, IMFs, nucleus-valence e-) REQUIRES energy (endothermic).

- Lattice energy and Coulomb's law:
    - MgO beats NaF (similar ionic radii, greater charge magnitude wins)
    - NaF beats KCl (same charge magnitude, smaller ionic radii wins)

- If the question says to justify your answer in terms of IMFs, mention ALL of the IMFs that each substance experiences. Do NOT say "like dissolves like" when justifying why two substances dissolve or mix together.

- Larger e-cloud = more London dispersion forces = more polarizable …this is dependent on SIZE, not MASS

- Stronger IMFs = higher boiling point = lower vapor pressure = greater viscosity

- Hydrogen bonds only occur between an H already bonded to F, N, or O and another F, N, or O …(H–H is NOT a hydrogen bond)

- Chromatography → distance traveled is based on affinity for the mobile phase and affinity for the stationary phase.

- Sometimes the data tells you something that is different than what you would have predicted (i.e. $CCl_4$ has stronger IMFs than HCl.) GO WITH THE DATA!!!

- Water is wet. ;)

- Do NOT use 1 mole = 22.4 L unless you are actually at STP (0°C & 298 K) …*STP is NOT "standard state" (which is 25°C & 298 K)

- Any two gases at the same temp. Have the same KE but NOT the same velocities

- Ideal gas conditions = high temperature & low pressure
    - Deviations from ideal gas law occur at low T & high P
    - Deviations also occur when gases are too sticky (polar) or too large (LD).

- MM =dRT/P (meow, meow)

- Larger = size. Heavier = mass. More = amount (like moles). Don't mix them up!

## Big Idea 3 – Chemical Reactions (including redox)

- Net Ionic Equations (NIE): Dissociate aqueous substances (strong electrolytes) and eliminate spectator ions.

- All equations must be balanced for atoms AND charge!

- Oxidation is loss of electrons/reduction is gaining of electrons
    - LEO goes GER
    - OIL RIG

- The more (+) $E_{red}$ is the reduction and the less (+) is the oxidation reaction.

- When adding two half-reactions together, the electrons must cancel out.
    - If you reverse the rxn, change the sign of $E_{red}$ to serve as $E_{ox}$.
    - If you double it, do NOT double the voltage.

- Reduction at the cathode, oxidation at the anode. (An Ox/Red Cat)

- Electrons travel in the wire from anode to cathode. Ions flow through the salt bridge: anions toward the anode, cations toward the cathode.

- Electroplating shortcut....grams = MM(I)(t)/nF

## Big Idea 4 – Kinetics

- Thermodynamics tells you IF it will happen. Kinetics tells you how FAST.

- Rate Laws can be determined via experimental data OR if you know the reaction mechanism & the rate-determining (slow) step.

- The only thing that changes the value of "k" is changing the temperature (or adding a catalyst.)

- High activation energy --- slow reaction rate
  Low activation energy --- fast reaction rate

- If the data shows that the half-life is constant over time, it's first-order kinetics for that substance.

- Determining order of reaction via graphs… which produces a straight line?
    - [A] vs. t → zero order
    - ln [A] vs. t → first order
    - 1/[A] vs. t → second order
    - **regardless of which order the rxn is, the absolute value of the slope = k

- Don't forget to include the proper UNITS for your k value!)

- Rate "k" HAS units; Equilibrium "K" does NOT have units

## Big Idea 5 – Thermodynamics

- Thermodynamics tells you IF it will happen. Kinetics tells you how FAST.

- If your answer is ΔH, ΔS, ΔG, or $E^o$, make sure your answer includes the proper **SIGN** and the proper **UNITS**.

- Thermodynamically favorable reactions → ΔG<0 …E>0 …K>1
    - At equilibrium, ΔG=0, E=0 (both essentially indicate how far away from equilibrium the system is)

- Raising the temperature does NOT affect ΔH or the activation energy.

- Breaking attractions (bonds, IMFs, nucleus–valence e-) REQUIRES energy (endothermic).

- Bonds breaking is endothermic & bonds forming is exothermic (ΔH is the net sum of this)

- Pay attention to units! (specifically, pay attention when you have a mixture of joules & kJ)

## Big Idea 6 – Equilibrium

- …At equilibrium, ΔG=0, E=0
  (both essentially indicate how far away from equilibrium the system is)

- Rate "k" HAS units; Equilibrium "K" does NOT have units

- The only thing that changes the value of "K" is changing the temperature.

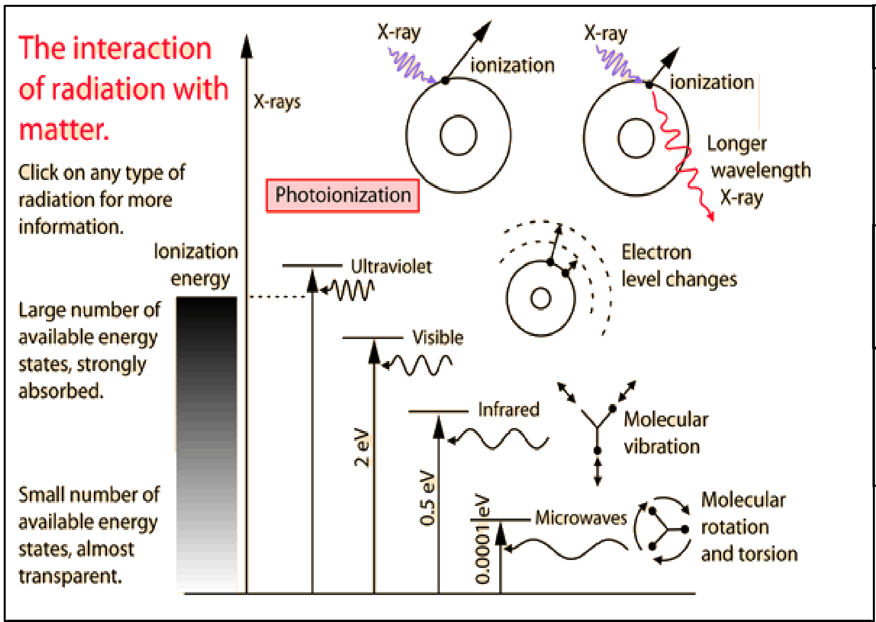
- Increasing temperature increases both the forward and the reverse rxn rates…it just increases the endothermic direction's rate more.

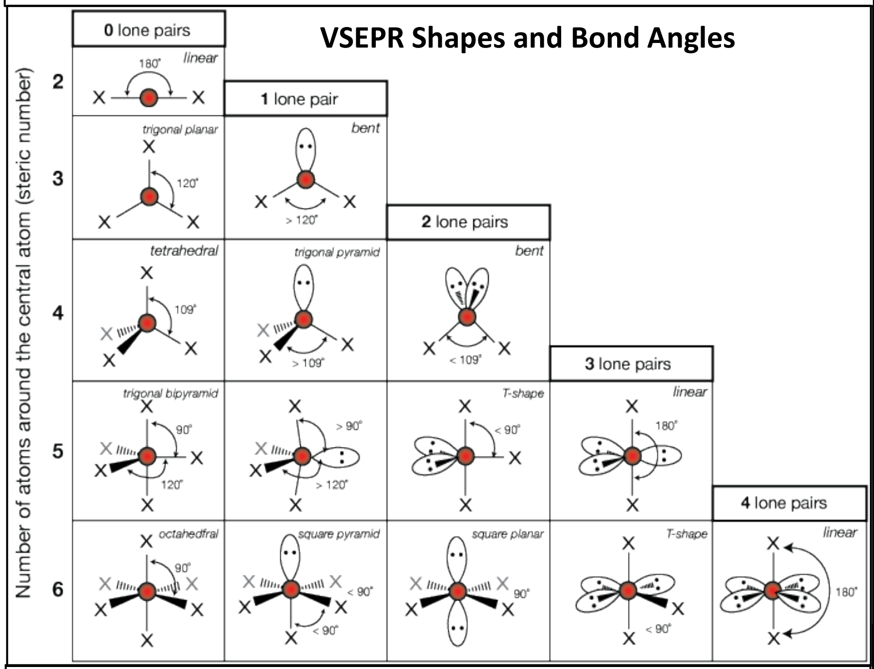
- Manipulating the equilibrium constant values (K)
    - Reverse the reaction → the new K is the reciprocal of the old K
    - Multiply the reaction by 2 → the new K is the old K squared
    - Add two reactions together → multiply $(K_1)x(K_2)$

- If you have a reaction with a HUGE value of K, assume the reaction essentially goes to completion, and treat it like a normal stoichiometry (or limiting reactant) problem; You don't need to make an ICE table
- Equilibrium *expressions* are determined via a balanced chemical equation

- Beware the pressure equilibrium expression. And if it's $K_p$, don't use brackets!
- If you complete an equilibrium calculation (ICE table) and find "x", you're not done! x maybe not the answer the question is asking for… answer what the questions is asking
- Discuss reaction quotient (Q) to explain a shift in equilibrium. Saying "LeChatelier's Principle" will get you NOTHING! If Q increases reaction goes towards the reactants. The same goes for a voltaic cell voltage change. If Q increases, the voltage decreases.
    - $Q<K$ …reaction shifts towards the products
    - $Q>K$ …reaction shifts towards the reactants
    - $Q=K$ …reaction is at equilibrium (no need to shift)
- Whenever finding Q can help determine which direction a reaction will proceed to re-establish equilibrium is a good thing.
- Inert gases and catalysts DO NOT shift an equilibrium
- If x = the solubility of an ionic solid (in mol/L)
    - $K_{sp}$ for AgCl = $(x)(x) = x^2$
    - $K_{sp}$ for $PbCl_2 = (x)(2x)^2 = 4x^3$
- "x" = molar solubility
- Larger $K_a$ = more ionizable
- Acid-base reactions proceed from the strong side to the weak side. Look at the magnitude of K to determine which way the reaction is favored.
- HX versus HY...If HX is the stronger acid, then Y- is the stronger base.
- The acidic species in a buffer neutralizes added base.
- weak acid & strong base titration: pH = pKa at the halfway point (also at this point, $[HA]=[A^-]$)
- If you titrate 10 mL of a 1 M weak acid and also titrate 10 mL of a 1 M strong acid, these samples would require the SAME amount of 1 M NaOH to reach the equivalence pt. (i.e. volume of titrant is based on moles, not acid strength) …BUT, the weak acid would have a higher pH at the equivalence point
- $M_1V_1=M_2V_2$ is not on the formula sheet, but extremely useful in dilutions and neutralizations

# Things to have Memorized in AP Chemistry





## A Sampling of Common Polyatomics

→DO NOT dissociate in water

→Oxidation numbers of their component atoms will sum to give the charge

| | | |
|---|---|---|
| $NH_4^+$ (Ammonium) | $C_2H_3O_2^-$ or $CH_3COO^-$ (Acetate) | |
| $OH^-$ (Hydroxide) | $ClO_3^-$ (Chlorate) | $NO_3^-$ (Nitrate) |
| $CO_3^{2-}$ (Carbonate) | $SO_4^{2-}$ (Sulfate) | $PO_4^{3-}$ (Phosphate) |

## Units for rate constant

$$k = \frac{1}{M^{(overall\ order-1)} \cdot s}$$

**1 g = 1 mL for water** (density)

Compounds containing

**$Na^+$, $K^+$, $NH_4^+$ and $NO_3^-$**

are considered fully soluble

**Group I and II hydroxides**

are strong bases

**HCl, HBr, HI, $HClO_4$, $H_2SO_4$, $HNO_3$**

are strong acids

**$H_2$, $N_2$, $O_2$, $F_2$, $Cl_2$, $Br_2$, $I_2$**

are diatomic elements

## Hybridization

4 electron groups around a central atom create 4 **$sp^3$** hybrid orbitals

→ same shape/bond angles as tetrahedral

3 electron groups around a central atom create 3 **$sp^2$** hybrid orbitals

→ same shape/bond angles as trigonal planar

2 electron groups around a central atom create 2 **sp** hybrid orbitals

→ same shape and bond angles as linear

## General Rules for Oxidation numbers:

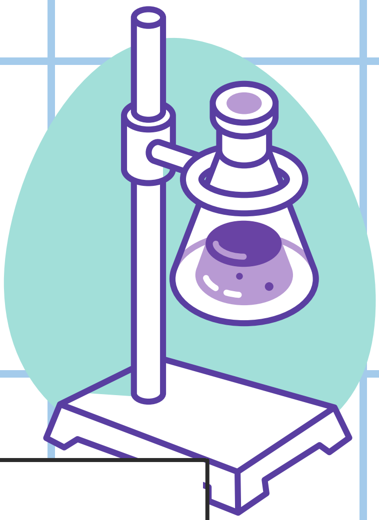
(ranked in order of priority)

| | |
|---|---|
| Elements (watch for diatomics!) | 0 |
| Monatomic ion | same as charge |
| 1A metals | +1 |
| 2A metals | +2 |
| Fluorine | -1 |
| Oxygen | -2 |
| Hydrogen | +1 |
| Common ions | usual charges |

Compiled by Nora Walsh, FJ Reitz High School, 2021

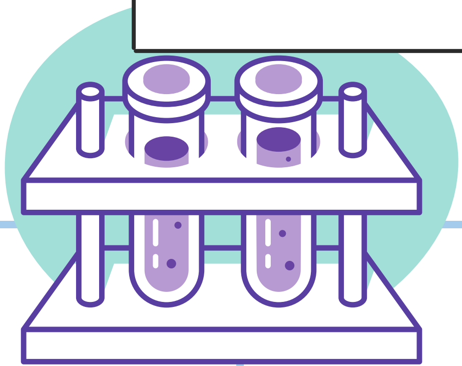
# College Board Live AP Chemistry Review Videos

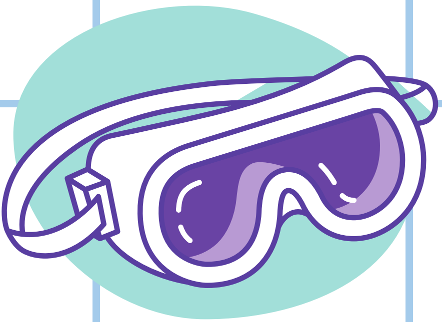
The video descriptions have handouts and resources specific to each video

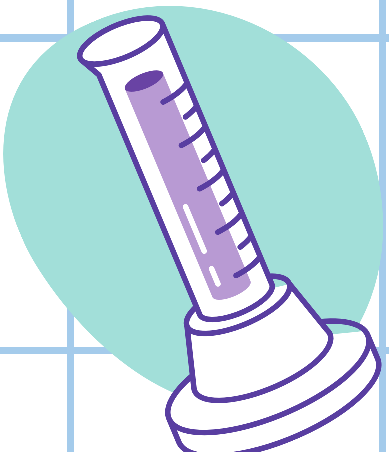


# UNIT REVIEWS

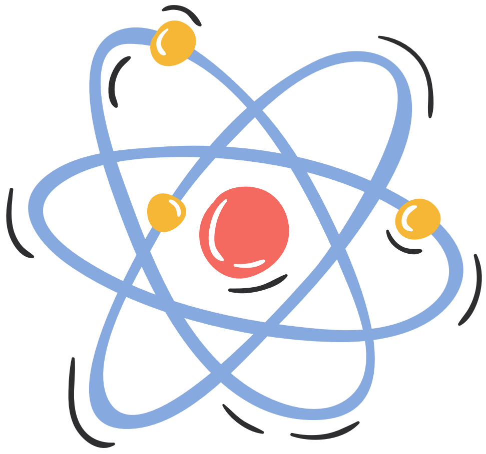
2022 AP Chemistry Review Mr. Nackers







# UNIT 1 - ATOMIC STRUCTURE AND PROPERTIES



| | |
|---|---|
| 1.1 | MOLES AND MOLAR MASS |
| 1.2 | MASS SPECTROSCOPY OF ELEMENTS |
| 1.3 | ELEMENTAL COMPOSITION OF PURE SUBSTANCES |
| 1.4 | COMPOSITION OF MIXTURES |
| 1.5 | ATOMIC STRUCTURE AND ELECTRON CONFIGURATION |
| 1.6 | PHOTOELECTRON SPECTROSCOPY |
| 1.7 | PERIODIC TRENDS |
| 1.8 | VALENCE ELECTRONS AND IONIC COMPOUNDS |

**7-9% of exam**

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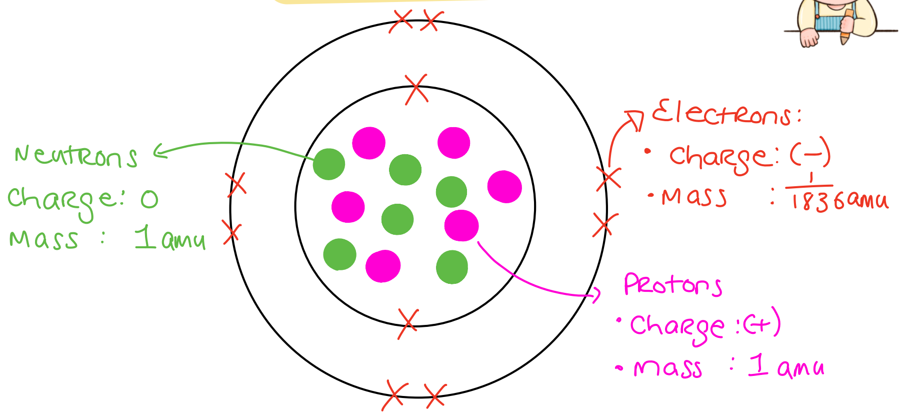
# Unit 1: Atomic Structure

## Atomic Structure



$X_2^A$ Mass Number (A): $p^+ + n^0$

Atomic Number (Z): $\# p^+$ / Nuclear charge

# neutrons (n) = A − Z.

# electrons = # protons

**Isotopes:** Atoms of the same element, same atomic number but a different mass number ($n^0$). $C^{12}$ and $C^{14}$

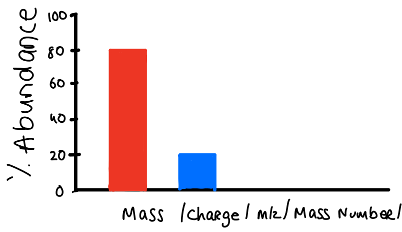
**Atomic Mass:** $\sum$ (isotopic mass) x (abundance)

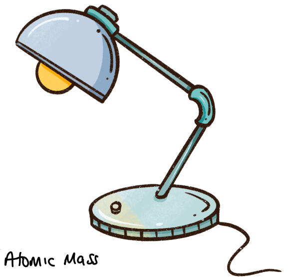
Average mass of isotopes by abundance

## Spectroscopy

**Mass Spectroscopy - identify isotopes**

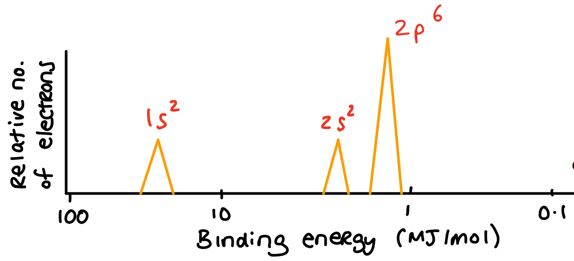
- Seperates elements by isotopes
- Each peak represents a different isotope
- Height = Relative abundance

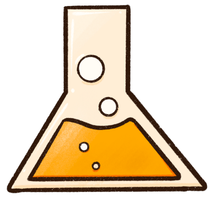




**Photoelectron Spectroscopy (PES) - Energy of $e^-$**

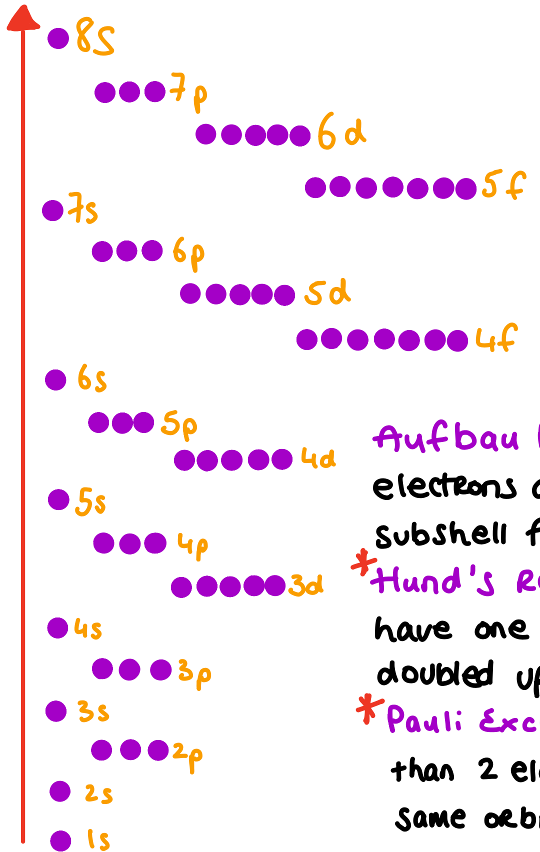
- uses X Rays to Remove electrons
- Imagine nucleus to the left
- Each peak = subshell · Height of peak = # $e^-$
- Further left = ↑Binding energy = ↓Energy level
- For same orbital, different element: Element with more $p^+$ will shift peaks left.





**Binding energy** = energy required to remove an electron from the corresponding shell.

## Electron Configuration



**Core Electrons** = inner electrons

**Valence Electrons** = outer electrons

s = 2e⁻

p = 6e⁻

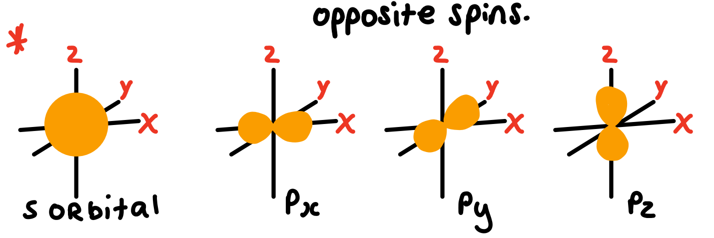
d = 10e⁻

f = 14e⁻

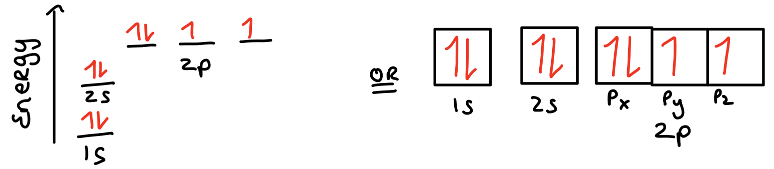
**Aufbau Principle:** "to build up" electrons are added to lowest subshell first.

***Hund's Rule:** Each subshell should have one electron before they are doubled up

***Pauli Exclusion principle:** No more than 2 electrons can occupy the same orbital and they must have opposite spins.



**Example: Oxygen = 8e⁻**



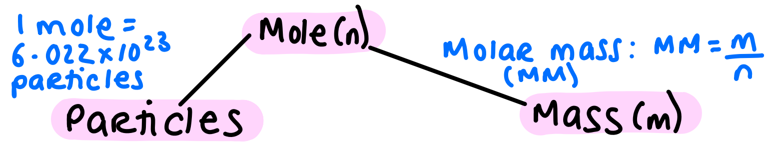
**Writing E.C. example Calcium**

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$

Shorthand: $[Ar]^{10}\,4s^2$ (Noble gas preceeding element)

*Not on AP exam

## Moles and Molar Mass



**Use of dimensional analysis:**

- Multiply known quantity by a conversion factor with the starting units in the denominator

Example: How many grams in 0.85 mol Carbon?

$0.85\,\cancel{mol}\,C \times \frac{12.g\,C}{1\,\cancel{mol}\,C} = 10.2g\,C$

## Periodic Trends

**Coulomb's Law:** $F = \frac{q1 \cdot q2}{r^2}$

F = Coulombic force

q = charge on particles

r = distance between particles

F increases when

- Charges increases
- Distance decreases

$+q^1$ $-q^2$ attraction

$+q^1$ $+q^2$ Repulsion

**Effective nuclear charge ($Z_{eff}$):** Approximate nuclear charge felt by the outer electron due to the shielding by core electrons. (Z − core e⁻)

**Ionization Energy (IE):** Energy required to remove electrons from an atom

$A + IE_1 \rightarrow A^+ + e^-$

$A^+ + IE_2 \rightarrow A^{2+} + e^-$

$A^{2+} + IE_3 \rightarrow A^{3+} + e^-$

**Electron Affinity (EA):** Energy Released when an electron is added to an atom. Has similar (but erratic) trend to IE.

$A + e^- \rightarrow A^- + Ea$

**Electronegativity:** How much an atom wants an electron from another atom. From 0-4. Similar trend as IE.

These are a piece of cake! 😂

**General Trends:**

- **Down Family:** ↑ Radius, ↓ IE/EA/EN
  Outer e⁻ in higher shells (↑ shielding), further away and less attracted to nucleus.
- **Across period:** ↓ Radius, ↑ IE/EA/EN
  More p⁺ (greater $Z_{eff}$) outer e⁻ more attracted to nucleus.
  Sample IE Exceptions: · Be to B (2p > 2s)
  · N to O (unpaired to paired e⁻).
- **Radius of Cation < Element < Anion:**
  As # of e⁻ increases, there's more e⁻ e⁻ Repulsions
- **Isoelectronic species:**
  More p⁺ (greater Zeff), outer e⁻ more attracted to nucleus, smaller Radius.

**Periodic properties:** Elements in the same family

- Same # valence e⁻, form similar ions, similar chemical props.

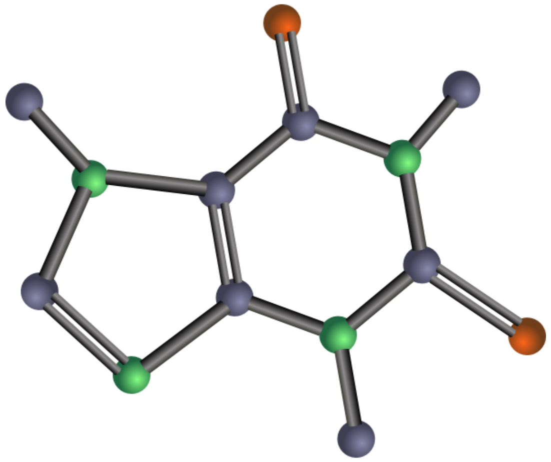
## Describing Compounds

**Empirical Formula:** Mole Ratio of elements in compound in simplest form

**Molecular Formula:** $\left(\frac{\text{Molar mass}}{\text{Mass of EF}}\right) \times (EF)$

**% Composition:** $\frac{\text{Mass of X}}{\text{Molar mass of compound}} \times 100\%$

# UNIT 2 - MOLECULAR & IONIC COMPOUND STRUCTURE AND PROPERTIES



2.1 TYPES OF CHEMICAL BONDS

2.2 INTRAMOLECULAR FORCE AND POTENTIAL ENERGY

2.3 STRUCTURE OF IONIC SOLIDS

2.4 STRUCTURE OF METALS AND ALLOYS

2.5 LEWIS DIAGRAMS

2.6 RESONANCE AND FORMAL CHARGE

2.7 VSEPR AND BOND HYBRIDIZATION

**7-9% of exam**

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# Unit 2 Molecular and Ionic Structure and Properties

Ms Kelleher

## Intramolecular Bonding

Intramolecular force: attraction within a molecule
- Strong
- Hard to break

### Ionic Bonding

Transfer of electrons from a metal to a non-metal.

$[K]^+[:\ddot{Cl}:]^-$

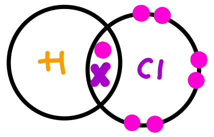
Coulomb's law : ↑ charge, ↓ size = ↑ bond energy

### Covalent Bonding

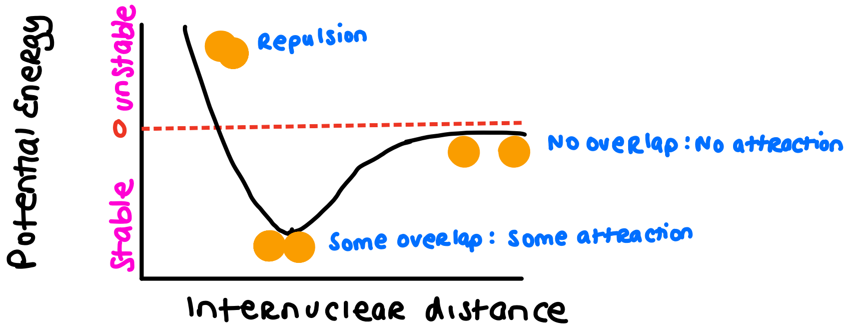
Sharing of electrons between non-metals.

**Polar**: Electrons not shared equally
Large Δ E.N.

**Non polar**: Electrons shared equally.
Small Δ E.N.



Balance of attraction and repulsion between atoms.



↑ Bond order = ↑ bond energy = ↓ bond length

**Bond polarity**: Difference in electronegativity of two elements

$\delta^-$ partial negative charge Atoms with a high E.N. difference

$\delta^+$ partial positive charge Atoms with a low E.N. difference

⟼

Dipole arrow points towards more electronegative atom

### Metallic Bonding

Electrons not associated with a single atom or molecule (delocalized electrons).

↑ delocalised $e^-$ = ↑ bond energy

---

Sigma bond (σ) $e^-$ shared between atoms

Pi bond (π) $e^-$ shared around atoms

Single bond : σ (bond rotation)

Double bond : σ + π (no rotation around bond)

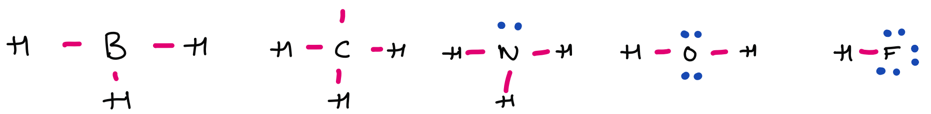
Triple bond : σ + 2π (no rotation around bond)

## Lewis, Resonance and Formal Charge

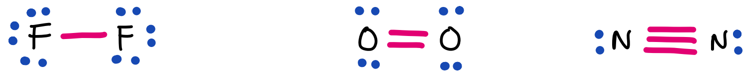
### P.T and valence $e^-$

| 1 | 2 | | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | He |
| Li | Be | Transitions: | B | C | N | O | F | Ne |
| Na | Mg | Variable valency | Al | Si | P | S | Cl | Ar |
| K | Ca | | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | | In | Sn | Sb | Te | I | Xe |

### Simple molecules



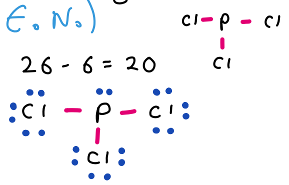
### Diatomic molecules



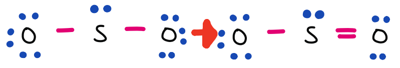
**Octet Rule**: Except for Hydrogen and Boron, all atoms end up with 8 electrons around them.

### Steps to draw Lewis Structures

1. Count and sum valence electrons (adjust for ions) $PCl_3 = 5 + 7(3) = 26$
2. Determine Central atom (Written 1st / Most E. N.)
3. Subtract bonding electrons from total 26 - 6 = 20
4. Add remaining electrons as lone pairs to reach an octet around each atom

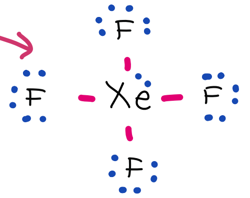


If octet has not been achieved:
Add multiple bonds (double, triple)

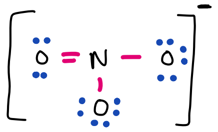


If all atoms have achieved an octet and not all valence electrons have been assigned:
Add remaining electrons to the central atom

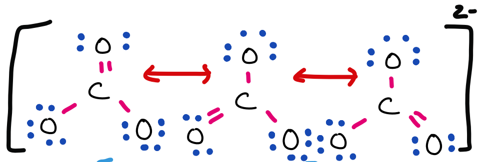
This is an expanded octet



Don't forget square brackets for ions!



Resonance



← π bond $e^-$ delocalised

**Formal Charge** : [Valence $e^-$] - [lone $e^-$ + ½ bond $e^-$]

Lower F.C (0, +1, -1) are better structures

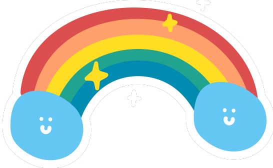
More negative F.C on more EN atom

Dont want F.C. with same signs on adjacent atoms

Sum of F.C = charge on chemical species

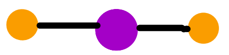
## VSEPR and Bond Hybridization

- Electrons repel due to Coulomb's forces
- Bonds and lone pairs are negative in nature so arrange themselves to minimise repulsion
- Steric Number: # of electron domains - influences geometry



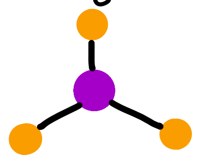
### Steric 2 (sp)

Linear
$AB_2$ (180°)

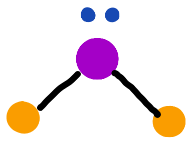


### Steric 3 ($sp^2$)

Trigonal planar
$AB_3$ (120°)

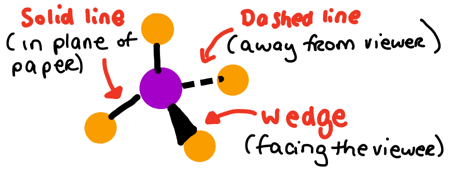


Bent
$AB_2E_1$ (120°)

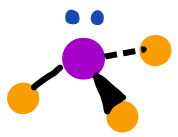


### Steric 4 ($sp^3$)

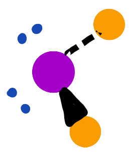
Tetrahedral
$AB_4$ (109.5°)



Trigonal Pyramid
$AB_3E_1$ (107°)

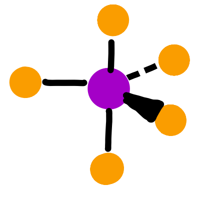


Bent
$AB_2E_2$ (104.5°)

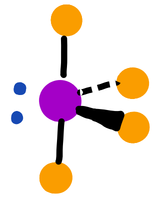


### Steric 5

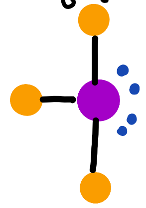
Trigonal bipyramidal
$AB_5$ (90°, 120°)



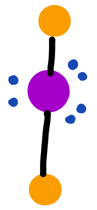
See-Saw
$AB_4E_1$ (90°, 120°)



T-shaped
$AB_3E_2$ (90°)

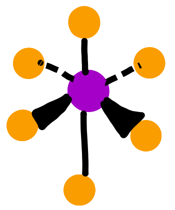


Linear
$AB_2E_3$ (180°)

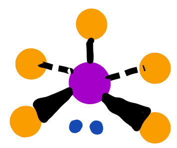


### Steric 6

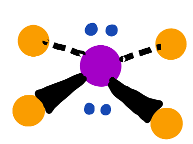
Octahedral
$AB_6$ (90°)



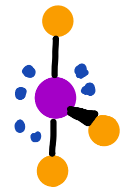
Square pyramid
$AB_5E_1$ (90°)



Square planar
$AB_4E_2$ (90°)



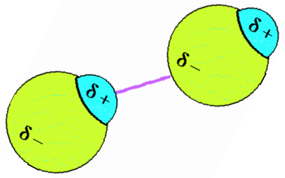
T-shaped
$AB_3E_3$ (90°)



**Polar compound**: A compound with an uneven distribution of charges
- polar bonds don't cancel out - asymmetrical
- lone pair $e^-$ disrupt electrical symmetry

**Non polar compound**: A compound with even distribution of charges - symmetrical and identical atoms.

# UNIT 3 - INTERMOLECULAR FORCES AND PROPERTIES



3.1 INTERMOLECULAR FORCES

3.2 PROPERTIES OF SOLIDS

3.3 SOLIDS, LIQUIDS, AND GASES

3.4 IDEAL GAS LAW

3.5 KINETIC MOLECULAR THEORY

3.6 DEVIATION FROM IDEAL GAS LAW

3.7 SOLUTIONS AND MIXTURES

3.8 REPRESENTATIONS OF SOLUTIONS

3.9 SEPARATION OF SOLUTIONS AND MIXTURES CHROMATOGRAPHY

3.10 SOLUBILITY

3.11 SPECTROSCOPY AND THE ELECTROMAGNETIC SPECTRUM

3.12 PHOTOELECTRIC EFFECT

3.13 BEER-LAMBERT LAW

**18-22% of exam**

CollegeBoard AP

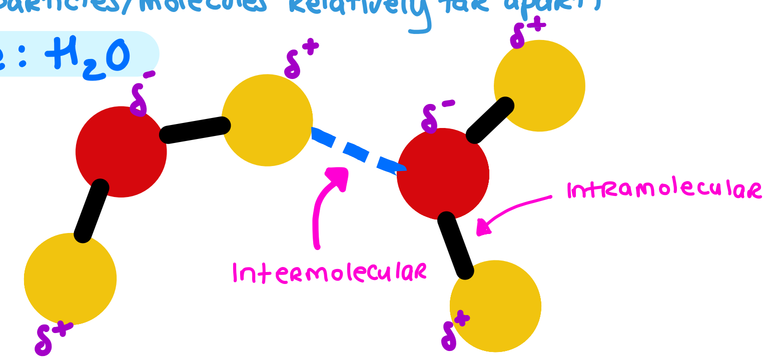
# Unit 3: Intermolecular Forces and Properties

## Intermolecular Forces

Intermolecular forces - attractive forces between molecules

- weak (particles/molecules relatively far apart)

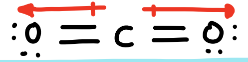
**Example: $H_2O$**



## Polar vs. Non polar

**Non-polar**

- Bond dipoles within a molecule cancel out

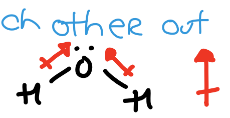

$:\ddot{O}=C=\ddot{O}:$

- Non polar molecules:

Linear, Trigonal planar, Tetrahedral, square planar, Trigonal bipyramidal, octahedral

**Polar**

- Bond dipoles do not cancel each other out



Polar molecules:

- Linear, trigonal planar, tetrahedral, If atoms around central atom are not identical

Polar geometry:

- Bent, trigonal pyramidal, see-saw, T-shaped, square pyramidal

## Intermolecular forces

weakest to strongest →

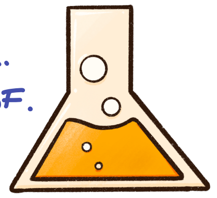
## Intramolecular forces

All strong, hard to compare — Strongest

| London Dispersion (LDF) | Dipole-Dipole | Hydrogen Bonding (Strong dipole-dipole) | Ionic | Metallic | Covalent |
|---|---|---|---|---|---|
| All substances<br>Only force in non polar molecules or single non-metal atoms | Polar molecules<br>Asymmetrical molecules with only non-metals | occurs in polar molecules that have hydrogen directly bonded to N, O or F. | metal + non-metal | Only metal atoms | non-metals |
| Ne, $H_2$, $CO_2$ | HCl, $CH_2O$, $CH_2Cl$ | HF, $H_2O$, $CH_3OH$ | NaCl, KBr, MgO | Au, Al, Zn | - C (diamond)<br>- C (graphite)<br>- $C_{60}$<br>- $SiO_2$<br>- SiC |

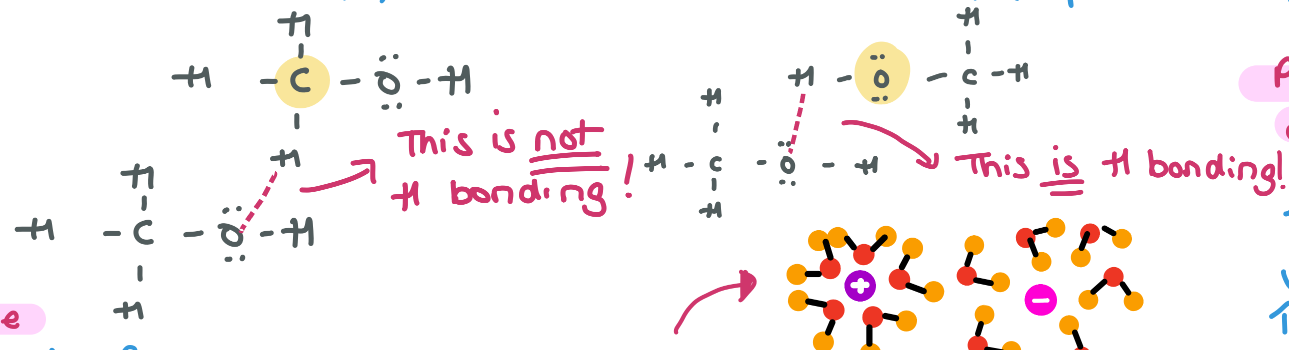
## London dispersion forces

- Interactions between particles or molecules as a result of temporary or instantaneous dipoles
- occur due to the continuous motion of electrons
  - Polarizability: the ease with which the charge distribution in an electron cloud can be distorted.
  - Larger the atom/molecule, the larger the electron cloud, thus more polarizable and greater LDF.



## Dipole-dipole

- An attraction between polar molecules in a way that the partial positive end ($\delta^+$) of one molecule is attracted to the partial negative ($\delta^-$) of nearby molecule.
- Hydrogen bonding: A strong dipole-dipole interaction between a Hydrogen atom (bonded to an N, O or F) on one molecule and an N, O, or F on another molecule (or another part of a large macromolecule)



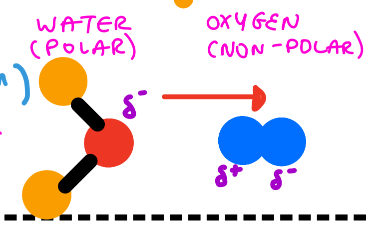
## Properties as a result of increasing IMF

↑ Melting and Freezing Pt.
↑ Enthalpy of fusion/vaporization
↓ Vapor pressure
↑ viscosity
↑ Surface tension
↓ Solubility (Depends on polarity of solvent + solute)
↑ Lattice energy

## Ion-dipole

- An attractive force between an ion and a polar molecule
- In solutions
- stronger than H bonding (Hence ↑ B.P of an ionic compound solution)

## Dipole induced dipole

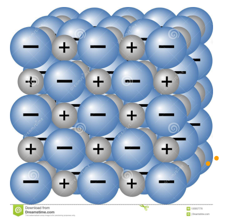


- An attractive force between a polar and non polar molecule
- Temporary, Relies on orientation

## Solids

### Ionic Solids (metal + non metal)

- Electrostatic attraction between cations (+) and anions (-) held by ionic bonds e.g. NaCl, KCl, KI, $FeCl_3$, $CaCO_3$, $CaCl_2$, $MgSO_4$, $Fe_2O_3$, $AgNO_3$



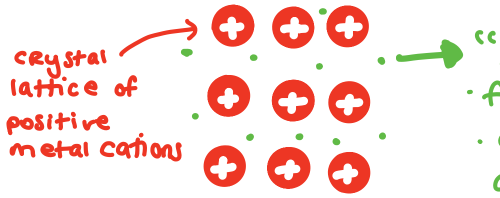
Properties:

- High Melting point
- Conducts electricity as a liquid or aqueous solution (ions free to move)
- Hard and brittle
- often dissolves in water

### Metallic Solids (metals)

- Lattice of metal cations with sea of mobile $e^-$ (metallic bond) e.g metals (Pb, Ag, Au, Cu, Fe, Zn)

Alloys: Brass (Cu + Zn), Bronze (Cu + Sn), Steel (Fe + C).

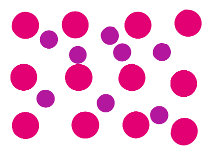


"sea" of delocalized $e^-$

- free to move
- can conduct electricity and heat

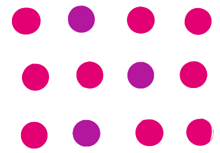
**Interstitial alloy:**

Small atoms fill gaps in metal lattice



**Substitutional alloy:**

Same sized metal replaces lattice



Properties

- High melting point
- Lustrous
- malleable and ductile
- Conducts heat + electricity

### Network Covalent Solids

Lattice of non-metal atoms with covalent bonds e.g. C (diamond) → $sp^3$ hybrid, C (graphite) → $sp^2$ hybrid, $SiO_2$ (sand, glass, quartz), SiC.

Properties:

- High Melting point
- Electrical insulator (except graphite)
- Very hard and brittle (except graphite)

### Molecular Solids (non-metals)

Lattice of molecules with weak IMFs e.g He, Kr, $N_2$, $F_2$, $B_2$, $I_2$, $P_4$, $S_8$; $H_2O$, $NH_3$, $CO_2$, $NO_2$, $C_6H_{12}O_6$, Organic Comp.

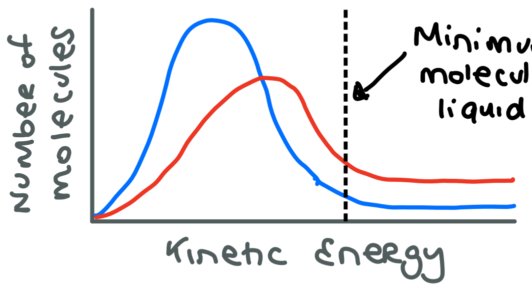
Properties:

- Low Melting point, poor electrical conductor, brittle.

## Properties of liquids

### Vapor pressure

- The pressure exerted by a gas in equilibrium with it's liquid phase at a given temperature



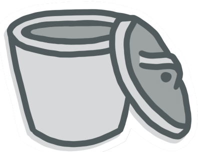
As temperature increases, a greater fraction of the molecules have the KE needed to escape the liquid and vapor pressure increases.

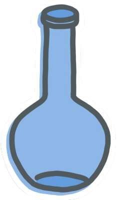
## Solid vs Liquid vs Gas

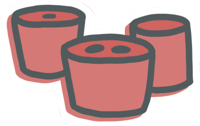
**Solid**
- Fixed shape
- Fixed volume
- Vibrational movement

**Liquid**
- Take shape of container
- Fixed volume
- Particles slide over each other
- BP IMP related to IMFs

**Gas**
- No fixed shape
- Negligible volume







## Gas Laws

**STP:**

1 atm = 760 torr = 760 mmHg = 101.325 kPa

0°C = 273 K  K = °C + 273.15

P = Pressure, atmospheres

V = Volume, litres

n = moles

T = temperature, Kelvin

R = 0.00821 L·atm/mol·K

**Ideal gas law** $P \cdot V = n \cdot R \cdot T$

Small, low IMF gases ideal at low P and high T

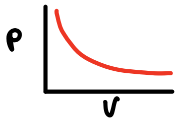
**Combined gas law** $\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2}$

**Dalton's Law** $P_A = \left(\frac{n_A}{n_{total}}\right)(P_{total}) = \frac{n_A \cdot R \cdot T}{V}$  $P_{(total)} = P_A + P_B + P_C$

**Graham's Law** $\frac{v_A}{v_B} = \sqrt{\frac{MM_B}{MM_A}}$  At same temp, lighter gas travels faster

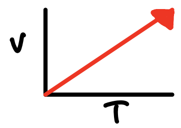
## Kinetic Molecular Theory and Gas Laws

**Pressure vs. Volume** (Boyle's Law)



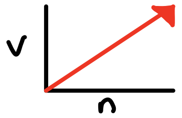
↓ V ↑ collisions ↑ pressure

**Volume vs. Temperature** (Charle's Law)



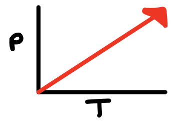
↑ temp ↑ collisions ↑ volume — pressure

**Volume vs. moles** (Avagadro's Law)



↑ n ↑ collisions ↑ volume — pressure

**Pressure vs. Temperature** (Guy Lussac's Law)



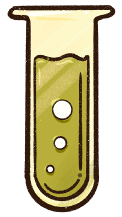
↑ T ↑ collisions ↑ pressure — volume

1. Gases consist of molecules in constant motion, moving in straight lines and change direction only when they collide with other molecules or walls of container
2. Pressure exerted by a gas in a container results from collisions between the gas and the container walls.
3. The average kinetic energy of gas molecules is proportional to the Kelvin temperature of the gas.
4. The molecules composing the gas are negligibly small compared to the distance between them.
5. Gas molecules exert no attractive or repulsive forces on each other; therefore, their collisions are elastic (do not involve a loss of energy).

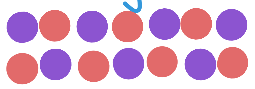
### Deviations from ideal gas law

1. Gas particles DO have volume
   At high pressures (low temperature and volume) the volumes of the particles is no longer negligible compared to the volume of the container
2. Some gas particles DO attract or repel one another
   At high pressure (low temp and volume) the attractive and repulsive forces can impact strengths of collisions.

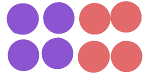
## Solutions and Mixtures



**Homogenous**
- Solid or Liquid
- Macroscopic properties do not vary in sample



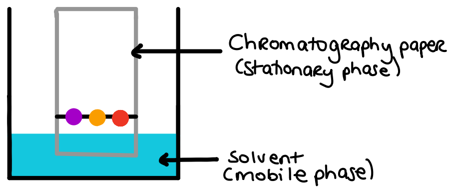
**Heterogenous**
- Macroscopic properties depend on location in mixture



Molarity = $\frac{\text{moles of solute}}{\text{litres of solution}}$

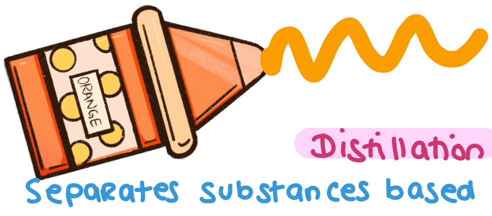
## Chromatography

- Paper, thin layer and column seperates components of a liquid solution based on the polarity of their IMFs and their ability to bind to the stationary phase



- Larger particles move slowly
- Particles with a polarity which matches the solvent will move further.

Retention factor (Rf): $\frac{\text{Distance moved by sample}}{\text{Distance travelled by solvent}}$



### Distillation

Separates substances based on their IMFs and their different vapor pressure/boiling points

## Solubility

- Substances with similar IMFs tend to be miscible (soluble)

Ionic compounds dissolve in polar solvents

Molecular compounds dissolve in non polar solvents

## Spectroscopy and the Electromagnetic Spectrum

← Increasing Energy/frequency (ν)

Increasing wavelength (λ) →

Gamma — X-Ray — U.V — Visible — I.R. — Microwave — Radio

- X-Ray → Core e⁻ (Photoelectron Spectroscopy)
- U.V, Visible → e⁻ transitions (Spectrophotometry)
- I.R. → Bond vibration
- Microwave → Molecular Rotations
- Radio → Nuclear Spins (NMR)

## Photoelectric effect

$C = \lambda \nu$

C = speed of light $3.0 \times 10^8$ m/s

λ = wavelength (m or nm)

ν = frequency (Hz or $s^{-1}$)

$E = h \cdot \nu$

E = Energy of photon (J)

h = planck's constant $6.626 \times 10^{-34}$ J.s

ν = Frequency (Hz or $s^{-1}$)

## Beer – Lambert Law

$A = \varepsilon b c$

A = Absorbence

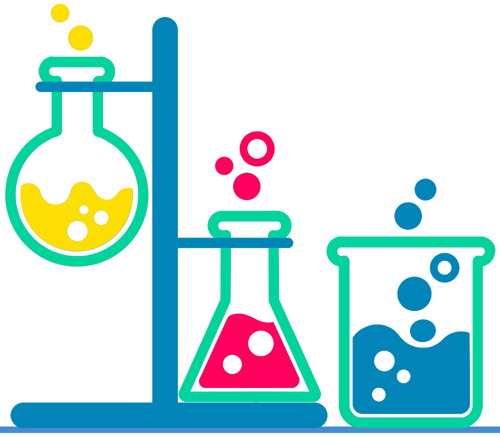
ε = molar absorbtivity (light of a specific λ)

b = path length

c = concentration

In most experiments, path length and wavelength of light are held constant. Absorbance is then proportional to concentration of absorbing molecules or ions.

# UNIT 4 - CHEMICAL REACTIONS



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# Unit 4: Chemical Reactions

## Physical versus Chemical change

A physical change: Substances has a change in properties, but not a change in chemical composition

Involves a change in intermolecular attractions

Usually doesn't involve bond breaking (except dissolution)

Phase changes (e.g. $H_2O\,(l) \rightarrow H_2O\,(g)$)

Separating mixtures (Distillation, filtration, chromatography)

Chemical change: Substance is transformed into a new substance, with different compositions.

Involves breaking or forming chemical bonds. Reversible

$2H_2O\,(l) \rightarrow 2H_2\,(g) + O_2\,(g)$

$AgNO_{3(aq)} + NaCl\,(aq) \rightarrow NaNO_3\,(aq) + AgCl\,(s)$

## Net ionic equations

YAY

Guide lines

1. Start with a molecular equation
2. Make the transition to ionic equation or not

Tips for when to transition or not

| · Break it up | Don't break it up |
|---|---|
| Strong Acid/Base | Solid substance |
| Ionic compound | Covalent substance |
| "Aqueous" substance | weak Acid/Base |
| | Gas |
| | Pure liquid/Solid |
| | Insoluble (slightly soluble) ionic solid |

3. Cross off spectator ions on both sides of the equation

Example:

1. $Ca(OH)_{2(aq)} + 2HBr_{(aq)} \rightarrow 2H_2O_{(l)} + CaBr_{2(aq)}$

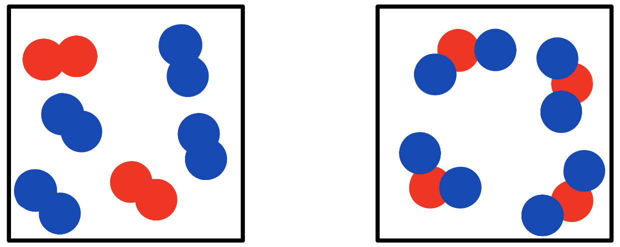
   S.B. S.A. Covalent Soluble ionic compound

2. $Ca^{2+} + 2OH^- + 2H^+ + 2Br^- \rightarrow 2H_2O + Ca^{2+} + 2Br^-$
3. $\cancel{Ca^{2+}} + 2OH^- + 2H^+ + \cancel{2Br^-} \rightarrow 2H_2O + \cancel{Ca^{2+}} + \cancel{2Br^-}$

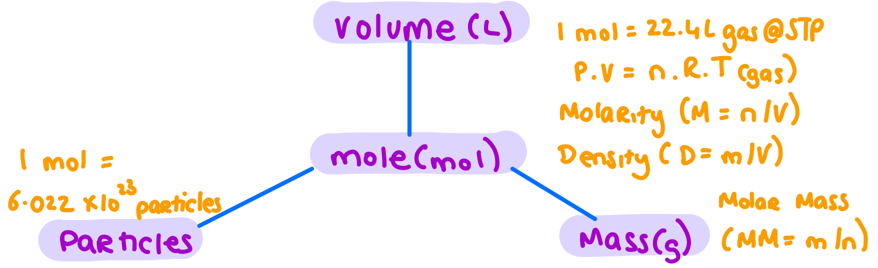
   $2OH^-_{(aq)} + 2H^+_{(aq)} \rightarrow 2H_2O_{(l)}$

## Particulate Diagrams

$2H_2 + O_2 \rightarrow 2H_2O$



## Stoichiometry



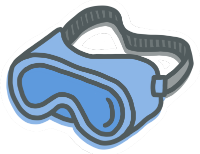
Example:

$Al\,(s) + HCl\,(aq) \rightarrow AlCl_3\,(aq) + H_2\,(g)$

Balance the equation: $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

moles to moles - If 0.36 mol of $AlCl_3$ is produced, how much $H_2$ is produced?

$$AlCl_3 \times \frac{3\text{ mol }H_2}{2\text{ mol }AlCl_3} = 0.54\text{ mol }H_2$$



Grams to grams How many grams of Al are required to produce 75 g of $H_2$. (Assume HCl is added in excess)

$$75\,g\,H_2 \times \frac{1\text{ mol }H_2}{2.016\,g\,H_2} \times \frac{2\text{ mol Al}}{3\text{ mol }H_2} \times \frac{26.98\,g\text{ Al}}{1\text{ mol Al}} = 670\,g\text{ Al}$$

Molarity How many mL of 5.0M HCl is needed to completely react with 4.25g of Al?

$$4.25\,g\text{ Al} \times \frac{1\text{mol}}{26.98\,g\text{ Al}} \times \frac{6\text{ mol HCl}}{2\text{ mol Al}} \times \frac{1L}{5.0\text{ mol HCl}} \times \frac{1000ml}{1L} = 94.5\text{ mL}$$

Ideal gas Law (PV = nRT) 35 g of Al reacts with excess HCl. What volume (in L) of $H_2$ is produced at 345K, 1.12 atm?

$$35\,g\text{ Al} \times \frac{1\text{ mol Al}}{26.98\,g\text{ Al}} \times \frac{3\text{ mol }H_2}{2\text{ mol Al}} = 1.95\text{ mol }H_2$$

$$V = \frac{nRT}{P} = \frac{(1.95\text{mol} \times 0.08206\text{ L.atm.mol}^{-1}\text{K}^{-1})(345\text{ K})}{(1.12\text{ atm})} = 49\text{ L }H_2$$

Limiting Reactant and theoretical yield

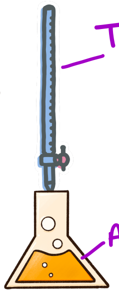
125 g of Al reacts with 2.50L of 3.20M HCl. Which is the limiting reactant? What is the theoretical yield of $H_2$?

$$125\,g\text{ Al} \times \frac{1\text{mol Al}}{26.98\,g\text{ Al}} \times \frac{3\text{mol }H_2}{2\text{ mol Al}} \times \frac{2.016\,g\,H_2}{1\text{ mol }H_2} = 14.0\,g\,H_2$$

$$2.50L\text{ HCl} \times \frac{3.20\text{mol HCl}}{1L\text{ HCl}} \times \frac{3\text{mol }H_2}{6\text{mol HCl}} \times \frac{2.016\,g\,H_2}{1\text{ mol }H_2} = 8.06\,g\,H_2$$

Limiting reactant is HCl and theoretical yield of $H_2$ is 8.06g.

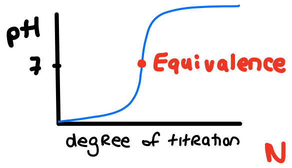
## Titrations



Titrant (solution of known concentration)
A.K.A. Standard solution

Analyte (solution of unknown concentration)

Equivalence point: just enough titrant has been added to react with analyte. *May be indicated by a color change* This observable event is known as the end point.



$M_a V_a = M_b V_b$

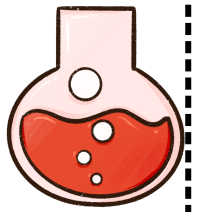
M = Molarity

V = volume

Neutralisation: Acid + Base → Salt + Water

| $HCl$ | + | $H_2O$ | → | $H_3O^+$ | + | $Cl^-$ |
|---|---|---|---|---|---|---|
| Bronsted Lowry Acid (proton donor) | | Bronsted Lowry Base (proton acceptor) | | Conjugate Acid | | Conjugate base |

## Types of Reactions



Sometimes REDOX

- Synthesis/Combination  A + X → AX
- Decomposition "Heating"  AX → A + X

Always REDOX

- Combustion "Burning"  CHO + $O_2$ → $CO_2$ + $H_2O$
- Single replacement  A + BX → B + AX

Never REDOX

- Double replacement  AX + BY → AY + BX

  Product is a precipitate, gas or weak electrolyte

- Bronsted-Lowry Acid Base  $HA + B \rightarrow A^- + BH^+$

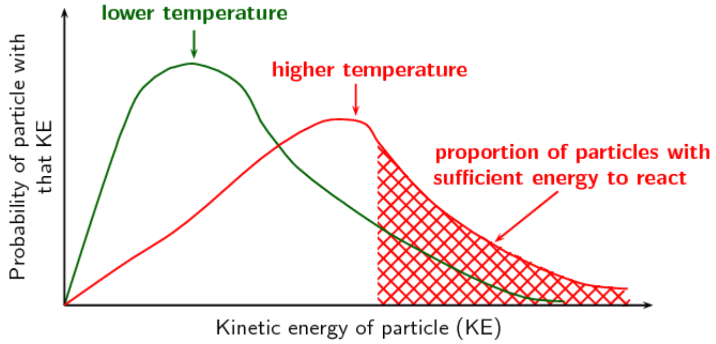
## Redox Reactions

| Oxidation | Reduction |
|---|---|
| · Loses $e^-$ | · Gain $e^-$ |
| · Ox # increases (more +) | · Ox # decreases (more −) |
| · $A \rightarrow A^+ + e^-$ | · $A + e^- \rightarrow A^-$ |
| · Reducing agent | · Oxidising agent |
| · Anode in electro cell | · Cathode in electro cell |

Assigning Oxidation States

- Ox # of elements = 0  Ox # of monoatmic ions = charge
- Break up ionic compounds into ions
- In compounds F = −1; O = −2 (except peroxide = −1); H = +1 (except hydride = −1)
- Balance half reactions
  - Balance elements (not H or O)
  - Balance O with $H_2O$, balance H with $H^+$
  - Balance charges with $e^-$
- Balance the electrons of each half reaction
- Add up half reactions. Add $OH^-$ in basic solution.

# UNIT 5 - KINETICS



5.1 REACTION RATES

5.2 INTRODUCTION TO RATE LAW

5.3 CONCENTRATION CHANGES OVER TIME

5.4 ELEMENTARY REACTIONS

5.5 COLLISION MODEL

5.6 REACTION ENERGY PROFILE

5.7 INTRODUCTION TO REACTION MECHANISMS

5.8 REACTION MECHANISM AND RATE LAW

5.9 STEADY-STATE APPROXIMATION

5.10 MULTISTEP REACTION ENERGY PROFILE

5.11 CATALYSIS

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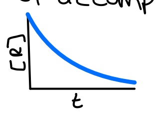
# Unit 5 Kinetics

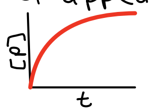
## Reaction rates

$2R_{(aq)} \rightarrow 2X_{(aq)} + P_{(aq)}$

Rate of decomposition = $\left(\frac{\text{change in concentration of reactant}}{\text{change in time}}\right) = \left(\frac{[R]_f - [R]_i}{t_2 - t_1}\right) = \left(\frac{\Delta[R]}{\Delta t}\right)$



Rate of appearance = $\left(\frac{\text{change in concentration of product}}{\text{change in time}}\right) = \left(\frac{[P]_f - [P]_i}{t_2 - t_1}\right) = \left(\frac{\Delta[P]}{\Delta t}\right)$



### Factors affecting rates:

YOU GOT THIS

Reactant concentrations: Higher concentrations ⇒ faster rates
Temperature: Higher temperature ⇒ faster rates
Surface area: Greater surface area ⇒ faster rates
Catalysts: It depends.. see catalyst section!

**Anything that increases collisions will increase the rate.**

## Rate Law

note to self: Must be found experimentally!

$X + Y \rightarrow 2 + W$

**Rate Law:** Rate = $k[X]^m[Y]^n$

- Reactants only
- m = order with respect to X
- n = order with respect to Y
- m + n = overall order of the reaction
- k = "rate constant"
  - temperature dependant
  - units reflect overall order

## Elementary Reactions

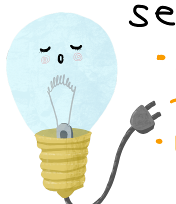
Reactions that occur in a single event or step.
Rate law for elementary reactions can be inferred or predicted from the stoichiometry of the molecules participating in the reaction

Examples: $O_3 + Cl \rightarrow O_2 + ClO$  rate = $k[O][Cl]$
$2NO + H_2 \rightarrow N_2 + H_2O$  rate = $k[NO]^2[H_2]$

## Reaction mechanism

This is the process by which a reaction occurs, over a series of elementary steps

- Sum of elementary steps must lead to final, overall reaction with correct stoichiometry
- Mechanism must agree with rate law expression



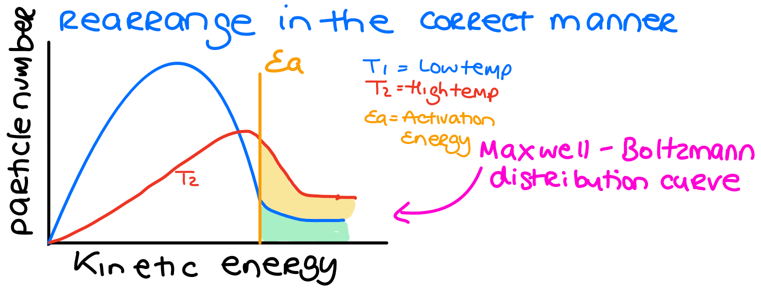
Step 1: $O_{3(g)} + Cl_{2(g)} \rightarrow ClO_{(g)} + O_{2(g)}$
Step 2: $ClO_{(g)} + O_{(g)} \rightarrow Cl_{(g)} + O_{2(g)}$
Overall: $O_{3(g)} + O_{(g)} \rightarrow Cl_{(g)} + O_{2(g)}$

Catalyst
- Present at beginning and end
- Not included in overall eq.
- Might show in rate law

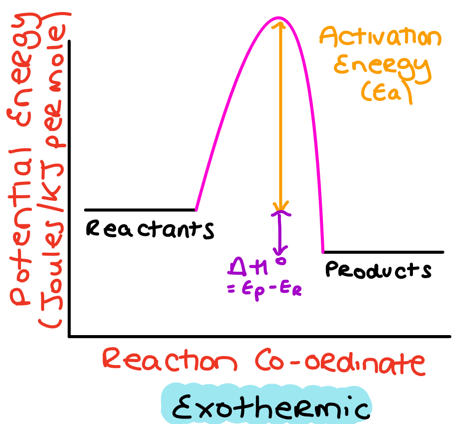
Intermediates
- Formed in one step, consumed in the next
- Not included in overall equation
  - Not in rate law → at AP!

## Collision Model

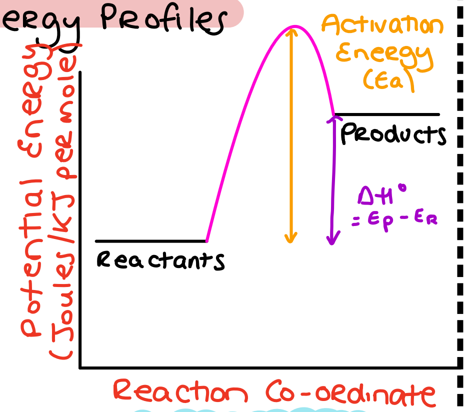
Sucessful collisions have
1. Sufficient energy to overcome activation energy (Ea)
2. The correct orientation that allow bonds to rearrange in the correct manner



## Reaction Energy Profiles



Exothermic

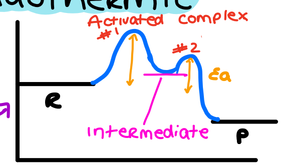


Endothermic

As Ea ↑ reaction rate ↓

Step 1: Slow step (Higher Ea)
Endothermic (P.E of intermediate higher than reactant)
Step 2: Exothermic (P.E of product lower than reactant)

Multi-step profiles:



## Arhenius - Temperature and orientation

Factors affecting rate constant, K

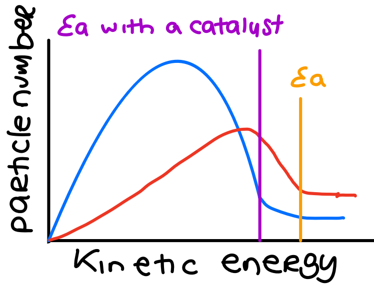
rate = $k \underbrace{[X]^m[Y]^n}_{\text{concentration (or partial pressure)}}$

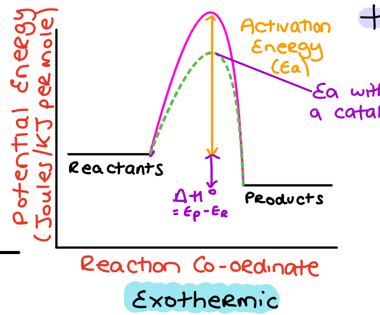
k: Every thing else!

↑ temperature → ↑ "k" → ↑ rate
↓ Ea → ↑ "k" → ↑ rate
Improve orientation → ↑ k → ↑ rate

## Catalysts

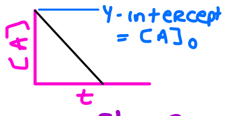
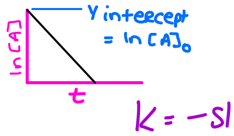
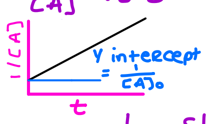
Homogenous: Catalyst in same phase as reactants





Heterogenous: Catalyst in different phase than reactants

when a catalyst is used, ↓ Ea → More collisions with sufficient energy → ↑ rate!

| | 0 order | 1st order | 2nd Order | 3rd Order |
|---|---|---|---|---|
| Rate law | Rate = K | Rate = k[A] | Rate = $k[A]^2$B / $k=[A][B]$ | Rate = $k[A]^2B$ / $k=[A][B]^2$ |
| units of K | mol $L^{-1}s^{-1}$ or $Ms^{-1}$ | $s^{-1}$ | $L\,mol^{-1}s^{-1}$ or $M^{-1}s^{-1}$ | $L^2 mol^2 s^{-1}$ or $M^{-2}s^{-1}$ |
| integrated rate law | $[A]_t = -kt + [A]_0$ | $\ln[A]_t = -kt + \ln[A]_0$ | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ | |
| Straight line plot and it's relationship to k | [A] vs t  Y-intercept = $[A]_0$<br>k = - slope | ln[A] vs t  Y intercept = $\ln[A]_0$<br>k = -slope | $\frac{1}{[A]}$ vs t  Y intercept = $\frac{1}{[A]_0}$<br>k = slope | |
| Half-life | $t_{1/2} = \frac{[A]_0}{(2k)}$ | $t_{1/2} = \frac{0.693}{k}$<br>If $t_{1/2}$ = constant rxn = 1st order<br>* example: Radioactive Decay | $t_{1/2} = \frac{1}{([A]_0 k)}$ | |

## Reaction mechanism, Rate law and Steady State approximation

- If the 1st step is slow, it determines rate
- If the 1st step is not rate limiting, use steady state approximation

Step 1: $O_{3(g)} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} O_{2(g)} + O_{(g)}$ FAST
Step 2: $O_{3(g)} + O_{(g)} \xrightarrow{K_2} 2O_{2(g)}$ SLOW  Rate = $K_2[O_3][O]$
Overall: $2O_{3(g)} \rightarrow 3O_{2(g)}$

must remove intermediate

At equilibrium:
Rate forward = Rate reverse

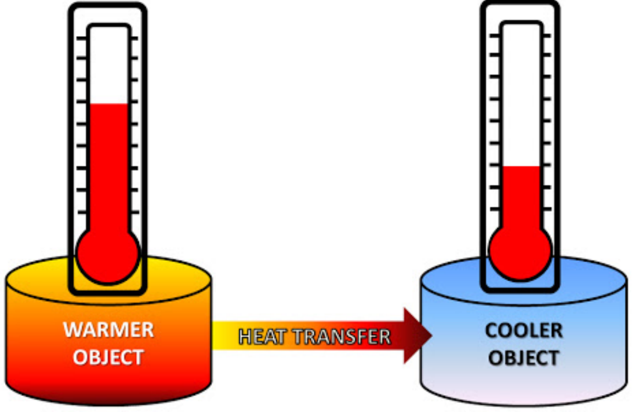
$\rightarrow K_1[O_3] = K_{-1}[O_2][O]$

$\frac{K_1[O_3]}{K_{-1}[O_2]} = [O]$  Solve for intermediate

Rate = $K_2[O_3]\frac{K_1[O_3]}{K_{-1}[O_2]}$  Sub into rate law

Combine like terms  $\left(\frac{K_1 K_2}{K_{-1}}\right)\frac{[O_3]^2}{[O_2]} \rightarrow K = \frac{[O_3]^2}{[O_2]}$

# UNIT 6 - THERMODYNAMICS



6.1 ENDOTHERMIC AND EXOTHERMIC PROCESSES

6.2 ENERGY DIAGRAMS

6.3 HEAT TRANSFER AND THERMAL EQUILIBRIUM

6.4 HEAT CAPACITY AND CALORIMETRY

6.5 ENERGY OF PHASE CHANGES

6.6 INTRODUCTION TO ENTHALPY OF REACTION

6.7 BOND ENTHALPIES

6.8 ENTHALPY OF FORMATION

6.9 HESS'S LAW

## 7-9% of exam

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# Unit 6: Thermodynamics

## Endothermic and Exothermic processes.

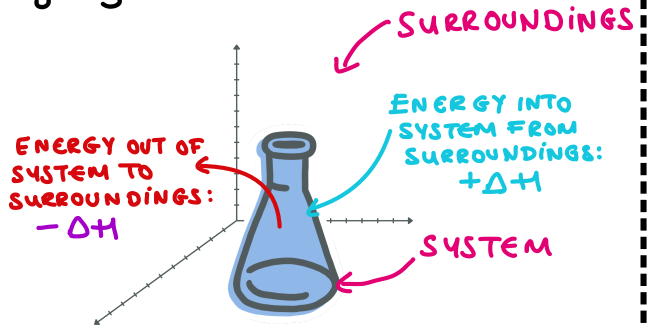
**Exothermic:** Energy is released into surroundings as heat.
- Temperature of surroundings increases.

**Endothermic:** Energy is absorbed from surroundings.
- Temperature of surroundings decreases.

**System:** The part of the experiment on which we focus our attention. Normally consists of reactants and products.

**Surroundings:** Everything else. Normally consists of the container and everything outside the container

When a solid is dissolved in water to form a solution, the thermometer that is used to record the temperature is considered to be part of the surroundings.



DON'T FORGET

**First law of thermodynamics:** Energy cannot be created or destroyed. It can change from one form to another.

| Endothermic examples | Exothermic examples |
|---|---|
| Melting | Freezing |
| Boiling | Condensation |
| Vaporization | Deposition |
| Sublimation | Changes involving: |
| Changes involving: | combining materials |
| Breaking | |
| Separation | |

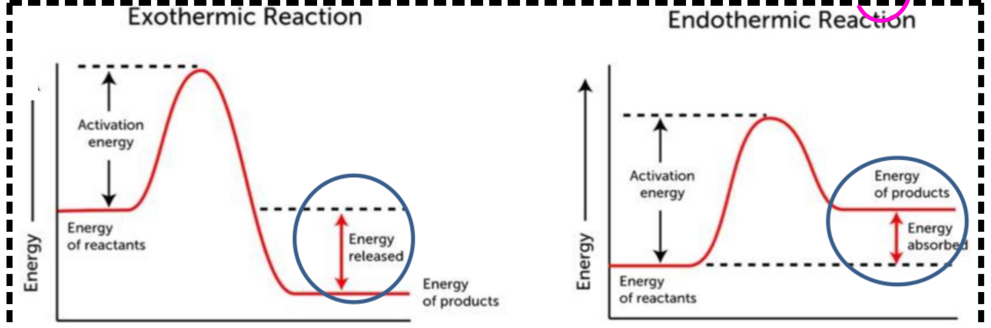
## Enthalpy and Heat

**Energy (E)** = capacity to do work or transfer heat
$\Delta E = q + w$

**Heat (q)** = the transfer of energy that takes place because of a difference in temperature, from hot to cold.
units: Joules or Kilojules

**Enthalpy (H)** = used to measure changes in energy for a constant-pressure system. Units: kJ/mol, kJ/mol rxn

REMINDER $\Delta H = q_p$ If $\Delta H > 0$, Endothermic, $+\Delta H$
If $\Delta H < 0$, Exothermic, $-\Delta H$
DON'T FORGET THE SIGN!!



## Thermal Equilibrium

When two substances at different temperatures come into contact:
The higher temperature substance will lose energy (via collision) and the lower temperature substance will gain energy (via collision)

$q\text{ loss} = -q\text{ gained}$

Eventually both objects will reach the same temperature and said to be at thermal equilibrium.

## Heat Capacity and Calorimetry

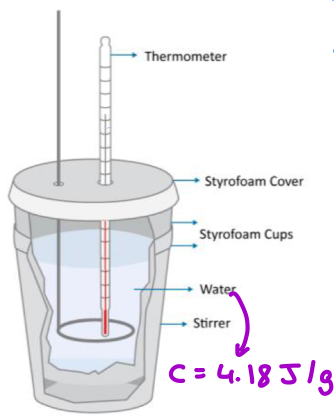
**Specific heat capacity:** Amount of energy needed to raise the temperature of one gram of a substance by one degree Celsius.

$$q = m\,c\,\Delta T$$

- q → Heat (joules / Calories)
- m → mass (kg) → sometimes n = moles
- c → Specific heat (J/kg °c)
- ΔT → Temperature (°c / K)

Calorimetry is the measure of the quantity of heat exchanged.

A calorimeter is a device used to measure the ~~heat transfer~~ by stopping the transfer of heat between the inside of the calorimeter and the surroundings.



$c = 4.18\ J/g°C$

To find (c) of a metal
- Heat metal to a known temperature and place into a calorimeter of water.
- Heat will transfer from metal to water to reach thermal equilibrium.

$$q(\text{metal}) = -q(\text{water})$$

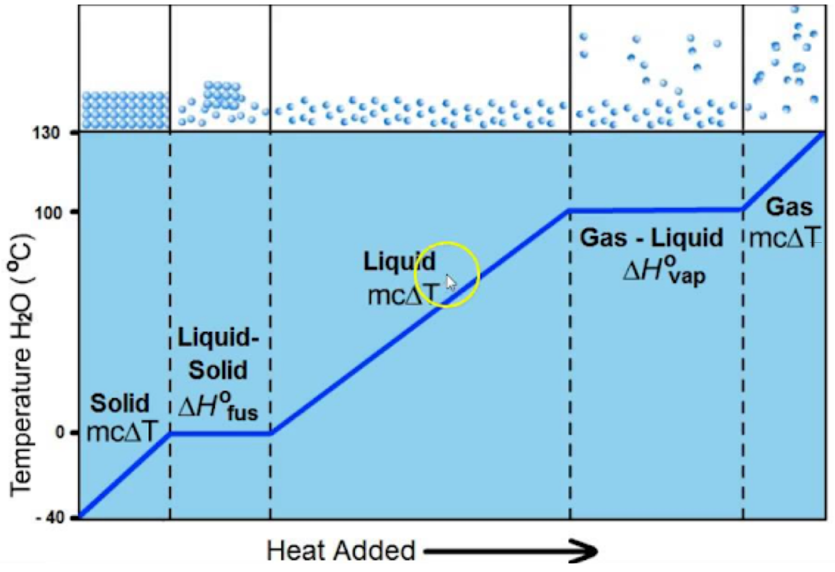
$$q = mc\Delta T$$

Sub in:

$$m_{(\text{metal})}\,C_{(\text{metal})}\,\Delta T_{(\text{metal})} = -\left[m_{(\text{water})}\,C_{(\text{water})}\,\Delta T_{(\text{water})}\right]$$

For two substances, when C is higher, ΔT is lower.

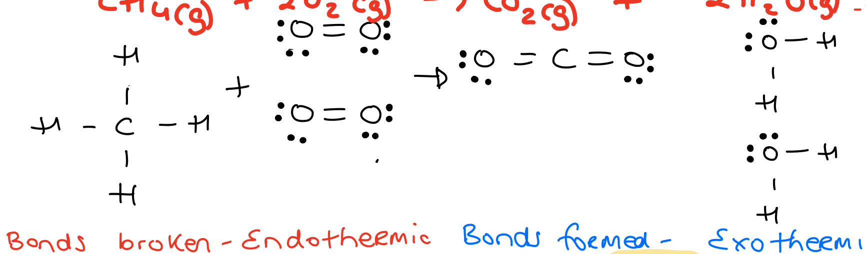
Molar heat capacity = C ÷ molar mass of that substance.



## Bond Enthalpies

**Endothermic** Energy required to break a bond
**Exothermic** Energy released when a bond is made

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -802\ kJ/mol_{rxn}$



Bonds broken - Endothermic $+\Delta H$
C−H: 4 × 413 = 1652
O=O : 2 × 498 = 996
2648 kJ

Bonds formed - Exothermic $-\Delta H$
C=O = 2 × 799 = 1598
O−H = 4 × 463 = 1852
3450 kJ

$$\Delta H_{rxn} = \Sigma \Delta H(\text{broken}) - \Sigma \Delta H(\text{formed})$$
$$= 2648\,kJ - 3450\,kJ$$
$$= -802\ kJ/mol_{rxn}$$

## Enthalpy of formation

$\Delta H^\circ_f$ represents the change in enthalpy associated with the formation (synthesis) of one mole of a compound from it's elements under standard conditions (1 atm and 25°C). $\Delta H^\circ_f$ for a pure element in it's standard state = 0.

$$\Delta H^\circ = \Sigma \Delta H^\circ_f \text{ products} - \Sigma \Delta H^\circ_f \text{ reactants}$$

REMINDER PAY ATTENTION TO PHASES!

## Hess's Law

- If equations are added together, add up total ΔH values
- If an equation is reversed, change sign of ΔH.
- If an equation is multiplied by N, multiply ΔH by N.

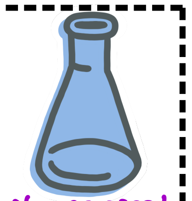
# UNIT 7 -EQUILIBRIUM

**7-9% of exam**

CollegeBoard AP

# Unit 7: Equilibrium

## Equilibrium

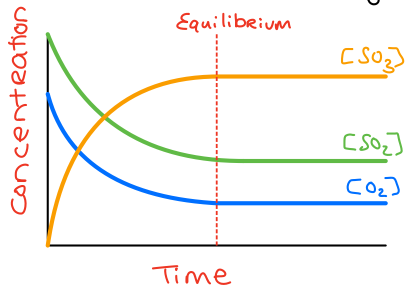


When equilibrium is reached:

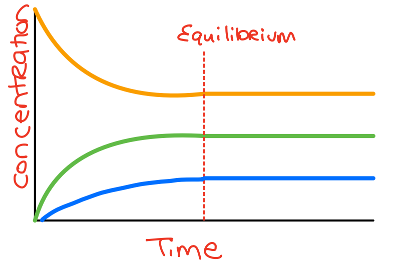
- Reactants and products are simultaneously present.
- The concentrations or partial pressures of all species remain constant
- No observable changes occur in the system
- The equilibrium state is dynamic; the forward and reverse processes continue to occur at equal rates, resulting in no net observable change.

Examples:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$



Start with all reactants, no products and achieve equilibrium.



Start with all products, no reactants and achieve equilibrium.

## Reaction Quotient and Equilibrium Constant

$$aA + bB \rightleftharpoons cC + dD$$

Q = Reaction Quotient

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

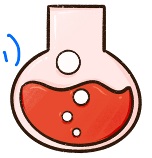
At any time in a reaction

K = Equilibrium Constant

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

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

At equilibrium



**Tips**

SOLIDS AND PURE LIQUIDS ARE NOT INCLUDED!

Example: $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

$$Q = \frac{[CO_2]}{[CH_4][O_2]^2}$$

## Direction of reaction

If $Q = K$, at equilibrium

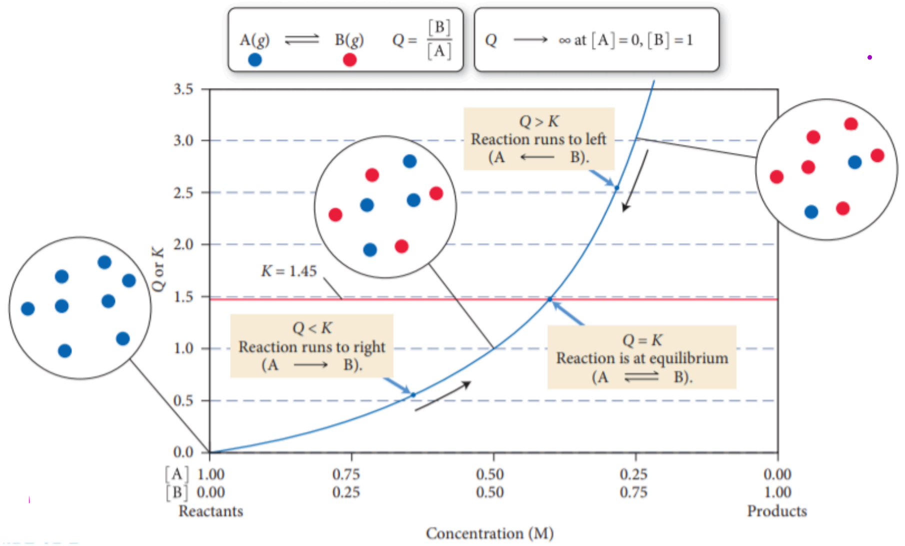
If $Q < K$, too many reactants.

Reaction proceeds left to right until $Q = K$ $K \rightarrow Q$

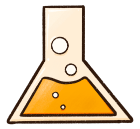
If $Q > K$, too many products

Reaction proceeds right to left until $Q = K$ $K \leftarrow Q$

## Q, K and direction of reaction



## Magnitude of K.



Small K values: Reactants favoured

Large K values: products favoured

## Properties of equilibrium constant

1. Reverse equation → Invert K.
2. Multiply co-efficients by a factor → Raise K to same factor
3. Add equations together → Multiply K constants

Example:

Reaction 1: $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ $K_1 = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$

Reaction 2: $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ $K_2 = \frac{[CO][H_2O]}{[CO_2][H_2]}$

Reaction 3: $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$ $K_3 = ?$

$$K_3 = \frac{1}{K_1} \times \frac{1}{K_2}$$

## Calculating Equilibrium concentrations

Ex. 1 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

At equilibrium $[H_2] = 0.100M$, $[I_2] = 0.100M$, $[HI] = 0.714M$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.714)^2}{(0.100)(0.100)} = 51.0$$

Ex. 2. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_c = 51.0$

Initial $[H_2] = [I_2] = 2.0M$, **Calc [Equil]**

| | $H_2$ + | $I_2$ ⇌ | $2HI$ |
|---|---|---|---|
| I | 2.0M | 2.0M | 0 |
| C | $-x$ | $-x$ | $+2x$ |
| E | $2-x$ | $2-x$ | $2x$ |

$[H_2] = 2 - 1.56 = 0.44$

$[I_2] = 2 - 1.56 = 0.44$

$[HI]^2 = 2(1.56) = 3.12$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} - 51.0 = \frac{2x^2}{(2-x^2)}, \quad x = 1.56$$

**Notes**

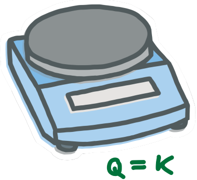
See more examples of ICE TABLES IN 'ICE ONE PAGER'!

## Equilibrium Concentrations

- Equilibrium concentrations of reactants and products depend on initial concentrations
- K is always the same at a given temperature, regardless of initial concentrations
- There is no such thing as law of conservation of moles (moles can change, grams cannot)

## Le Chatelier's principle

If a system at equilibrium experiences an external stress, the position of equilibrium will shift in the direction that relieves that stress.



- Concentration

| | | | |
|---|---|---|---|
| Add Reactant | ↓ Q | $Q < K$ | Shift right |
| Remove Reactant | ↑ Q | $Q > K$ | Shift left |
| Add product | ↑ Q | $Q > K$ | Shift left |
| Remove product | ↓ Q | $Q < K$ | Shift right |

Adding/Removing (s) or (l) / inert substance / catalyst: No shift

- Temperature

| | | | | |
|---|---|---|---|---|
| $\Delta H > 0$ (endo) | ↑ temp | ↑ K | $Q < K$ | Shift right |
| | ↓ temp | ↓ K | $Q > K$ | Shift left |
| $\Delta H < 0$ (exo) | ↑ temp | ↓ K | $Q > K$ | Shift left |
| | ↓ temp | ↑ K | $Q < K$ | Shift right |

- Volume / pressure

Gas: ↑P/↓V Shift to fewer moles of gas

↓P/↑V Shift to more moles of gas

Aqueous: Add $H_2O(l)$ Shift to more moles of (aq)

Remove $H_2O(l)$: Shift to fewer moles of (aq)

## Solubility Equilibrium

Solubility of insoluble salts

$$A_mX_n(s) \rightleftharpoons mA^+ + nX^-$$

$K_{sp} = [A^+]^m[X^-]^n = (ms)^m(ns)^n$ s = molar solubility

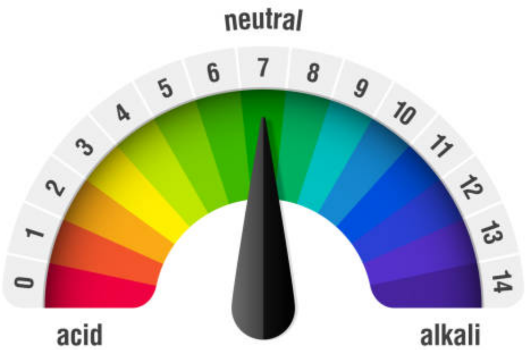
Precipitation: $Q_{sp} > K_{sp}$ Precipitate forms

$Q_{sp} < K_{sp}$ No precipitate forms

Common Ion effect:

- Solubility of a salt decreases when dissolved in a solution with an ion common with the salt.
- Solubility increases when an ion in solution reacts with an ion in the salt.

# UNIT 8 - ACIDS AND BASES



## 11-15% of exam

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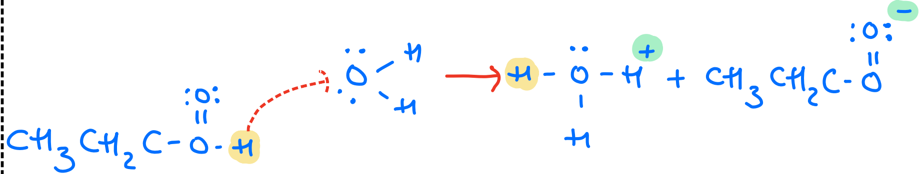
# Unit 8 Acids and Bases



$CH_3CH_2C(=O)-O-H + H_2O \rightarrow H_3O^+ + CH_3CH_2C(=O)-O^-$

Acid : $H^+$ donor  Base : $H^+$ acceptor  Conjugate acid  Conjugate base

water is amphoteric - can behave as an acid or base

$H_2O + HCO_3^- \rightarrow H_2CO_3 + OH^-$
ACID  BASE

$H_2O + HCO_3^- \rightarrow H_3O^+ + CO_3^{2-}$
BASE  ACID


Ms Kelleher

$pH = -\log[H_3O^+]$  $pOH = -\log[OH^-]$

$pH = -\log[H^+]$  $10^{-pH} = [H^+]$

Henderson-Hasselbach:
$pH = pKa + \log\left[\frac{[A^-]}{[HA]}\right]$

## Autoionization of water

$H_2O_{(l)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$
BASE  ACID  C.A.  C.B

$K_w = [H_3O^+][OH^-]$ @ 25°C , $K_w = 1\times10^{-14}$ very small!

$[H_3O^+] = \frac{1.0\times10^{-14}}{[OH^-]}$  $[OH^-] = \frac{1.0\times10^{-14}}{[H_3O^+]}$

## Pure water

$[H_3O^+] = [OH^-]$  $pH = pOH = 7$

$pK_w = 14.0$  $pH = -\log(1.0\times10^{-14})$ @ 25°C

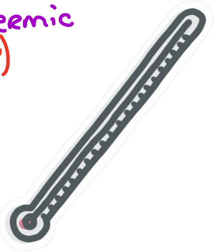
$pK_w = pH + pOH$

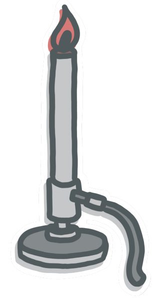
As temperature increases ↑ $pK_w$ decreases ↓

As temperature increases ↑ $K_w$ increases

Endothermic

| Temp. | $pK_w$ $(-\log K_w)$ | $K_w$ $(10^{-pK_w})$ |
|---|---|---|
| 10 | 14.5 | $3.2\times10^{-15}$ |
| 20 | 14.2 | $6.3\times10^{-15}$ |
| 25 | 14.0 | $1.0\times10^{-14}$ |
| 30 | 13.8 | $1.6\times10^{-14}$ |
| 40 | 13.5 | $3.2\times10^{-14}$ |





$aA + bB \rightarrow cC + dD$

$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$  $Q_p = \frac{P_C^{\,c} P_D^{\,d}}{P_A^{\,a} P_B^{\,b}}$

concentration  pressure (gases)

**Reaction Quotient:** Quantities of products or reactants at any time in a Reaction

DON'T FORGET SOLIDS (S) AND PURE LIQUIDS (l) ARE NOT INCLUDED IN Q

$Q_c \neq Q_p$

K = Equilibrium constant, used instead of Q when a system is at equilibrium.

$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$  $K_p = \frac{P_C^{\,c} P_D^{\,d}}{P_A^{\,a} P_B^{\,b}}$

K is dependant on concentrations or pressures of reactants and products. If temperature changes, K will change.

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

Directly proportional to K i.e. if products are favored, K is larger

Numerator (products)

Denominator (Reactants)

Inversely proportional to K, i.e if reactants are favoured, K is smaller

K > 1 : products > Reactants
K = 1 : products = Reactants
K < 1 : products < Reactants

K > 1000: Reaction goes to completion, no reverse reaction

K < 0.0001: the forward reaction does not take place.

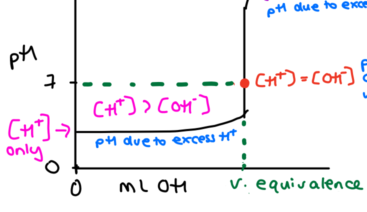
At Equilibrium Q = K

If Q > K, the numerator must decrease to make Q = K. Products decrease and reverse reaction is favoured

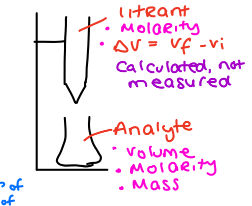
If Q < K, the numerator must increase to make Q = K, the products must increase and forward reaction is favoured

## Titration Curves

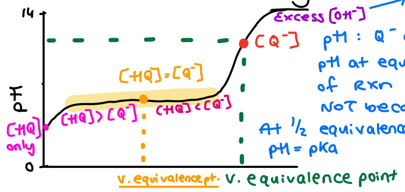
### Strong Acid ($H^+$) and Strong Base



pH = 7 due to auto dissociation of water not rxn of CA/CB with water



### Weak Acid (HQ) + Strong Base



pH : excess $OH^-$. ($Q^-$ is weak, negligible contribution)

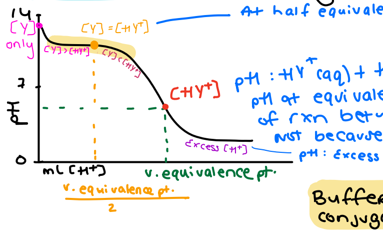
pH : $Q^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HQ_{(aq)} + OH^-_{(aq)}$

pH at equivalence point is basic because of rxn between conjugate base and water NOT because titrant is a strong base

At ½ equivalence pH = pKa

Buffer zone: weak Acid (HQ) and it's conjugate ($Q^-$) Resists change in pH upon addition of $OH^-$

### weak base (Y) + strong Acid



At half equivalence pOH = pKb ∴ pH = 14 - pKb

pH : $HY^+_{(aq)} + H_2O_{(l)} \rightleftharpoons Y_{(aq)} + H_3O^+_{(aq)}$

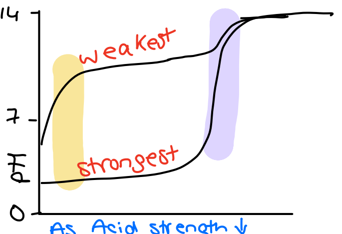
pH at equivalence point is acidic because of rxn between conjugate acid with water, not because titrant is a strong acid.

pH : Excess $H^+$ ($HY^+$ is weak and contribution is negligible)

Buffer zone: Weak Base (Y) and it's conjugate base ($HY^+$)

### Buffer zones

#### weak Acid + Strong Base



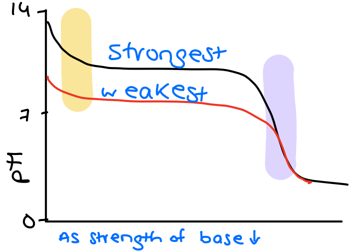
As Acid strength ↓ starting pH ↑

Bigger jump to buffer zone

Higher pH at equivalence pt

As Acid strength ↓, conjugate base strength ↑

#### weak base + Strong Acid



As strength of base ↓ starting pH ↓

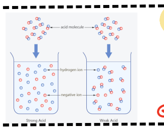
Bigger drop to buffer zone

Lower pH at equivalence pt.

As base strength ↓ conjugate acid strength ↑

### Strong Acids

Fully dissociate in water to produce $H_3O^+$/$H^+$ ions
HCl, HBr, HI, $HClO_3$, $HNO_3$ and $H_2SO_4$



### Strong Bases

Fully dissociate in water to produce $OH^-$ ions
LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
Group 1 + 2 metal hydroxides

## Effect of dilution on pH

$$M_1 \times V_1 = M_2 \times V_2$$

Example:

If volume doubles, concentration halves

| Original | Add 100ml → New | Change in pH |
|---|---|---|
| 100.0ml of 0.10M HCl | 200.0M of 0.05M HCl | 1.30 - 1.00 = 0.30 |
| 200.0ml of 0.50M NaOH | (0.50)(0.200) = (x)(0.300)<br>0.33M = x<br>300.0ml of 0.33M NaOH | 13.52 - 13.70 = -0.17 |
| 300.0ml distilled water | 400.0ml distilled water | pH = 7.00 |

* The larger the change in concentration, the larger the change in pH

No change

## Weak Acid and Base equilibrea

weak acids partially ionize in water to produce $H_3O^+$ ions

### Ka of weak acid

- Acid dissociation constant. A measure of acid strength
- Ka < 1 for a weak acid.
- A solution of weak acid involves equilibrium between an un-ionized acid and it's conjugate

$Ka = \frac{[H_3O^+][A^-]}{[HA]}$  $pKa = -\log(Ka)$

when [HA] = [A⁻], pH = pKa
when [HA] > [A⁻], pH < pKa
when [HA] < [A⁻], pH > pKa

when comparing two weak acids
Larger Ka/Kb = stronger acid/base
Smaller pKa/pKb = stronger acid/base

weak bases partially ionize in water to produce $OH^-$ ions

### Kb of weak base

- A solution of a weak base involves equilibrium between an un-ionized base and it's conjugate acid

$Kb = \frac{[HB^+][OH^-]}{[B]}$  $pKb = -\log(Kb)$

Adding a common ion to weak acid/base decreases % ionization

### % ionization

As $[H_3O^+]$ decreases, % ionization increases. Adding $H_2O$ increases ionization

Acid: $\frac{[H_3O^+]}{[HA]_{original}} \times 100\%$  Base: $\frac{[OH^-]}{[B]_{original}} \times 100$

## Buffers

pH range = pKa ± 1

- A solution that resists change in pH when a small amount of strong acid or it's base is added to solution
- Made of a weak acid and it's CB (salt) or weak base and it's C.A. (salt) e.g $HNO_2$ and $NO_2^-$ (sourced for e.g from sodium salt of C.A. like $NaNO_2$)

$[H_3O^+] = Ka$ . pH = pKa when concentrations of weak acid and conjugate base are equal.

# A Guide to Titrations and Finding the pH

## Strong Acid/Strong Base:

Here, there's nothing special happening – we either have excess acid or base, unless we're at the equivalence point where the pH=7

- 0mL: Here, you just have a solution of a strong acid with a known concentration.
    - $[HA]=[H^+]$ because it's a strong acid
    - $-\log[H^+]=pH$
- Prior to Equivalence point: Each mole of base neutralizes a mole of acid, but there is still an excess of acid.
    - Subtract moles of base added from the initial moles of acid and find new concentration of acid
    - Still, $[HA]=[H^+]$ because it's a strong acid
    - $-\log[H^+]=pH$
- At Equivalence Point: We've added sufficient base to exactly neutralize the acid, leaving just the salt present.
    - pH=7 because neither conjugate is able to interact with water to act as an acid or base
- Past Equivalence Point: Since all acid was neutralized at the equivalence point, any base added past that point is just making a solution of the strong base.
    - Subtract initial moles of acid from moles of base added to determine excess moles of base. Find concentration of base which is $[OH^-]$. $pOH=-\log[OH^-]$, $pH=14-pOH$

**Weak Acid/Strong Base:**

(Just invert pH and pOH completely throughout if you have a weak base/strong acid titration).

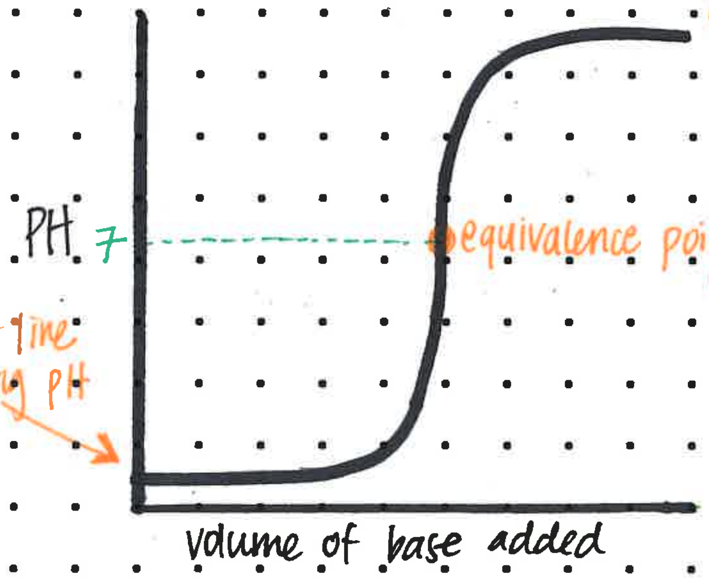
- 0mL: Here, you just have a solution of weak acid with a known concentration.
  - $HA \leftrightarrow H^+ + A^-$, so $K_a = \frac{[H^+][A^-]}{[HA]}$.
  - Since all $H^+$ and $A^-$ come from the dissociation of HA, $[H^+]=[A^-]$
  - If we set both as x, $K_a = \frac{x^2}{[HA]-x} \approx \frac{x^2}{[HA]}$ and pH=-log(x)
- Prior to equivalence point: Each mole of base neutralizes a mole of acid – creating a mole of base – but there is still an excess of acid.
  - mol $A^-$= (mol $OH^-$)$_{added}$
  - mol HA = (mol HA)$_{initial}$ – (mol $OH^-$)$_{added}$
  - Use Henderson-Hasselback here $pH = pK_a + \log\left(\frac{mol\ A^-}{mol\ HA}\right)$
    - HH on the equation sheet says concentration, but since they're always in the same solution, they have the same volume and that part cancels out!
- Half-equivalence point: When the volume of base added is exactly half of what is needed to neutralize the acid initially present. This means that half of the acid has been turned to salt, yielding an equal number of moles of acid and salt ($[A^-]=[HA]$ and mol $A^-$=mol HA).
  - $pH = pK_a + \log\left(\frac{mol\ A^-}{mol\ HA}\right) = pK_a + \log(1) = pK_a$
  - At this point, pH ALWAYS equals $pK_a$. This is important enough to remember because it comes up all the time.
- Equivalence Point: The equivalence point is the conjugate base's one moment of glory. Here, we have a solution of just the conjugate base. Find the concentration of it by dividing the moles of salt (equal to the initial moles of acid) and dividing by the new volume. Then you just have a solution of a weak base with a known concentration.
  - Find $K_b$ of the conjugate using $K_b = \frac{10^{-14}}{K_a}$
  - Then find new concentration of that salt by $[A^-] = \frac{mol\ HA_{initial}}{V_{new}}$
  - $A^- + H_2O \leftrightarrow HA + OH^-$, so $K_b = \frac{[HA][OH^-]}{[A^-]}$.
  - Since all HA and $OH^-$ come from the reaction of $A^-$ with water, $[HA]=[OH^-]$
  - If we set both as x, $K_b = \frac{x^2}{[A^-]}$ and pOH=-log(x)
  - Subtract 14-pOH=pH
- Past Equivalence Point: Since all acid was neutralized at the equivalence point, any base added past that point is just making a solution of the strong base.
  - Subtract initial moles of acid from moles of base added to determine excess moles of base. Find concentration of base. pOH=-log[$OH^-$], pH=14-pOH

# TITRATION CURVES

🟧 THINGS TO NOTE
🟪 CALCULATIONS

## STRONG ACID/STRONG BASE

*3 CALCULATIONS*



Levels off @ pH of base

Calculate excess $OH^-$ mol, then divide by the total volume to get $[OH^-]$ $-\log[OH^-] = pOH$ $14 - pOH = pH$

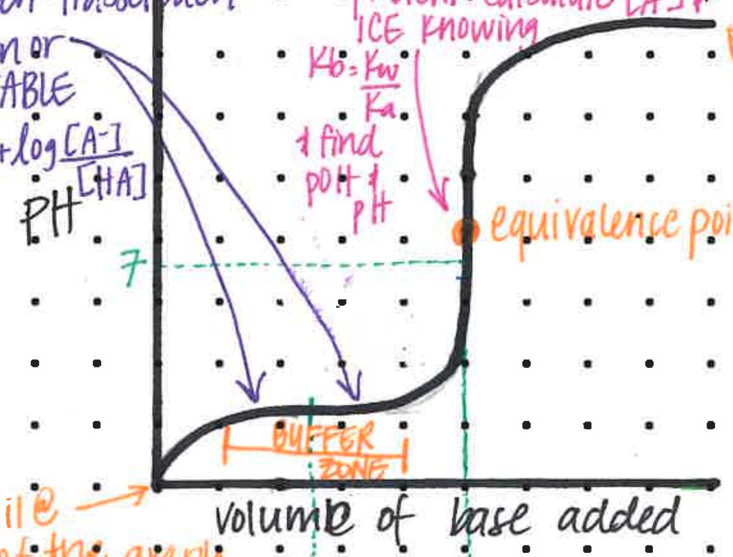
equivalence point @ pH = 7

Volume of base needed to reach equivalence point using $M_1V_1 = M_2V_2$

Straight line @ starting pH $-\log[H^+]$

## WEAK ACID/STRONG BASE

*5 CALCULATIONS*



Before & after half equivalence pt. Can use Henderson-Hasselbach equation or RICE TABLE $pH = pKa + \log\frac{[A^-]}{[HA]}$

$M_1V_1 = M_2V_2$ for amount of base needed. Hydrolysis problem. Calculate $[A^-]$ & ICE knowing $Kb = \frac{Kw}{Ka}$ & find pOH & pH

pH depends on excess base added. Calculate excess mol $OH^-$ & divide by total volume = $[OH^-]$. Find pOH & pH.

levels off @ pH of the base

equivalence point

Slightly above 7 (strong base) $[HA] = 0$

$pH = pKa$ or $[HA] = [A^-]$ & can find Ka of an unknown acid by $10^{-pKa}$ or $10^{-pH}$

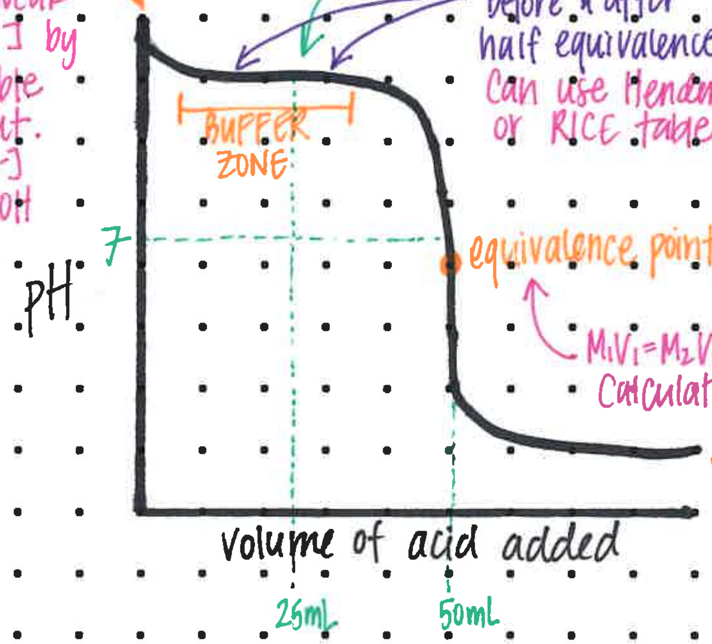
little tail @ start of the graph

Initial weak acid [ ] by using ICE table shortcut $X = [H^+]$ Find pH.

half equivalence point = MAXIMUM buffering $\frac{[HA]}{[A^-]} = 1$

## WEAK BASE/STRONG ACID

*5 CALCULATIONS*



Tail @ starting pH of base

Initial weak base [ ] by RICE table shortcut. $X = [OH^-]$ Find pOH

half equivalence point = MAXIMUM BUFFERING

Before & after half equivalence point. Can use Henderson-Hasselbach or RICE table. $pOH = pK_b + \log\frac{[BH^+]}{[B]}$

$pOH = pK_b$ or $\frac{[B]}{[HB^+]} = 1$. Find $K_b$ of unknown base by $10^{-pK_b}$ or $10^{-pOH}$

equivalence point ← slightly below 7 (strong acid) $[B] = 0$

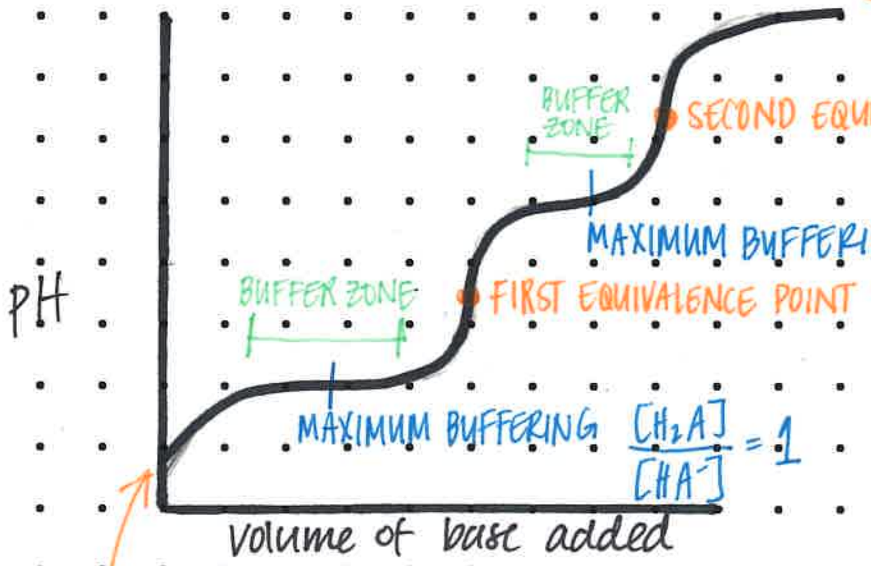
$M_1V_1 = M_2V_2$ for amount of acid needed. Hydrolysis problem. Calculate $[BH^+]$ & ICE knowing $K_a = \frac{K_w}{K_b}$ & find pH.

Levels off of pH of acid

pH depends on excess acid added. Calculate excess mol of $H^+$ & divide by total volume = $[H^+]$. Find pH.

## WEAK DIPROTIC ACID/STRONG BASE

*NO CALCULATIONS*



levels off @ pH of base

SECOND EQUIVALENCE POINT

MAXIMUM BUFFERING $\frac{[HA^-]}{[A^{2-}]} = 1$

FIRST EQUIVALENCE POINT

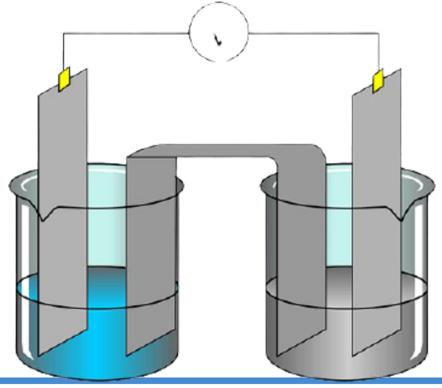
MAXIMUM BUFFERING $\frac{[H_2A]}{[HA^-]} = 1$

tail @ start of graph!

EXAMPLES OF WEAK DIPROTIC ACIDS: $H_2C_2O_4$ OR $H_2CO_3$

*You just really need to know the shape of graph and identify 2 equivalence points*

# UNIT 9 - APPLICATIONS OF THERMODYNAMICS



| | |
|---|---|
| 9.1 | INTRODUCTION TO ENTROPY |
| 9.2 | ABSOLUTE ENTROPY AND ENTROPY CHANGE |
| 9.3 | GIBBS FREE ENERGY AND THERMODYNAMIC FAVORABILITY |
| 9.4 | THERMODYNAMIC AND KINETIC CONTROL |
| 9.5 | FREE ENERGY AND EQUILIBRIUM |
| 9.6 | COUPLED REACTIONS |
| 9.7 | GALVANIC (VOLTAIC) AND ELECTROLYTIC CELLS |
| 9.8 | CELL POTENTIAL AND FREE ENERGY |
| 9.9 | CELL POTENTIAL UNDER NONSTANDARD CONDITIONS |
| 9.10 | ELECTROLYSIS AND FARADAY'S LAW |

**7-9% of exam**

CollegeBoard AP

# Unit 9: Applications of Thermodynamics

## Entropy

Entropy is a measure of how dispersed (spread out) the energy of a system is at a specific temperature.

Entropy increases when..

- Matter / Energy spreads out
- a substance changes phase
  - solid → liquid
  - liquid → gas
  - solid → gas

- Particles occupy a larger volume
- Gas expands to larger volume (constant temp)
- Total moles of gas products > Total moles of gas reactants
- Temperature of a gas increases → broader distribution of kinetic energies of gas particles

The temperature increases.

## Calculating Entropy

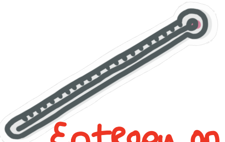
$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

Note $\Delta S^\circ = 0$ only at 0 Kelvin (−273°)

$\Delta H^\circ_f = 0$ for a pure element, This isn't the case for $\Delta S^\circ$

## Temperature, Entropy and Gibbs Free Energy

| $\Delta H^\circ$ | $\Delta S^\circ$ | Symbols | $\Delta G^\circ<0$, favored at | Reaction driven by |
|---|---|---|---|---|
| <0 | >0 | < > | all temp | Enthalpy + Entropy |
| >0 | <0 | >< | no temp. | |
| >0 | >0 | >> | high temp | Entropy only |
| <0 | <0 | << | low temp. | Enthalpy only |



## Gibbs free energy

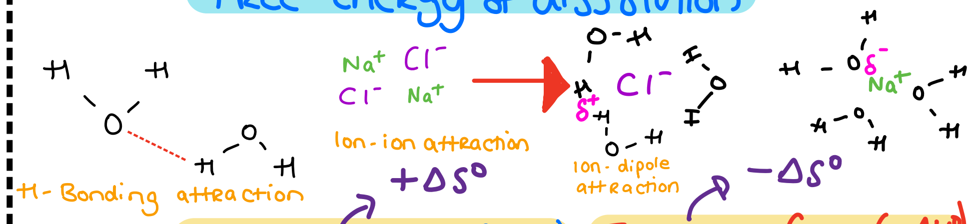
$\Delta G^\circ$ = Energy that is "free" and available to do work.
- Standard state (1.0 M, 1.0 atm, 298 K)

$$\Delta G^\circ = \sum \Delta G^\circ_f \text{ products} - \sum \Delta G^\circ_f \text{ reactants}$$

$\Delta G^\circ < 0$ : Thermodynamically favored (spontaneous)

$\Delta G^\circ > 0$ : Thermodynamically unfavored (non spontaneous)

## Free energy of dissolution



Takes to break ($+\Delta H^\circ$) Frees to form ($-\Delta H^\circ$)

Favorable: $-\Delta H^\circ, +\Delta S^\circ$ Unfavorable: $+\Delta H^\circ\ -\Delta S^\circ$

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

If $\Delta G^\circ > 0$ : Thermodynamically unfavored - Slightly soluble / insoluble salts

If $\Delta G^\circ < 0$ : Thermodynamically favorable - Soluble salts **S.N.A.P.**

## Kinetic Control

- $\Delta G^\circ$ is negative, occurs extremely slowly
- Large activation energy, catalyst used to lower it

## Coupled Reactions

Making a reaction with a $\Delta G^\circ > 0$ occur.

1. External source of energy
2. A thermodynamically favored rxn. coupled with unfavored

Share a common intermediate

Use Hess's Law to determine $\Delta G$

Sum of reactions $\Delta G^\circ$ values <0, ∴ thermodynamically favorable

| Galvanic (Voltaic) Cell | Electrolytic Cell |
|---|---|
| Thermodynamically favorable. | Thermodynamically unfavorable |
| Anode and cathode in separate chambers (half cells). | Anode and cathode often in the same chamber. |
| Salt bridge needed | Power source needed (e.g battery) |
| Produces electrical energy (+V) | Uses electrical energy (−V). |

Both cells:

- Oxidation at anode, Reduction at cathode
- Require ion flow in the cell for a reaction to occur
  Cations → Cathode; anions → anode

## Faraday's Law

$$I = \frac{q}{t}$$

I = current, Amperes (A)
q = amount of charge
t = time, seconds (s)

- Moles of $e^-$ determined from chemical equation
- Pay attention to unit
- Use dimensional analysis
- Moles and Molar mass used: g → moles

## Cell potential and Free energy

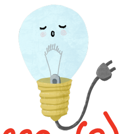
$$E^\circ \text{cell} = E^\circ \text{cathode} - E^\circ \text{anode}$$

- Units: Volts (V)
- Standard reduction potentials $E^\circ$red (1 M solutions, 1 atm, 25°C) used to compare reduction potentials
- For an oxidation process, the reduction half reaction equation and sign of voltage are reversed.
- Don't multiply ½ rxn. potentials by coefficients in equation.

$E^\circ$ cell > 0 : thermodynamically favorable Galvanic Cells

$E^\circ$ cell < 0 : thermodynamically unfavorable Electrolytic cells

$$\Delta G^\circ = -nFE$$



Faraday's constant, F is the amount of charge (q) in coulombs (C) per mole of electrons. F = 96,485 C/mol $e^-$

n = moles of electrons

## Non standard conditions

Standard conditions (1M solution, 1atm gas, 25°C)

Q = 1, not at equilibrium. COMPARE Q to K

- Voltaic cell (K>1)
  - ↑Q ↓ $E^\circ$cell closer to equilibrium
  - ↓Q ↑ $E^\circ$cell further from equilibrium
- Electrolytic cell (K<1
  - ↑Q ↑ $|E^\circ\text{cell}|$
  - ↓Q ↓ $|E^\circ\text{cell}|$

Absolute value because these cell potentials are negative.

## Equilibrium and Thermodynamics

At Non-standard states

$$\Delta G = \Delta G^\circ + R.T\ln Q$$

$$E = E^\circ - \frac{R.T}{n.F}\ln Q$$

Nernst Equation

R = 8.314 J mol⁻¹ K⁻¹

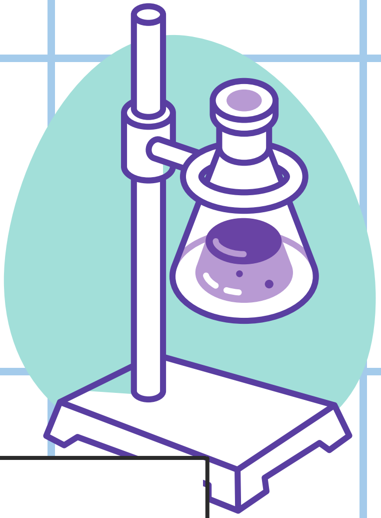
At Equilibrium

Q = K, ΔG = 0

$$K = e^{\frac{-\Delta G^\circ}{R.T}} = e^{\frac{E^\circ n.F}{R.T}}$$

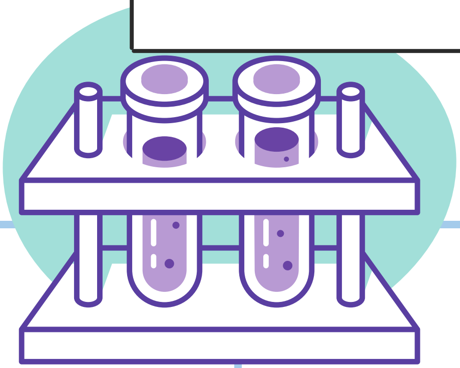
If $\Delta G^\circ < 0$, $E^\circ > 0$, K >> 1 Thermodynamically favorable

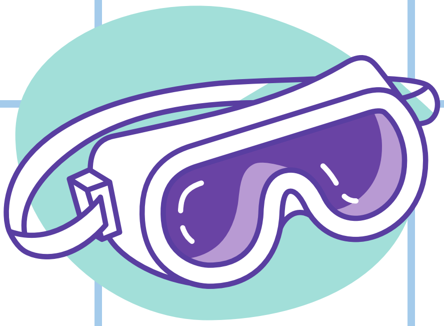
If $\Delta G^\circ > 0$, $E^\circ < 0$, K << 1 Thermodynamically unfavorable

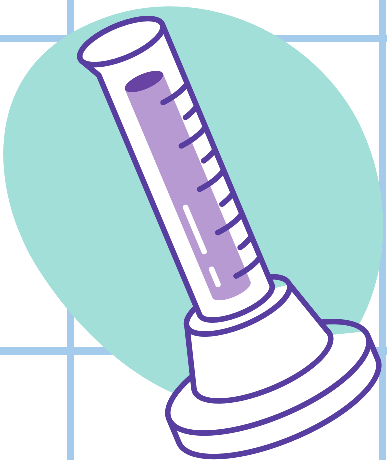


# THOU SHALT NOT FORGET!

2022 AP Chemistry Review Mr. Nackers







# AP Chemistry

# Thou Shalt Not Forget

*Adapted from the original document by Dan Reid*

## Unit 1: Atomic structure and properties

1. When an electron is in a higher the energy level, it is farther away from the nucleus and therefore has less Coulombic attraction to the nucleus and is therefore easier to remove (...it has a lower 1st ionization energy.)
2. Moving across a row on the periodic table, the $Z_{eff}$ increases, therefore the valence electrons are more attracted to the nucleus, therefore the atomic radius decreases and the ionization energy increases.
3. When reading a PES graph, the higher the peak, the more electrons there are in that sublevel, and a larger binding energy means that the electrons are closer to the nucleus.
4. $1s^2\ 2s^2\ 2p^6 3s^2\ 3p^6 4s^2\ 3d^{10}\ 4p^6$
5. When writing the electron configuration for a cation, remove the valence electrons first...the ones in the p-orbital and s-orbital...then you can remove d-orbital electrons if necessary. (note: if the last orbital filled using the Aufbau principle was a d orbital, the s orbital electrons are still the first to be removed).
6. Isotopes of an element have the same number of protons, but different numbers of neutrons.
7. Mass spectroscopy graphs measure atomic masses of isotopes.
8. Elements in the same group (vertical columns) have similar chemical and physical properties.
9. Metals are on the left side of the zig-zag line and nonmetals are on the right side of this line on the periodic table.
10. Cations (+) are smaller than their atoms since you are removing valence electrons that are farther from the nucleus; cations also have a higher Zeff, so a greater positive force pulling on electrons. Anions (−) are larger than their atoms since adding extra electrons increases electron-electron repulsions.

## Unit 2: Molecular and ionic compound structure and properties

1. Covalent bonds are formed between two nonmetals sharing electrons.
2. Ionic bonds are formed when a metal transfers electrons to a nonmetal and the opposite charges attract.
3. The greater the electronegativity difference between 2 atoms, the more polar the bond becomes.
4. Combustion reactions make $CO_2$ and $H_2O$.
5. Carbon makes a total of 4 bonds in a compound.
6. Bond angles: 4 domains = 109.5° 3 domains = 120° 2 domains = 180°

7. Hybrid orbitals: 4 domains = $sp^3$ 3 domains = $sp^2$ 2 domains = sp
8. Asymmetrical molecules = dipoles DO NOT cancel = polar molecule; symmetrical = dipoles cancel = nonpolar molecule
9. Single bond = sigma double bond = sigma + pi bond triple bond = sigma + 2 pi bonds
10. Lattice energy is the energy to break an ionic bond in a compound. Lattice energy increase as the ion's charge increases. Lattice energy decreases as the radii of the ions increase. (This can be deduced from Coulomb's Law.)
11. Formal charge involves comparing the # of valence electrons an atom has to the # of electrons around it in the Lewis structure. (Remember to "split" the bonded electrons evenly between the atoms.)
    Formal charge = valence electrons – lone pair electrons -1/2 bonding electrons
12. Obey the octet rule first when drawing the Lewis Dot Structure then use formal charge if necessary. Extra electrons can go on the larger central atom, and if you have too few electrons, start making some double or triple bonds.
13. Metallic bonds are between metals, and they ALWAYS conduct electricity, and their hardness varies.
14. Interstitial alloys are made when a smaller atom fits into the gaps between the larger atoms of a metallic crystal. Substitutional alloys are made when the radii of the metals are similar in size and are substituted into the crystal lattice.

## Unit 3: Intermolecular forces and properties

*Intermolecular forces*

1. IMF's from weakest to strongest: London Dispersion, dipole-dipole, hydrogen bonding, ion-dipole.
2. All molecules contain LD forces, and this force gets stronger as the molecule is larger...Larger electron cloud = more LD = more polarizable.
3. All polar molecules contain dipole-dipole forces, and this force gets stronger as the molecule is more polar.
4. H-bonds are between a NOF in one compound to a hydrogen that's already bonded to a NOF in another compound.
5. Boiling point and melting point increase as IMF's increase.
6. Vapor pressure and volatility decrease as IMF's increase.

*Structures of solids*

1. Molecular solids have low melting/boiling points, and they do not conduct electricity.
2. Ionic solids have high melting/boiling points, and don't conduct electricity as a solid, but DO conduct as a liquid or (aq).
3. $SiO_2$ (quartz) and diamonds are covalent network solids, and they have very high boiling/melting points.
4. When a molecular solid melts or boils, it is the IMF's between the molecules that break, not the covalent bonds.

*Gases:*

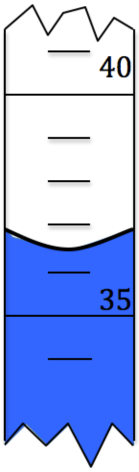
1. Gas mixtures are homogeneous b/c of the constant random motion of the particles.
2. Gases are compressible b/c of the large spaces between the particles.
3. Gas pressure is caused by collisions of particles with the walls of the container. More Collisions = More Pressure
4. P and V are inversely related...doubling the volume of a container will cut the pressure of the gas in half.
5. T and V are directly related...If you heat a balloon, it will expand.
6. T and P are directly related...If you heat a rigid container, the pressure of the gas will increase.
7. PV=nRT Units: Temperature = Kelvin; Volume = Liters; Pressure = atm Use this gas constant→ R=0.08206
8. One mole of an ideal gas = 22.4 Liters ONLY at STP!!
9. Gas pressure and # of moles are directly related...if you double the mole of gas in a container, the pressure will double.
10. Molar Mass = dRT/P The "d" stands for density in units of g/L Use this gas constant→ R=0.08206
11. The more molar mass a gas has, the slower it moves at a given temperature.
12. Temperature = Average Kinetic Energy (Gases at the same temperature have the same average kinetic energy.)
13. When collecting a gas by water displacement: $P_{total} = P_{dry\ gas} + P_{water\ vapor}$
14. Real gases behave most like an ideal gas at high temperature and at low pressure. The more polar a gas is and the larger a gas is, the more it will **deviate** from ideal behavior. Consequently, small, nonpolar gases are the most ideal.

*Solutions and mixtures*

1. Compounds can be separated into elements by chemical changes, and mixtures can be separated by physical changes.
2. Filtering separates mixtures based on differences in particle size...the large particles are trapped on the filter paper while the soluble component goes through the filter paper and stays in the "filtrate".
3. Distillation separates mixtures based on differences in boiling point.
4. Chromatography separates mixtures based on differences in polarity.
5. In paper chromatography, the component that is most similar in polarity to the "mobile phase" moves up the farthest.
6. Density = mass/volume
7. The % composition by mass for a pure compound does not change.
8. $M_1V_1 = M_2V_2$ This is not on the formula sheet, but it is extremely useful for dilution calculations.

*Laboratory:*

1. When reading a volume of a liquid in a container, you can estimate by reading in between the graduated markings. That can give you one more sig. fig. in your volume. Read at the bottom of the meniscus. For example, in the picture you would read this as 36.5 and not 37 or 37.0.
2. Ranking measuring devices from least precise to most precise→ beaker, graduated cylinder, volumetric flasks, burette



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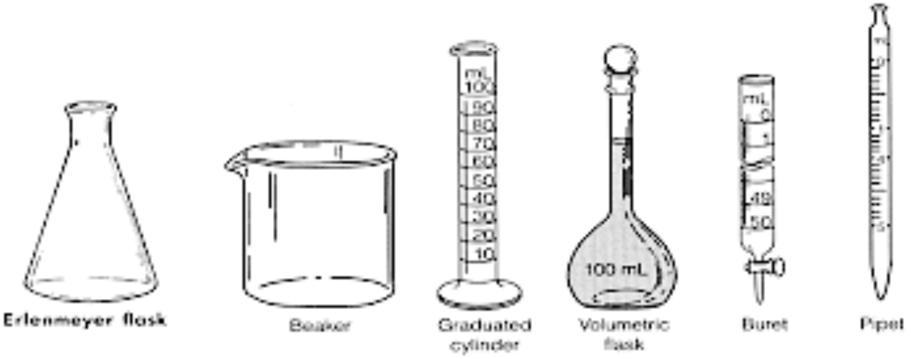
(The volumetric flask only has ONE line on it to measure one specific volume.)



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## Unit 4: Chemical reactions

1. $H_2O_2N_2Cl_2Br_2I_2F_2$ -- the diatomic elements ("I Have No Bright Or Clever Friends" or just "Honclbrif". When they are in a compound, their # of atoms can vary.
2. Empirical formula rhyme→

% to mass
mass to mole
divide by small
times until whole

*...Get the simplest whole # ratio of the moles (or atoms) in the compound.*

3. The molecular formula for a compound is a whole # multiple of the empirical formula ratio.
4. % yield = (experimental/theoretical) x 100%
5. % error= (experimental - theoretical)/theoretical x 100%
6. The amount of product for a reaction is determined by the limiting reactant.
7. Mass is conserved during both chemical and physical changes.

## Unit 5: Kinetics

1. In order for a reaction to occur, particles must collide at the correct orientation & with a minimum energy to break bonds...(This minimum energy is called the activation energy...the height of the "hill".)
2. How to write a rate law for an elementary step... $2A + B \rightarrow C + D$ Rate = $k[A]^2[B]^1$
3. Rate constant (k) Units: 1st order = $s^{-1}$; 2nd order = $M^{-1}s^{-1}$
4. Graphs: 1st order is linear for ln[A] vs time; 2nd order is linear for 1/[A] vs time ... Absolute value of the slope = k
5. Ways to speed up a reaction: (1) Add a catalyst...lowers the activation energy (2) Increase reactant concentration...more collisions (3) Increase surface area...more collisions (4) Increase pressure of gases...increases the concentration of the gas, so there are more collisions (5) increase temperature...more collisions AND more of them have the minimum activation energy.
6. ½ life for a 1st order process: $t_{1/2} = 0.693/k$
7. A 1st order reaction has a constant half-life regardless of the initial concentration. (Radioactive decay is a 1st order process.)
8. The taller the "hill" (or activation energy) the slower the reaction.
9. The slow step (rate-determining step) will dictate the speed of the reaction, and this step will determine the rate law.
10. Reaction Mechanisms: Intermediates are produced in one step and used up in a later step.
11. Reaction Mechanisms: Catalysts are used up in one step, and produced in a later step.

## Unit 6: Thermochemistry

1. Exothermic reactions: (−) ΔH; feels hot; heat is a product; temperature goes up…(endothermic is the opposite.)
2. $\Delta H_{rxn}$ = Bonds broken − Bonds formed…(reactant bonds are broken; product bonds are formed)
3. Breaking bonds is endothermic. Forming bonds is exothermic.
4. $\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$ ...Don't forget to multiply by the coefficients!!
5. If a reaction is exothermic, then the bonds formed in the products are stronger/more stable than the reactant bonds.
6. Doubling a reaction? ΔH will double. Reversing a reaction? The sign for ΔH changes. Adding reactions? Add the ΔH's.

## Unit 7: Equilibrium

1. $K_{eq}$ = [products]$^x$/[reactants]$^y$ … x and y represent the coefficients in the balanced chemical equation.
2. Only (aq) and (g) appear in an equilibrium expression. Use [ ] for Molarity and ($P_{gas}$) for atm.
3. A large $K_{eq}$ means that there are more products at equilibrium. A small $K_{eq}$ means there are more reactants at equilibrium.
4. Reversing a reaction? 1/$K_{eq}$ Doubling a reaction? $(K_{eq})^2$ Adding reactions? Multiply the K's together
5. Le Chatelier's Principle: It's all about determining Q!! If Q >$K_{eq}$ , then the reaction shifts to the left, towards the reactants.
6. Catalysts and inert gases DO NOT shift an equilibrium.
7. Changes in pressure (caused by changing the volume of a container) can shift an equilibrium ONLY IF the # of gas particles are different on each side...An increase in the pressure favors a shift in the equilibrium towards the side with LESS moles of gas. (Reminder: As V↓ , P↑)
8. Molar solubility is the moles/L concentration of the particular species in a saturated solution at equilibrium
9. Solubility Equilibrium: 2 ions....$K_{sp} = x^2$ ; 3 ions...$K_{sp} = 4x^3$ "x" = Molar Solubility in units of moles/Liter. Some people use "s" as the variable instead of x (see topic 7.11)
10. The larger the "x" value, the more soluble the salt is.
11. If Q > $K_{sp}$, a precipitate forms.
12. Group I cations ($Na^+$,$K^+$, $Li^+$) $NH_4^+$, and $NO_3^-$ salts are always soluble in water. These are usually the spectator ions in a chemical reaction

## Unit 8: Acids and bases

1. The pH of acids are less than 7, and bases are greater than 7. The pH of pure water is only 7 when the temp. is 25°C.
2. Acids donate [$H^+$]; bases accept [$H^+$].
3. The hydronium ion is $H_3O^+$. [$H^+$] is a proton.
4. Strong acids: $HNO_3$ $H_2SO_4$ $HClO_4$ and HBr, HI, HCl…"NO SO ClO 3, 4, 4 and BrICl"
5. Strong bases: Group 1 hydroxides Group 2 hydroxides *Some Group II hydroxides are only slightly soluble, but whatever dissolves can completely ionize.
6. pH = −log [$H^+$] [$H^+$] = $10^{-pH}$
7. The stronger the acid, the weaker its conjugate base.
8. Acid-Base reactions favor the direction of the "strong side" to the "weak side"...If K>1, then the reactants are stronger.
9. [$H^+$] =Square Root of $M_aK_a$…(This shortcut only works if "x" is really small compared to $M_a$ . Also, don't use this shortcut if you are given the pH of the solution and you are asked to solve for $K_a$ because the pH can be used to find "x" in the ICE box.)
10. "x" in the ice box calculation is [$H^+$] for a weak acid, and [$OH^-$] for a weak base.

11. % Ionization of a weak acid = $[H^+]$ /$M_a$
12. % ionization increases as the acid concentration decreases...adding more water will increase the amount of ionization.
13. If a salt contains a conjugate base of a weak acid, the salt is going to be slightly basic...CBOWA's are (-) ions.
14. If a salt contains a conjugate acid of a weak base, the salt is going to be slightly acidic...CAOWB's are (+) ions.
15. If a salt contains conjugates of strong acid/bases, the ion is neutral. Example -- KBr is a neutral salt (KOH + HBr)
16. A larger $K_a$ value means a stronger acid. A larger $K_b$ means a stronger base.
17. Relative strengths of acids: (a) Smaller cations are more acidic. (b) More (+) charge on the cation makes it more acidic. (c) More oxygens (or more electronegative atoms) on an anion makes it more acidic since the proton is "more ionizable".

*Titrations and buffers*

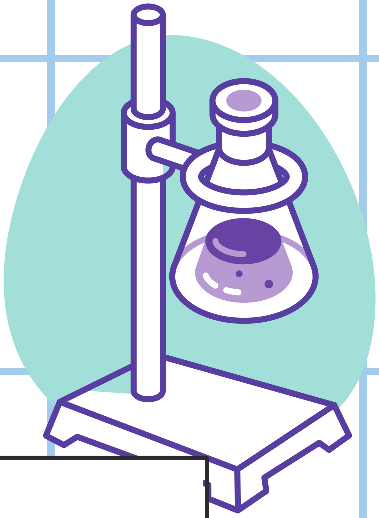
1. Buffers are created by a weak acid + CB (salt) or by a weak base + CA (salt).
2. $[H^+] = M_aK_a/[\text{salt}]$...You can use # of moles instead of molarity in this formula.
3. Adding a common ion to a weak acid (or base) decreases the % ionization, and therefore the pH gets closer to 7.
4. $M_aV_a= M_bV_b$ ...This is only true at the equivalence point.
5. Titrations: Weak acid + Strong Base has a pH at the equivalence point that's above 7. Weak Base + Strong Acid has a pH at the equivalence point that's below 7. Strong Acid + Strong Base has a pH =7 at the equivalence point.
6. pH = $pK_a$ at the ½ equivalence point for a "weak + strong" titration. Also, when pH = pKa, then $[HA] = [A^-]$
7. More buffer capacity = more moles of weak acid & CB (or weak base and CA).

## Unit 9: Applications of thermodynamics

1. Thermodynamically favorable (spontaneous) reactions have a $(-)\Delta G$.
2. Reactions with $(-)\Delta H$ and $(+)\Delta S$ are ALWAYS thermodynamically favorable…"enthalpy driven & entropy driven"
3. Reactions that increase the # of moles of gas have a $(+)\Delta S$.
4. If $\Delta G$ is $(-)$, then $K_{eq} > 1$.
5. $\Delta H$ and $\Delta S$ are usually NOT given in the same units!! When using $\Delta G^o = \Delta H^o - T\Delta S^o$, make sure they match units.
6. $\Delta G = 0$ at equilibrium.
7. When using $\Delta G^o = -RT \ln K$, the value for R is 8.314 J/mol K so the answer for $\Delta G$ will be in the units of Joules.
8. Sometimes a reaction with a $(-)\Delta G$ does not proceed at a measurable rate. They are said to be under "kinetic control." High activation energy is a common reason for a process to be under kinetic control.

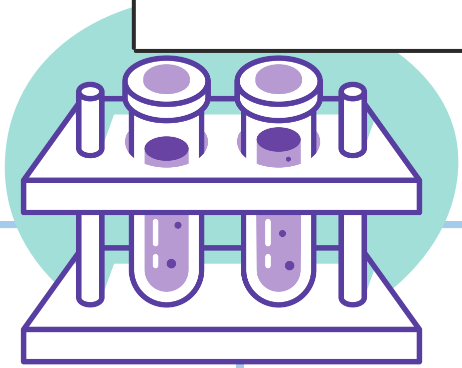
*Electrochemistry:*

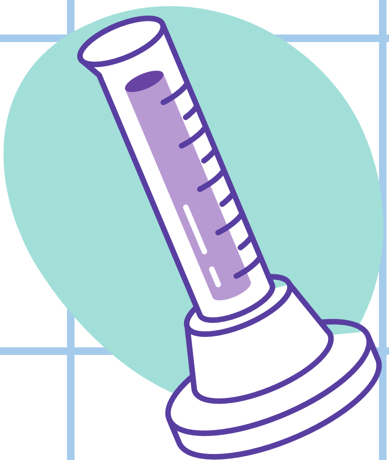
1. Oxidation #'s: H = +1 (except in a hydride when it is -1) O = −2 (except in a peroxide when it is -1).
2. LEO goes GER … Oxidation always occurs at the anode in both a battery and an electrolytic cell.
3. Electrons in a battery flow from anode (−) to cathode (+).
4. Salt bridge: Cations flow to the cathode, and the anions flow to the anode.
5. While a battery is discharged, the cathode gains mass and the anode loses mass.
6. If you reverse a reaction, the sign of $E^o{}_{cell}$ changes, but if you double a reaction, $E^o{}_{cell}$ DOES NOT change!!
7. $E^o{}_{cell} = E^o{}_{Red\ (GER)} - E^o{}_{Red\ (LEO)}$ (The other way to calculate $E^o{}_{cell} = E^o{}_{Reduction} + E^o{}_{Oxidation}$ ...but that involves reversing one of the reactions and changing the sign for $E^o{}_{Red}$)
8. The half-reaction with a more (+) $E^o{}_{Red}$ is the reaction that takes place at the cathode...GER.
9. When adding the two half reactions together, the electrons MUST cancel out.
10. $\Delta G^o = -nFE^o$ If $\Delta G^o$ is (−), then $E^o{}_{cell}$ is (+). Reminder: n = # of electrons transferred
11. If Q increases, then the voltage ($E^o{}_{cell}$) of the battery goes down.
12. Electroplating/Electrolysis Calculation: grams = (Molar Mass of the metal)(amps)(seconds)/(n)(F) … g=(MM)(I)(t)/nF



# LABORATORY

2022 AP Chemistry Review Mr. Nackers





# Quick Guide to Experimental Procedures

## Gravimetric Analysis:

| | | | | |
|---|---|---|---|---|
| **Weighing the sample to be analyzed.** | **Dissolving this sample in water.** | **Adding a suitable chemical to form a precipitate.** | **Filtering to collect the precipitate** | **Repeated drying and weighing until a constant mass of precipitate is obtained.** |

## Common Mistakes:

- **Precipitate is not dry when you take the final mass.**
    - Results in the appearance of more precipitate than was actually produced because some mass is water.
    - Percent yield would be higher than it should be.

## Common Applications:

- Mixtures of solids—determining the amount of a particular ion in a solution

## Important to Remember:

- All sodium, nitrate, ammonium, and potassium compounds are soluble. Net ionic equations would not include these ions.

# Quick Guide to Experimental Procedures

## Making a solution:

**The AP Readers would prefer that you use a pipet at this point to make sure you hit the line perfectly.**

**(a) An amount of solute is weighed out on an analytical balance and then**

**(b) A portion of the solvent is added to the volumetric flask.**

**(c) The mixture is swirled until *all* of the solute is dissolved.**

**(d) Additional solvent is added up to the mark on the volumetric flask.**

## Common Mistakes:

- **Overfilling the volumetric flask**
  - Results in a dilute solution
- **Not using distilled water.**
  - Other ions could affect the experiment for which the solution is used
- **Not using a volumetric flask (beaker or Erlenmeyer instead)**
  - Loss of precision in concentration of prepared solution

## Common Applications:

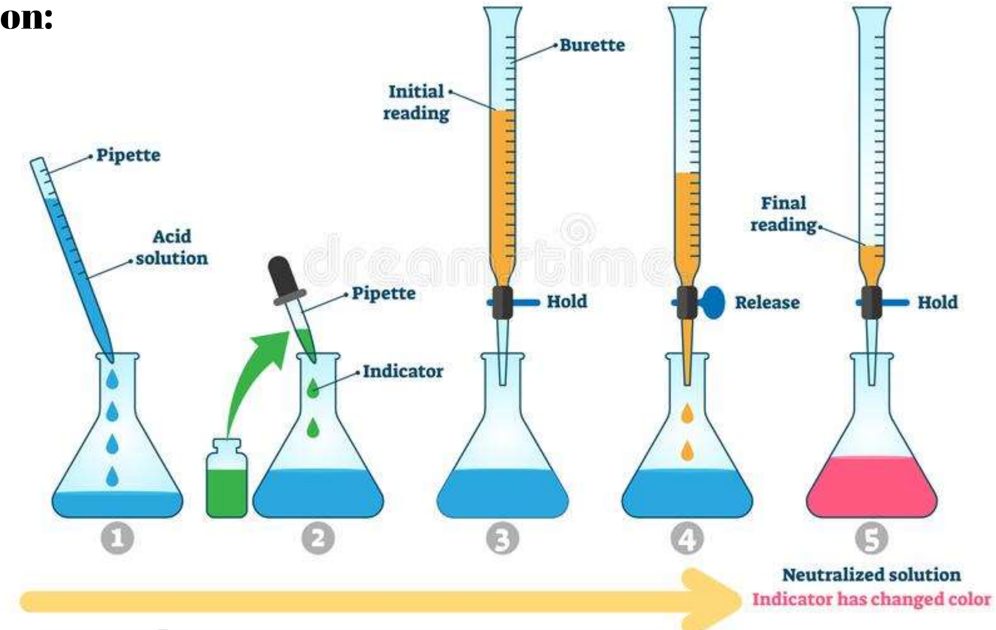
- Making solutions to dissolve substances for analysis, particularly in titrations.

## Important to Remember:

- Molarity = moles solute/L of solution

# Quick Guide to Experimental Procedures

## Titration:



## Common Mistakes:

- **Overshooting the titration (too dark of a color at the end)**
    - Results in the concentration of the unknown solution in the flask appearing to be higher than it actually is, since too much titrant has been added.
- **Not using indicator.**
    - No perceivable endpoint.
- **Using incorrect indicator.**
    - pH at the equivalence point should be approximately equal to the pKa of the indicator.

## Common Applications:

- Solving for the concentration of an unknown substance (analyte).
- Acid/Base, Redox

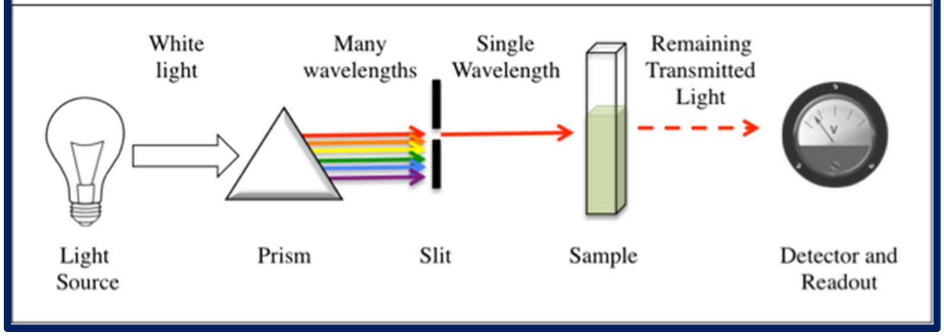
## Important to Remember:

- Molarity = moles solute/L of solution
- **Analyte:** substance in flask
- **Titrant:** substance in buret
- **Standard solution:** solution of known concentration, usually goes into the buret.
- **$M_1V_1 = M_2V_2$** is helpful for solving for the concentration of the analyte solution at the equivalence point.
- **Endpoint:** point in titration where flask solution changes color
- **Equivalence point:** point in the titration where the moles of acid are equal to the moles of base

# Quick Guide to Experimental Procedures

## Analyzing Concentration of Solutions Using Beer’s Law):

Diagram 1: Spectrophotometer



**Step 1: Pick the wavelength for the solution where absorbance is highest (for solute).**

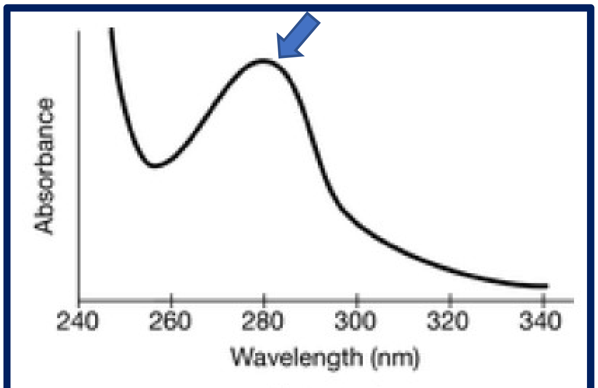
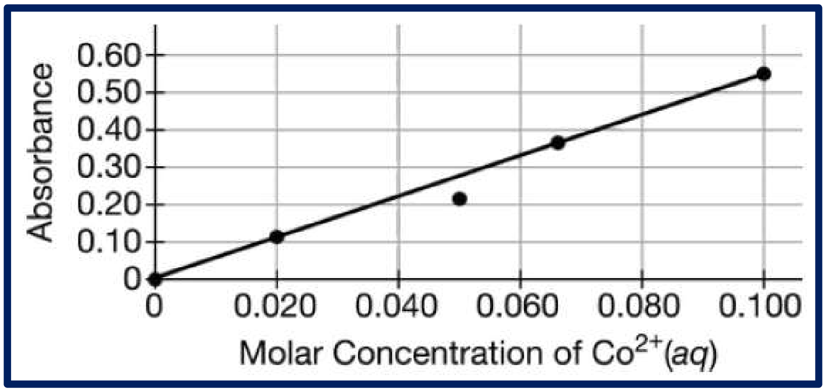


Diagram 2

**Step 2: Measure absorbance for different concentrations at that wavelength. Graph the results.**



$$A = \varepsilon bc$$

**Absorbance = (molar absorptivity)(cuvette pathway length)(concentration)**

# Quick Guide to Experimental Procedures

## Common Mistakes:

- **Absorbance is lower than it should be (point falls below the line)**
  - Cuvette was cleaned with distilled water and then immediately filled with solution, creating a more dilute solution
  - Too little solute in the prepared solution
- **Absorbance is higher than it should be (point falls above the line)**
  - Cuvette is dirty with fingerprints/dust, etc.
  - Too much solute in the prepared solution
  - Contamination with a more concentrated solution
  - Used a cuvette with a longer path for one data point
- **Did not use the correct wavelength of maximum absorbance for the solute.**
  - Absorbances could be too low especially for dilute solutions
- **Overfilled the cuvette**
  - Should not have an impact on data
- **Picked a wavelength where it is high absorbance for the solvent**
  - Won't be able to distinguish absorbance due to solvent vs. solute

## Common Applications:

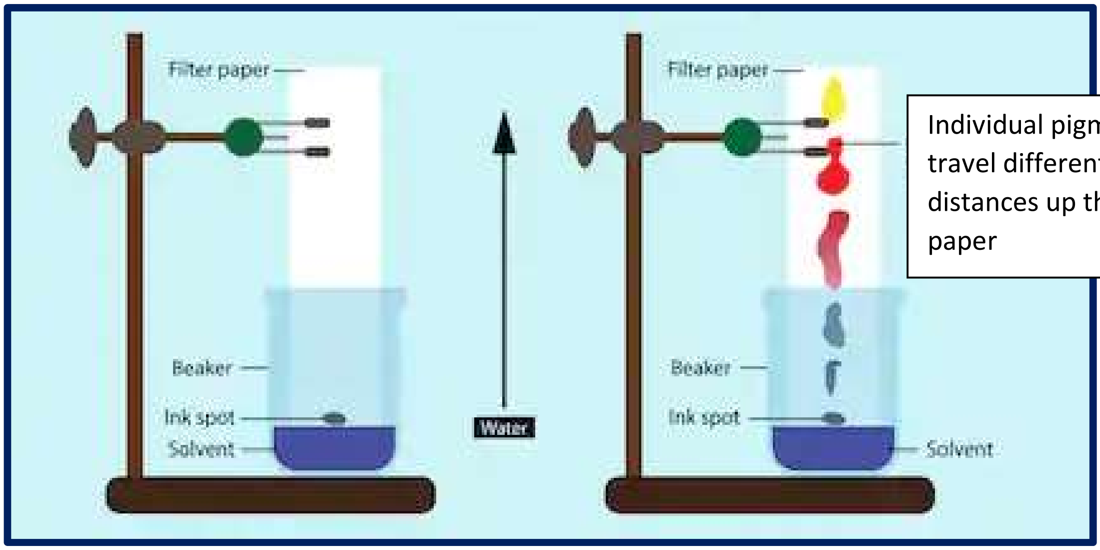
- Determining the concentration of a solution of unknown concentration using solutions of known concentration
- Kinetics reactions (like bleach + blue food dye)

## Important to Remember:

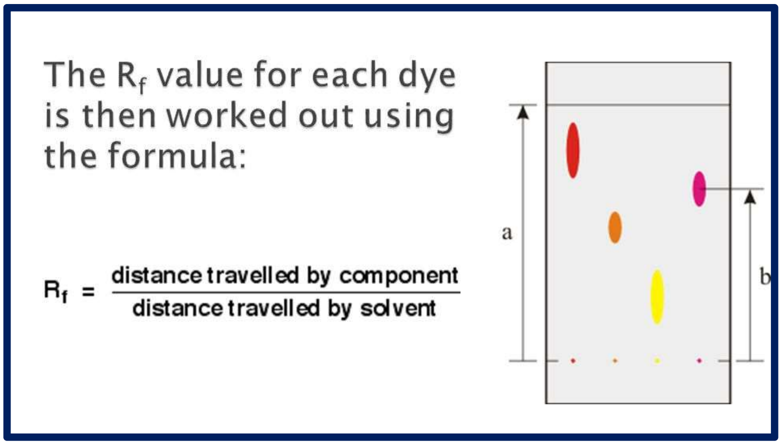
- Before using, you need to calibrate the spectrophotometer with a blank of just solvent (in order to account for any absorbance due to solvent and cuvette itself)
- Molarity = moles solute/L of solution
- Absorbance is the amount of light the solution absorbs at a specific wavelength
- Molar absorptivity (1/M*cm) describes how intensely a sample absorbs light at a specific wavelength (constant unique to the substance at a specific wavelength)
- Path length of sample is the length of the cuvette where the light will travel (cm)
- Concentration is molarity

# Quick Guide to Experimental Procedures

## Chromatography



Individual pigments travel different distances up the filter paper



The $R_f$ value for each dye is then worked out using the formula:

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$$

## Common Mistakes:

- **Solvent reaches the top of the paper strip.**
  - Rf values cannot be calculated as we do not know how far the solvent would have traveled had their been more paper.
- **No major difference in polarity between paper and solvent**
  - Substances cannot be adequately separated
- **No major differences in polarity of components of mixture**
  - Substances cannot be adequately separated

## Common Applications:

- Determining the components of a mixture

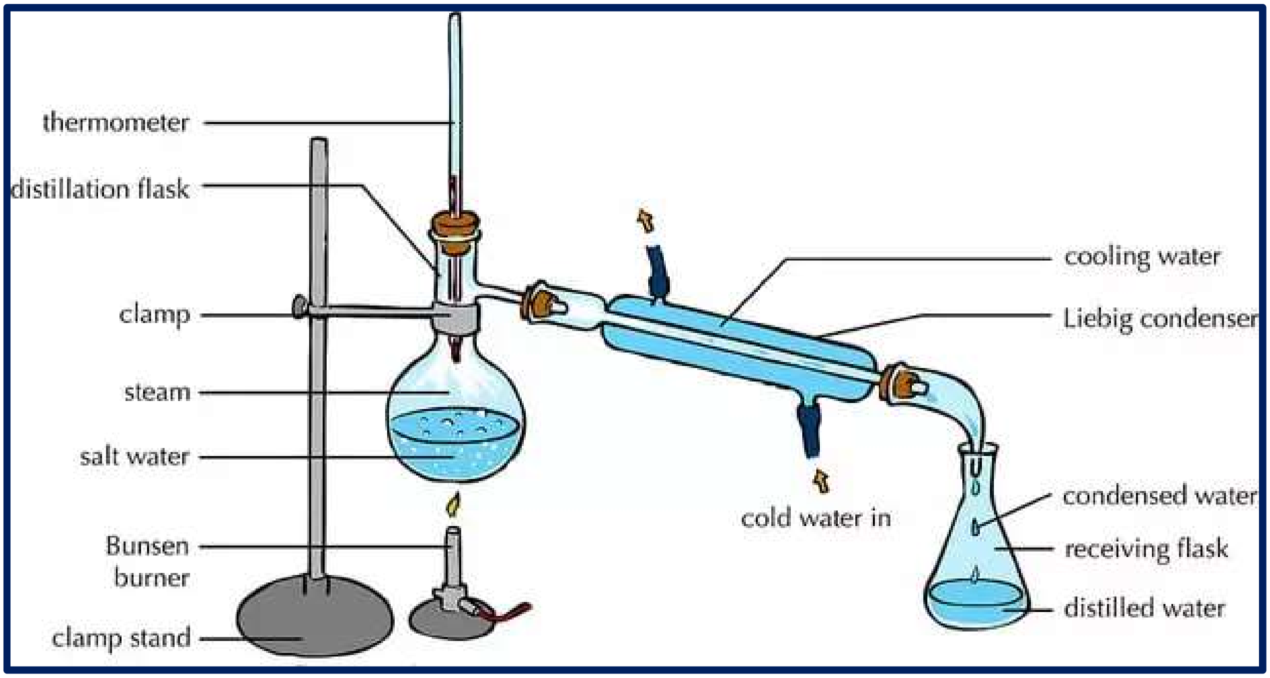
## Important to Remember:

# Quick Guide to Experimental Procedures

- Paper is usually relatively nonpolar in comparison to the solvent.
- The substance that travels further up the paper is more attracted to the solvent.
- The substance that travels the least is most attracted to the paper.
- If multiple trials are run, compare Rf values, not relative heights.
- Polar substances tend to lack symmetry, have polar bonds, and have lone pairs on the central atom. They are most soluble in other polar substances.
- Nonpolar substances tend to be symmetrical, have identical bonds, and have no lone pairs on the central atom. They are most soluble in other nonpolar substances.

# Quick Guide to Experimental Procedures

## Fractional Distillation



## Common Applications:

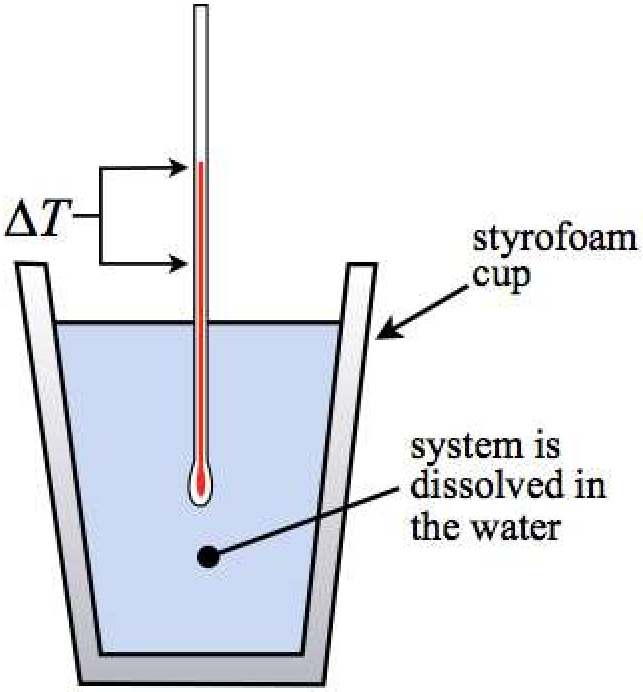
- Separating components in a solution/mixture based on differences in boiling point

## Important to Remember:

- The substance with the lower boiling point has a greater vapor pressure and weaker intermolecular forces
- The substance with the higher boiling point has a lower vapor pressure and stronger intermolecular forces
- The temperature of the solution will remain constant while a component is boiling off

# Quick Guide to Experimental Procedures

## Coffee Cup Calorimetry



## Common Mistakes:

- The final temperature is the highest (for exothermic) or lowest (for endothermic) temperature recorded during the reaction/process

## Applications:

- Solving for the specific heat of a metal or the heat of reaction

## Important to Remember:

- Endothermic processes have a drop in temperature.
- Exothermic processes have an increase in temperature.
- The water is not part of the system. It is part of the surroundings.
- $q = mC\Delta T$
    - q = heat in Joules or calories
    - m = mass of entire solution OR object, grams or kilograms
    - C = specific heat capacity, J/g°C (or a variation of the above)
    - $\Delta T = T_{final} - T_{initial}$

AP Chemistry Name: ________________________________

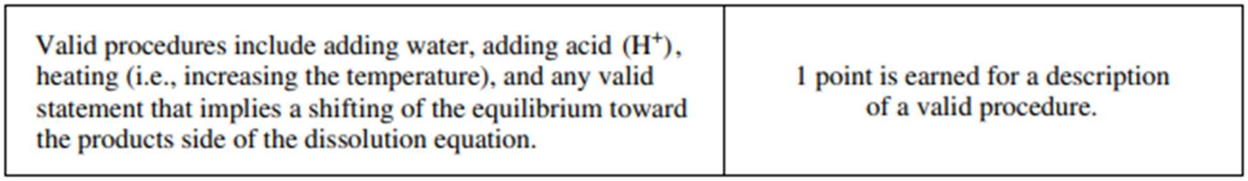
Lab Based Free Response Questions

1. There are several ways to dissolve salts with limited solubility. Describe one method to redissolve a precipitate of a salt with a small $K_{sp}$.

AP Chemistry Name: _________________________________

Lab Based Free Response Questions

1. (2013, #1) There are several ways to dissolve salts with limited solubility. Describe one method to redissolve a precipitate of a salt with a small $K_{sp}$.



| | |
|---|---|
| Valid procedures include adding water, adding acid ($H^+$), heating (i.e., increasing the temperature), and any valid statement that implies a shifting of the equilibrium toward the products side of the dissolution equation. | 1 point is earned for a description of a valid procedure. |

Name: ________________________________

2. A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net ionic equation below. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

$$MgO\ (s) + 2\ H^+\ (aq) \rightarrow Mg^{2+}\ (aq) + H_2O\ (l)$$

| **Trial** | **Volume of 1.0 M HCl (mL)** | **Mass of MgO (s) Added (g)** | **Initial Temperature of Solution (°C)** | **Final Temperature of Solution (°C)** |
|---|---|---|---|---|
| 1 | 100.0 | 0.25 | 25.5 | 26.5 |
| 2 | 100.0 | 0.50 | 25.0 | 29.1 |
| 3 | 100.0 | 0.25 | 26.0 | 28.1 |
| 4 | 100.0 | 0.50 | 24.1 | 28.1 |

a. Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.

b. The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

c. Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of ΔH° for the reaction between MGO (s) and HCl (aq).

| **Substance** | **$\Delta H^\circ_f$ (kJ/mol)** |
|---|---|
| MgO (s) | -602 |
| $H_2O$ (l) | -286 |
| $H^+$ (aq) | 0 |
| $Mg^{2+}$ (aq) | -467 |

d. A student used a coffee cup calorimeter and determined the $\Delta H^\circ_f = -140\ kJ/mol_{rxn}$. If the calorimeter leaked heat energy to the environment, would it account for the discrepancy between the accepted and the experimental values? Justify your answer.

2. (2013, #3) A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net ionic equation below. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

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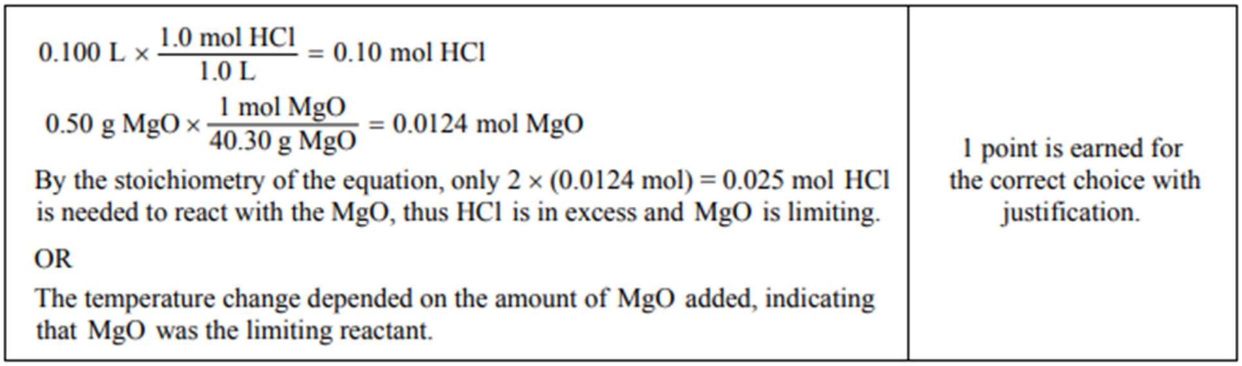
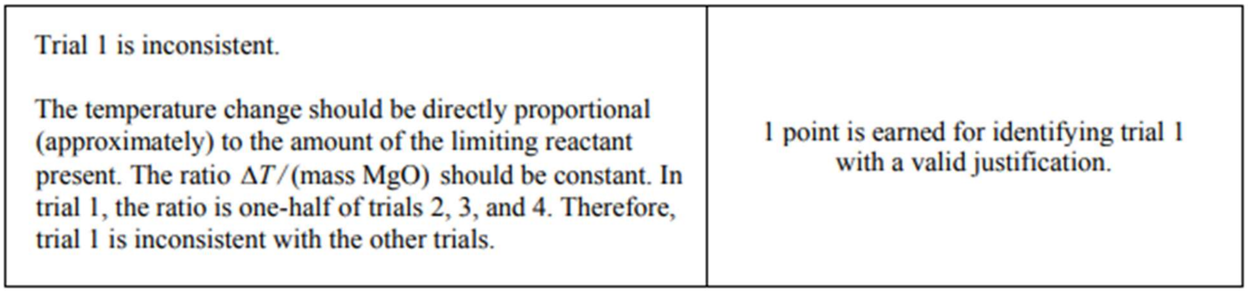
| 3 | 100.0 | 0.25 | 26.0 | 28.1 |
| 4 | 100.0 | 0.50 | 24.1 | 28.1 |

a. Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.



| | |
|---|---|
| $0.100\text{ L} \times \frac{1.0\text{ mol HCl}}{1.0\text{ L}} = 0.10\text{ mol HCl}$<br>$0.50\text{ g MgO} \times \frac{1\text{ mol MgO}}{40.30\text{ g MgO}} = 0.0124\text{ mol MgO}$<br>By the stoichiometry of the equation, only 2 × (0.0124 mol) = 0.025 mol HCl is needed to react with the MgO, thus HCl is in excess and MgO is limiting.<br>OR<br>The temperature change depended on the amount of MgO added, indicating that MgO was the limiting reactant. | 1 point is earned for the correct choice with justification. |

b. The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.



| | |
|---|---|
| Trial 1 is inconsistent.<br>The temperature change should be directly proportional (approximately) to the amount of the limiting reactant present. The ratio $\Delta T/(\text{mass MgO})$ should be constant. In trial 1, the ratio is one-half of trials 2, 3, and 4. Therefore, trial 1 is inconsistent with the other trials. | 1 point is earned for identifying trial 1 with a valid justification. |

Name: ______________________________

c. Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of ΔH° for the reaction between MGO (s) and HCl (aq).

| **Substance** | **$\Delta H^\circ_f$ (kJ/mol)** |
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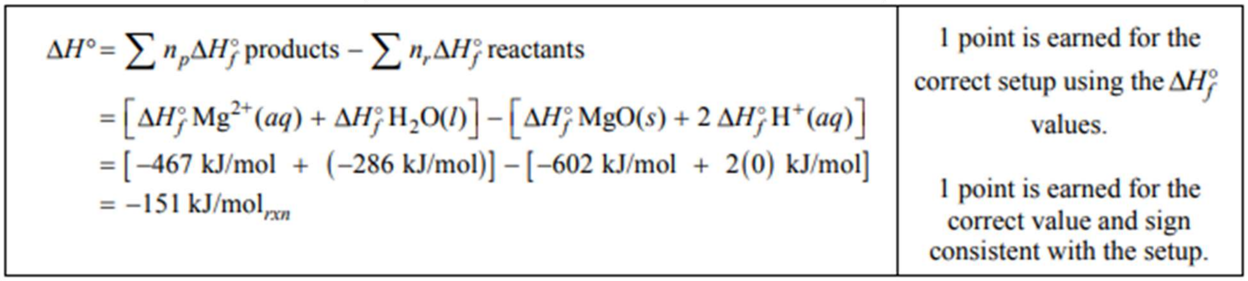
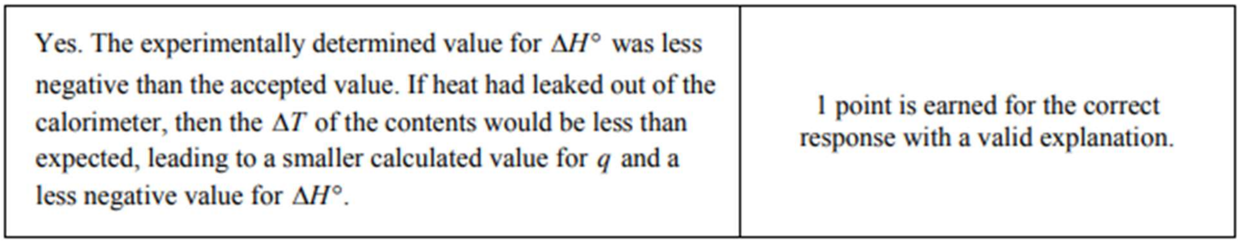


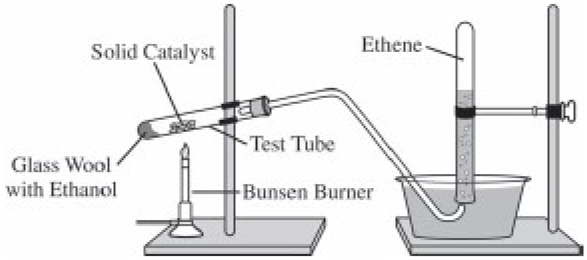
| | |
|---|---|
| $\Delta H^\circ = \sum n_p \Delta H^\circ_f \text{ products} - \sum n_r \Delta H^\circ_f \text{ reactants}$<br>$= [\Delta H^\circ_f \, Mg^{2+}(aq) + \Delta H^\circ_f \, H_2O(l)] - [\Delta H^\circ_f \, MgO(s) + 2\,\Delta H^\circ_f \, H^+(aq)]$<br>$= [-467 \text{ kJ/mol} + (-286 \text{ kJ/mol})] - [-602 \text{ kJ/mol} + 2(0) \text{ kJ/mol}]$<br>$= -151 \text{ kJ/mol}_{rxn}$ | 1 point is earned for the correct setup using the $\Delta H^\circ_f$ values.<br>1 point is earned for the correct value and sign consistent with the setup. |

d. A student used a coffee cup calorimeter and determined the $\Delta H^\circ_f$ = -140 $\text{kJ/mol}_{rxn}$. If the calorimeter leaked heat energy to the environment, would it account for the discrepancy between the accepted and the experimental values? Justify your answer.



| | |
|---|---|
| Yes. The experimentally determined value for $\Delta H^\circ$ was less negative than the accepted value. If heat had leaked out of the calorimeter, then the $\Delta T$ of the contents would be less than expected, leading to a smaller calculated value for $q$ and a less negative value for $\Delta H^\circ$. | 1 point is earned for the correct response with a valid explanation. |

3. Ethene, $C_2H_4$ (g) (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH$ (g) (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram below. The equation for the dehydration reaction is given below.



$$C_2H_5OH\ (g) \xrightarrow{catalyst} C_2H_4\ (g) + H_2O\ (g) \qquad \Delta H° = 45.5\ kJ/mol_{rxn}$$

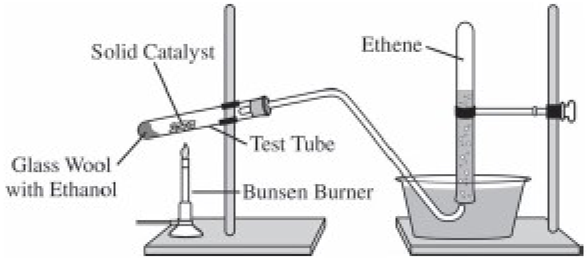
A student added a 0.200 g sample of $C_2H_5OH$ (l) to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $C_2H_5OH$ (l) evaporated and gas generation stopped. When the reaction stopped, the volume of collected gas was 0.0854 L at 0.822 atm and 305 K. The vapor pressure of water at 305 K is 35.7 torr.

a. Calculate the number of moles of $C_2H_4$ (g)
    i. that are actually produced in the experiment and measured in the gas collection tube and

    ii. that would be produced if the dehydration reaction went to completion.

b. During the dehydration experiment, $C_2H_4$ (g) and unreacted $C_2H_5OH$ (g) passed through the tube into the water. The $C_2H_4$ was quantitatively collected as a gas, but the unreacted $C_2H_5OH$ was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

3. (2015, #2) Ethene, $C_2H_4$ (g) (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH$ (g) (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram below. The equation for the dehydration reaction is given below.



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a. Calculate the number of moles of $C_2H_4$ (g)
   i. that are actually produced in the experiment and measured in the gas collection tube and

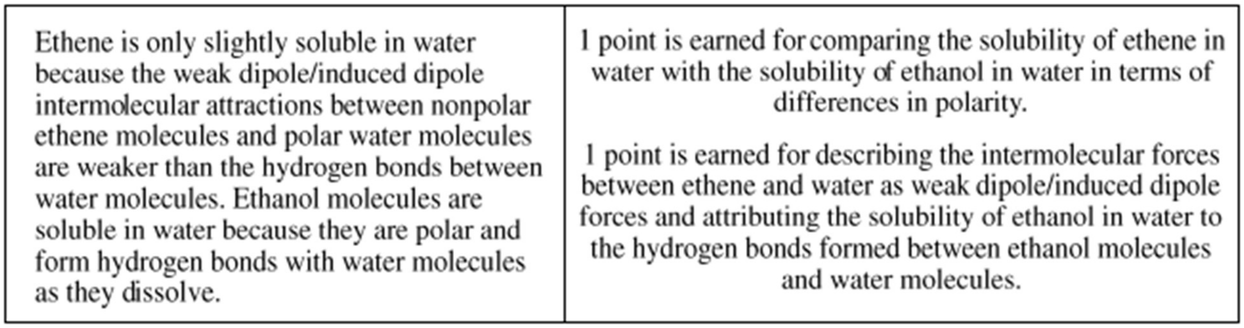
| | |
|---|---|
| $35.7\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 0.0470\ \text{atm}$<br>$P_{\text{ethene}} = P_{\text{total}} - P_{\text{water}} = 0.822\ \text{atm} - 0.0470\ \text{atm} = 0.775\ \text{atm}$ | 1 point is earned for the calculation of the pressure of the dry ethene. |
| $n = \frac{PV}{RT} = \frac{(0.775\ \text{atm})(0.0854\ \text{L})}{(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(305\ \text{K})} = 0.00264\ \text{mol}$ | 1 point is earned for the correct number of moles of ethene gas. |

   ii. that would be produced if the dehydration reaction went to completion.

| | |
|---|---|
| $0.200\ \text{g}\ C_2H_5OH \times \frac{1\ \text{mol}\ C_2H_5OH}{46.1\ \text{g}\ C_2H_5OH} \times \frac{1\ \text{mol}\ C_2H_4}{1\ \text{mol}\ C_2H_5OH}$<br>$= 0.00434\ \text{mol}\ C_2H_4$ produced | 1 point is earned for the correct number of moles of ethene produced. |

Name: ________________________________

b. During the dehydration experiment, $C_2H_4$ (g) and unreacted $C_2H_5OH$ (g) passed through the tube into the water. The $C_2H_4$ was quantitatively collected as a gas, but the unreacted $C_2H_5OH$ was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

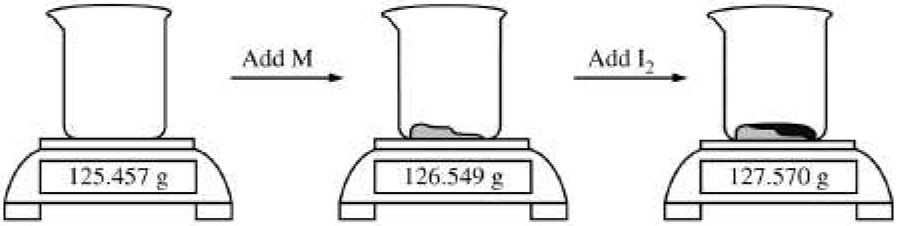


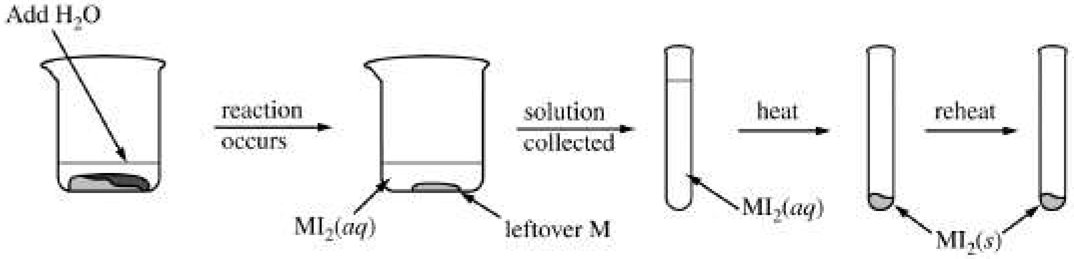
| | |
|---|---|
| Ethene is only slightly soluble in water because the weak dipole/induced dipole intermolecular attractions between nonpolar ethene molecules and polar water molecules are weaker than the hydrogen bonds between water molecules. Ethanol molecules are soluble in water because they are polar and form hydrogen bonds with water molecules as they dissolve. | 1 point is earned for comparing the solubility of ethene in water with the solubility of ethanol in water in terms of differences in polarity.<br>1 point is earned for describing the intermolecular forces between ethene and water as weak dipole/induced dipole forces and attributing the solubility of ethanol in water to the hydrogen bonds formed between ethanol molecules and water molecules. |

4. To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound $MI_2$, as represented by the equation below.

$$M + I_2 \rightarrow MI_2$$

The reaction proceeds until all of the $I_2$ is consumed. The $MI_2$ (aq) solution is quantitatively collected and heated to remove the water, and the product is dried and weighed to constant mass. The experimental steps are represented below, followed by a data table.





| Data for Unknown Metal Lab | |
|---|---|
| Mass of Beaker | 125.457 g |
| Mass of Beaker + metal M | 126.549 g |
| Mass of Beaker + metal M + $I_2$ | 127.570 g |
| Mass of $MI_2$, first weighing | 1.284 g |
| Mass of $MI_2$, second weighing | 1.284 g |

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

a. Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.

4. (2016, #3) To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound $MI_2$, as represented by the equation below.

$$M + I_2 \rightarrow MI_2$$

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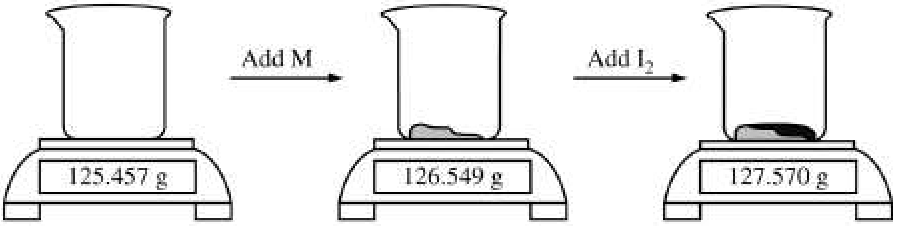

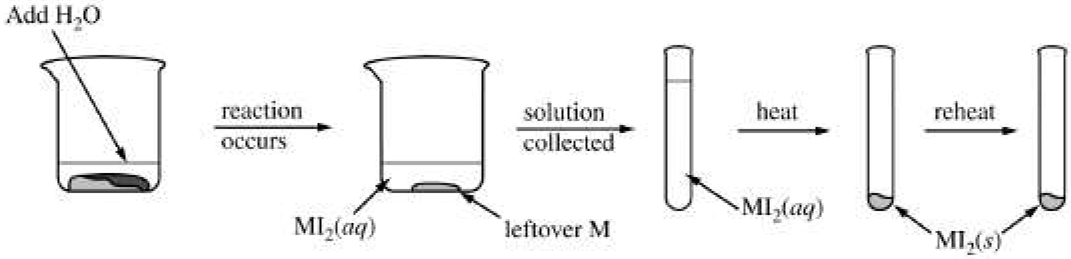

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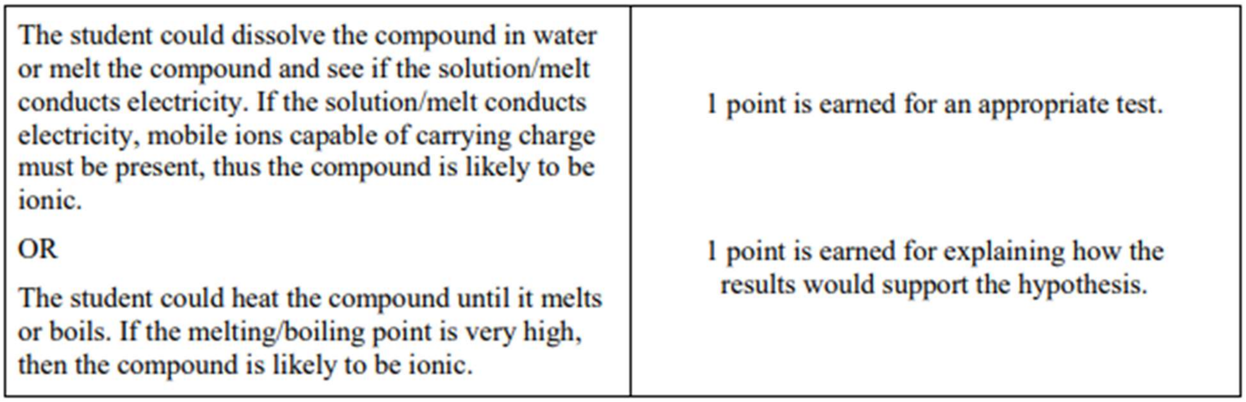
| Mass of $MI_2$, second weighing | 1.284 g |

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

a. Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.



| | |
|---|---|
| The student could dissolve the compound in water or melt the compound and see if the solution/melt conducts electricity. If the solution/melt conducts electricity, mobile ions capable of carrying charge must be present, thus the compound is likely to be ionic.<br>OR<br>The student could heat the compound until it melts or boils. If the melting/boiling point is very high, then the compound is likely to be ionic. | 1 point is earned for an appropriate test.<br>1 point is earned for explaining how the results would support the hypothesis. |

Name: ________________________________

5. The polyatomic ion $C_{10}H_{12}N_2O_8^{4-}$ is commonly abbreviated as $EDTA^{4-}$. The ion can form complexes with metal ions in aqueous solutions. A complex of $EDTA^{4-}$ with $Ba^{2+}$ ion forms according to the equation below.

$$Ba^{2+}\,(aq) + EDTA^{4-} \rightleftharpoons Ba(EDTA)^{2-}\,(aq) \qquad K = 7.7 \times 10^{7}$$

A 50.0 mL volume of a solution that has an $EDTA^{4-}$ (aq) concentration of 0.30 M is mixed with 50.0 mL of 0.20 M $Ba(NO_3)_2$ to produce 100.0 mL of solution.

   a. Considering the value of K for the reaction, determine the concentration of $Ba(EDTA)^{2-}$ (aq) in the 100.0 mL of solution. Justify your answer.

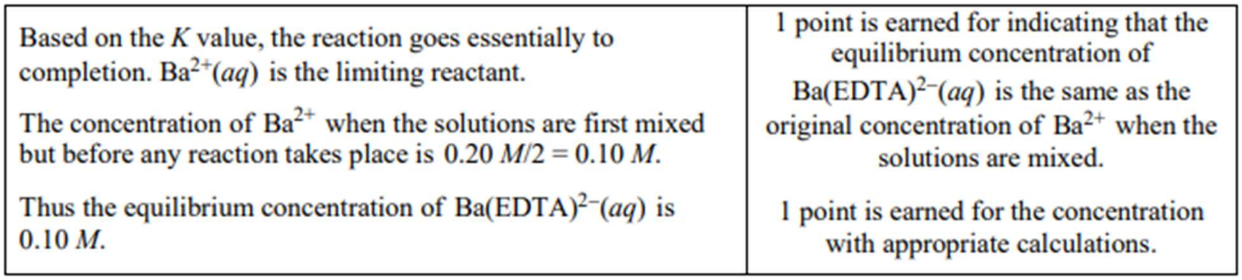
   b. The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of $Ba^{2+}$ (aq) present in the solution greater than, less than, or equal to the number of moles of $Ba^{2+}$ (aq) present in the original solution before it was diluted? Justify your answer.

5. (2016, #6) The polyatomic ion $C_{10}H_{12}N_2O_8^{4-}$ is commonly abbreviated as $EDTA^{4-}$. The ion can form complexes with metal ions in aqueous solutions. A complex of $EDTA^{4-}$ with $Ba^{2+}$ ion forms according to the equation below.

$$Ba^{2+}(aq) + EDTA^{4-} \rightleftharpoons Ba(EDTA)^{2-}(aq) \qquad K = 7.7 \times 10^7$$

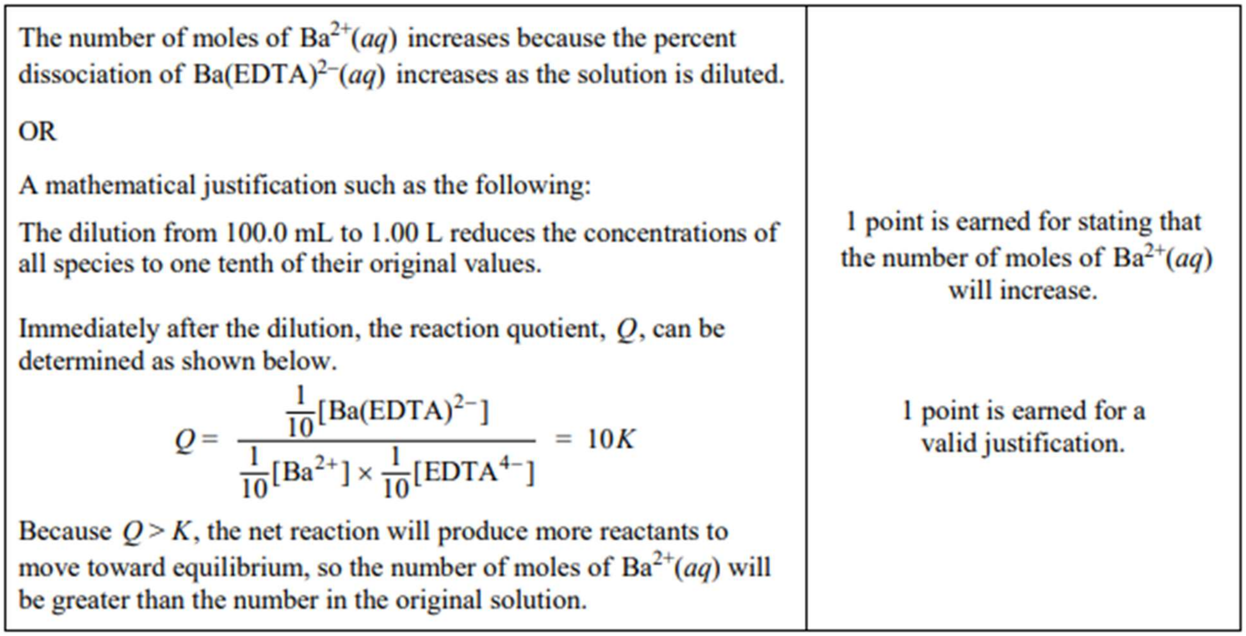
A 50.0 mL volume of a solution that has an $EDTA^{4-}$ (aq) concentration of 0.30 M is mixed with 50.0 mL of 0.20 M $Ba(NO_3)_2$ to produce 100.0 mL of solution.

   a. Considering the value of K for the reaction, determine the concentration of $Ba(EDTA)^{2-}$ (aq) in the 100.0 mL of solution. Justify your answer.



| | |
|---|---|
| Based on the *K* value, the reaction goes essentially to completion. $Ba^{2+}(aq)$ is the limiting reactant.<br>The concentration of $Ba^{2+}$ when the solutions are first mixed but before any reaction takes place is $0.20\ M/2 = 0.10\ M$.<br>Thus the equilibrium concentration of $Ba(EDTA)^{2-}(aq)$ is $0.10\ M$. | 1 point is earned for indicating that the equilibrium concentration of $Ba(EDTA)^{2-}(aq)$ is the same as the original concentration of $Ba^{2+}$ when the solutions are mixed.<br>1 point is earned for the concentration with appropriate calculations. |

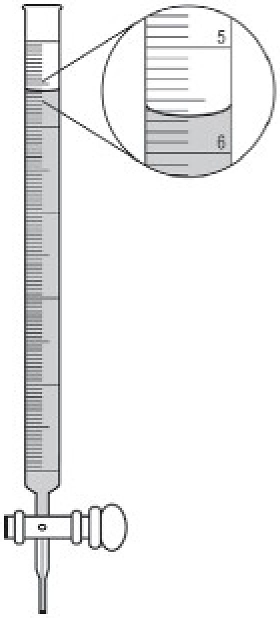
   b. The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of $Ba^{2+}$ (aq) present in the solution greater than, less than, or equal to the number of moles of $Ba^{2+}$ (aq) present in the original solution before it was diluted? Justify your answer.

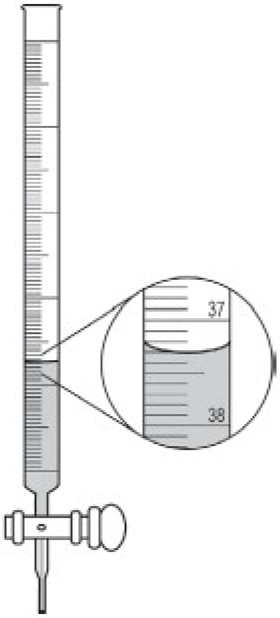


| | |
|---|---|
| The number of moles of $Ba^{2+}(aq)$ increases because the percent dissociation of $Ba(EDTA)^{2-}(aq)$ increases as the solution is diluted.<br>OR<br>A mathematical justification such as the following:<br>The dilution from 100.0 mL to 1.00 L reduces the concentrations of all species to one tenth of their original values.<br>Immediately after the dilution, the reaction quotient, *Q*, can be determined as shown below.<br>$Q = \dfrac{\frac{1}{10}[Ba(EDTA)^{2-}]}{\frac{1}{10}[Ba^{2+}] \times \frac{1}{10}[EDTA^{4-}]} = 10K$<br>Because $Q > K$, the net reaction will produce more reactants to move toward equilibrium, so the number of moles of $Ba^{2+}(aq)$ will be greater than the number in the original solution. | 1 point is earned for stating that the number of moles of $Ba^{2+}(aq)$ will increase.<br>1 point is earned for a valid justification. |

6. A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 M NaOH (aq), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.

    a. The images below show the buret before the titration begins (below lweft) and at the end point (below right). What should the student record as the value of NaOH (aq) delivered to the flask?



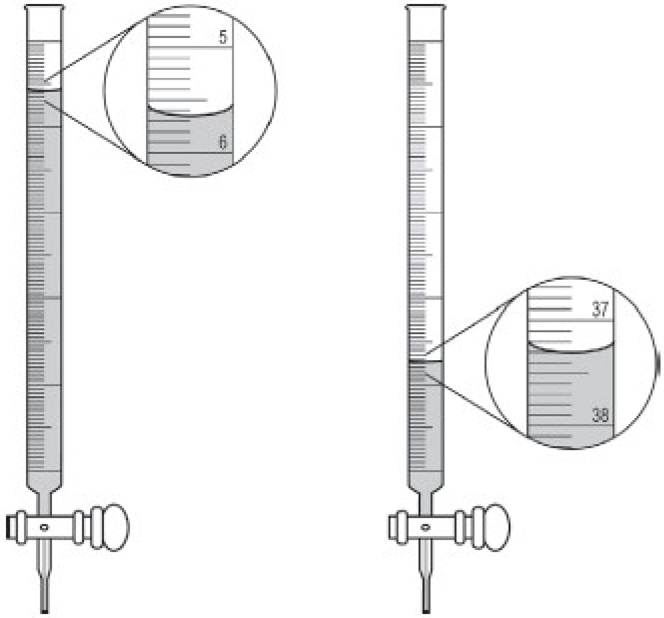


    b. Based on the given information and your answer to part (a), determine the value of the concentration of the acid that should be recorded in the student's lab report.

    c. In a second trial, the student accidentally added more NaOH (aq) to the flask than was needed to reach the end point, and then recorded the final volume. Would this error increase, decrease, or have no effect on the calculate acid concentration for the second trial? Justify your answer.

6. (2016, #7) A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 M NaOH (aq), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.

   a. The images below show the buret before the titration begins (below lweft) and at the end point (below right). What should the student record as the value of NaOH (aq) delivered to the flask?

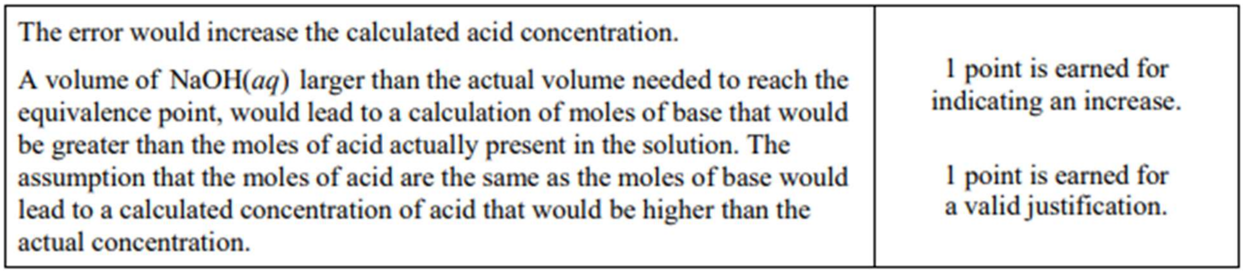


| | |
|---|---|
| 37.30 mL – 5.65 mL = 31.65 mL | 1 point is earned for the correct volume. |

   b. Based on the given information and your answer to part (a), determine the value of the concentration of the acid that should be recorded in the student's lab report.

| | |
|---|---|
| At the equivalence point, moles $OH^-$ added = moles of $H^+$ consumed.<br>Because HA is monoprotic:<br>$(0.110\ M)(0.03165\ \text{L}) \times \frac{1\ \text{mol HA}}{1\ \text{mol NaOH}} \times \frac{1}{0.0250\ \text{L}} = 0.139\ M$<br>OR<br>moles of $H^+$ consumed $= M_a V_a$<br>$M_a V_a = M_b V_b$<br>Therefore, $M_a = \frac{M_b V_b}{V_a} = \frac{(0.110\ M)(0.03165\ \text{L})}{0.0250\ \text{L}} = 0.139\ M$ | 1 point is earned for the correct setup and molarity. |

c. In a second trial, the student accidentally added more NaOH (aq) to the flask than was needed to reach the end point, and then recorded the final volume. Would this error increase, decrease, or have no effect on the calculate acid concentration for the second trial? Justify your answer.

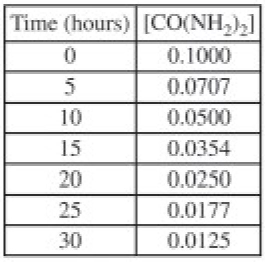


| | |
|---|---|
| The error would increase the calculated acid concentration.<br>A volume of NaOH(*aq*) larger than the actual volume needed to reach the equivalence point, would lead to a calculation of moles of base that would be greater than the moles of acid actually present in the solution. The assumption that the moles of acid are the same as the moles of base would lead to a calculated concentration of acid that would be higher than the actual concentration. | 1 point is earned for indicating an increase.<br>1 point is earned for a valid justification. |

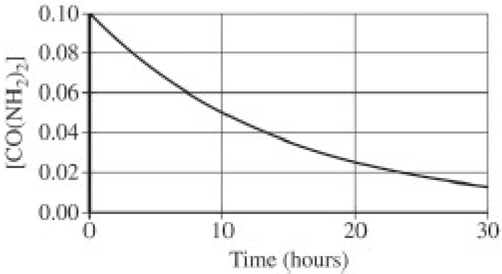
7. Urea decomposes according to the reaction below:

$$CO(NH_2)_2\ (aq) \rightleftharpoons NH_4^+\ (aq) + OCN^-$$

A student studying the decomposition reaction runs the reaction at 90 °C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.



| Time (hours) | $[CO(NH_2)_2]$ |
|---|---|
| 0 | 0.1000 |
| 5 | 0.0707 |
| 10 | 0.0500 |
| 15 | 0.0354 |
| 20 | 0.0250 |
| 25 | 0.0177 |
| 30 | 0.0125 |



a. The student proposes that the rate law is rate = k $[CO(NH_2)_2]$.

   i. Explain how the data support the student's proposed rate law.

   ii. Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

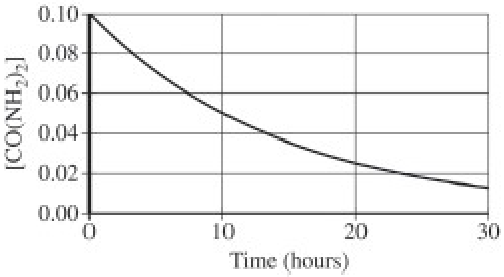
b. The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-$ (aq).

7. (2017, #2) Urea decomposes according to the reaction below:

$$CO(NH_2)_2\ (aq) \rightleftharpoons NH_4^+\ (aq) + OCN^-$$

A student studying the decomposition reaction runs the reaction at 90 °C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

| Time (hours) | $[CO(NH_2)_2]$ |
|---|---|
| 0 | 0.1000 |
| 5 | 0.0707 |
| 10 | 0.0500 |
| 15 | 0.0354 |
| 20 | 0.0250 |
| 25 | 0.0177 |
| 30 | 0.0125 |



a. The student proposes that the rate law is rate = k $[CO(NH_2)_2]$.
   i. Explain how the data support the student's proposed rate law.

| | |
|---|---|
| From inspecting the data table or the graph, it is evident that the decomposition reaction has a constant half-life, which indicates that the reaction is a first-order reaction. | 1 point is earned for a correct explanation. |

   ii. Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

| | |
|---|---|
| Since the reaction is first order,<br>$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.\text{ h}} = 0.069\text{ h}^{-1}$<br>OR<br>$k = \frac{\ln[A]_0 - \ln[A]_t}{t} = \frac{\ln(0.1000) - \ln(0.0500)}{10.\text{ h}} = 0.069\text{ h}^{-1}$ | 1 point is earned for the correct value of $k$ with correct units. |

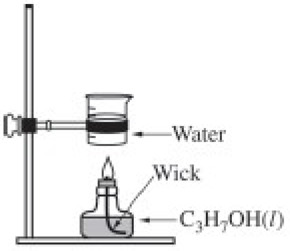
b. The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-$ (aq).

| | |
|---|---|
| Perform the experiment at a different concentration of $OH^-$(*aq*) and measure how the concentration of $CO(NH_2)_2$ changes over time. (Other variables, such as temperature, should be held constant.) | 1 point is earned for the description of a valid experiment. |

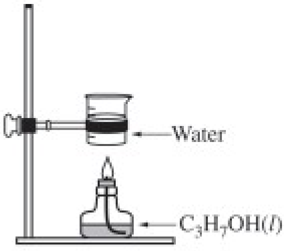
8. A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $C_3H_7OH$ (l), which combusts in oxygen according to the equation below.

$$2\ C_3H_7OH\ (l) + 9\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 8\ H_2O\ (g)$$

The student heats a sample of water by burning some of the $C_3H_7OH$ (l) that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of $C_3H_7OH$ (l) combusted is determined by weighing the alcohol burner before and after combustion.



Initial



Final

Data from the experiment are given in the table below.

| | |
|---|---|
| Mass of $C_3H_7OH$ (l) combusted | 0.55 g |
| Mass of water heated | 125.00 g |
| Initial temperature of water | 22.0 °C |
| Final temperature of water | 51.1 °C |
| Specific heat of water | 4.18 J/(g·°C) |

a. Calculate the magnitude of the heat energy, in kJ, absorbed by the water. Assume that the energy released from the combustion is completely transferred to the water.

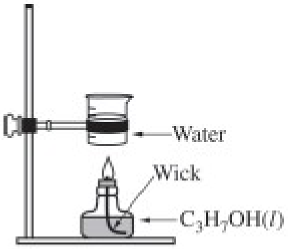
b. Based on the experimental data, if one mole of $C_3H_7OH$ (l) is combusted, how much heat, in kJ, is released?

c. A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing $C_3H_7OH$ (l) that is contaminated with water, which is miscible with $C_3H_7OH$ (l). The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

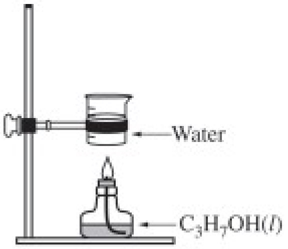
8. (2017, #5) A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $C_3H_7OH$ (l), which combusts in oxygen according to the equation below.

$$2\ C_3H_7OH\ (l) + 9\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 8\ H_2O\ (g)$$

The student heats a sample of water by burning some of the $C_3H_7OH$ (l) that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of $C_3H_7OH$ (l) combusted is determined by weighing the alcohol burner before and after combustion.



Initial

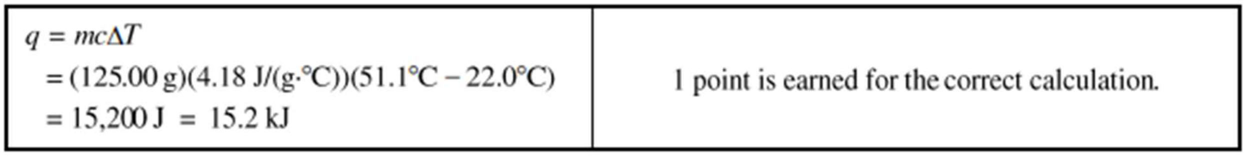


Final

Data from the experiment are given in the table below.

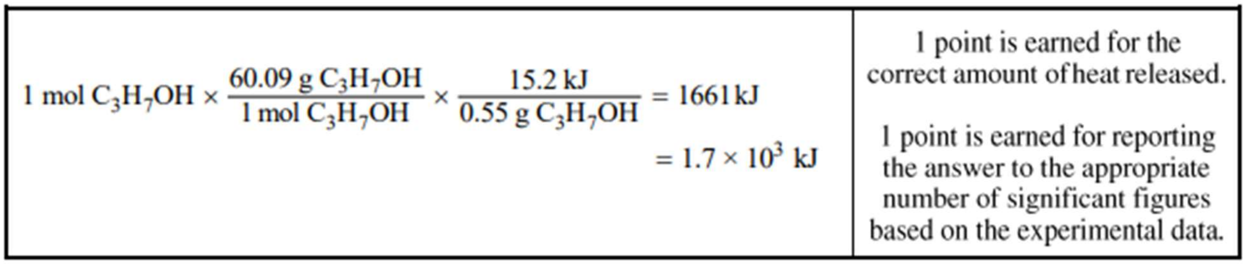
| | |
|---|---|
| Mass of $C_3H_7OH$ (l) combusted | 0.55 g |
| Mass of water heated | 125.00 g |
| Initial temperature of water | 22.0 °C |
| Final temperature of water | 51.1 °C |
| Specific heat of water | 4.18 J/(g·°C) |

a. Calculate the magnitude of the heat energy, in kJ, absorbed by the water. Assume that the energy released from the combustion is completely transferred to the water.



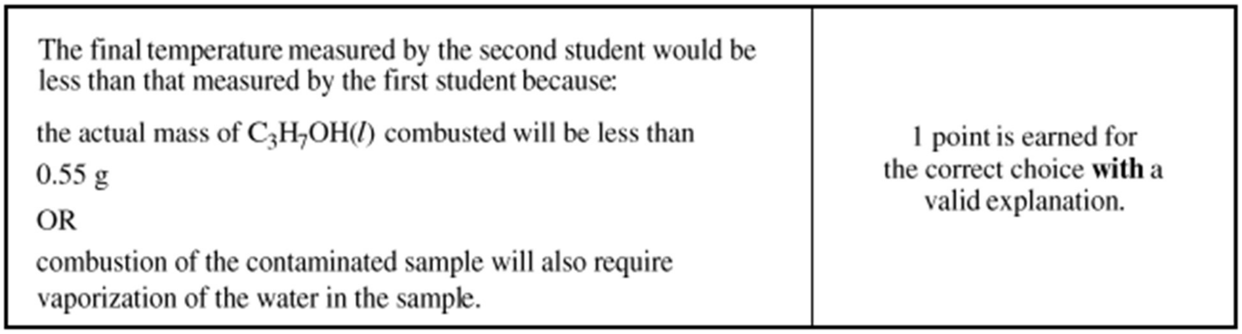
| | |
|---|---|
| $q = mc\Delta T$<br>$= (125.00\text{ g})(4.18\text{ J/(g·°C)})(51.1\text{°C} - 22.0\text{°C})$<br>$= 15{,}200\text{ J} = 15.2\text{ kJ}$ | 1 point is earned for the correct calculation. |

b. Based on the experimental data, if one mole of $C_3H_7OH$ (l) is combusted, how much heat, in kJ, is released?



| | |
|---|---|
| $1\text{ mol } C_3H_7OH \times \frac{60.09\text{ g } C_3H_7OH}{1\text{ mol } C_3H_7OH} \times \frac{15.2\text{ kJ}}{0.55\text{ g } C_3H_7OH} = 1661\text{ kJ}$<br>$= 1.7 \times 10^3\text{ kJ}$ | 1 point is earned for the correct amount of heat released.<br>1 point is earned for reporting the answer to the appropriate number of significant figures based on the experimental data. |

c. A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing $C_3H_7OH$ (l) that is contaminated with water, which is miscible with $C_3H_7OH$ (l). The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.



| | |
|---|---|
| The final temperature measured by the second student would be less than that measured by the first student because:<br>the actual mass of $C_3H_7OH(l)$ combusted will be less than 0.55 g<br>OR<br>combustion of the contaminated sample will also require vaporization of the water in the sample. | 1 point is earned for the correct choice **with** a valid explanation. |

Name: ________________________________

9. The student reads in a reference text that NO (g) and $NO_2$ (g) will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO\ (g) + NO_2\ (g) \rightleftharpoons N_2O_3\ (g)$$

| $\Delta H^\circ_{298}$ | $\Delta S^\circ_{298}$ | $\Delta G^\circ_{298}$ |
|---|---|---|
| - 40.4 $kJ/mol_{rxn}$ | - 138.5 $J/(K{\cdot}mol_{rxn})$ | 0.87 $kJ/mol_{rxn}$ |

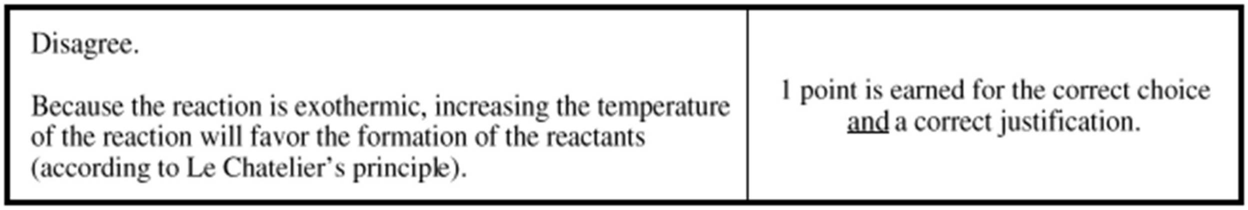
   a. The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3$ (g) in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

9. (2018, #2) The student reads in a reference text that NO (g) and $NO_2$ (g) will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO\,(g) + NO_2\,(g) \rightleftharpoons N_2O_3\,(g)$$

| $\Delta H^\circ_{298}$ | $\Delta S^\circ_{298}$ | $\Delta G^\circ_{298}$ |
|---|---|---|
| - 40.4 kJ/$mol_{rxn}$ | - 138.5 J/(K·$mol_{rxn}$) | 0.87 kJ/$mol_{rxn}$ |

   a. The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3$ (g) in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.



| | |
|---|---|
| Disagree.<br>Because the reaction is exothermic, increasing the temperature of the reaction will favor the formation of the reactants (according to Le Chatelier's principle). | 1 point is earned for the correct choice <u>and</u> a correct justification. |

AP Chemistry Name: ________________________________

Lab Based Free Response Questions

10. A student obtains a solution that contains an unknown concentration fo $Fe^{2+}$ (aq). To determine the concentration of $Fe^{2+}$ (aq) in the solution, the student titrates a sample of the solution with $MnO_4^-$ (aq), which converts $Fe^{2+}$ (aq) to $Fe^{3+}$ (aq), as represented by the following equation.

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

   a. The student titrates a 10.0 mL sample of the $Fe^{2+}$ (aq) solution. Calculate the value of $[Fe^{2+}]$ in the solution if it takes 17.48 mL of added 0.0350 M $KMnO_4$ (aq) to reach the equivalence point of the titration.

To deliver the 10.0 mL sample of the $Fe^{2+}$ (aq) solution in part (a), the student has the choice of using one of the pieces of glassware listed below.

25 mL buret　　25 mL beaker　　25 mL graduated cylinder　　25 mL volumetric flask

   b. Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of $Fe^{2+}$ (aq) solution.

In a separate experiment, the student is given a sample of powdered Fe (s) that contains an inert impurity. The student uses a procedure to oxidize the Fe (s) in the sample to $Fe_2O_3$ (s). The student collects the following data during the experiment.

| | |
|---|---|
| Mass of Fe (s) with inert impurity | 6.724 g |
| Mass of $Fe_2O_3$ (s) produced | 7.531 g |

   c. Calculate the number of moles of Fe in the $Fe_2O_3$ (s) produced.

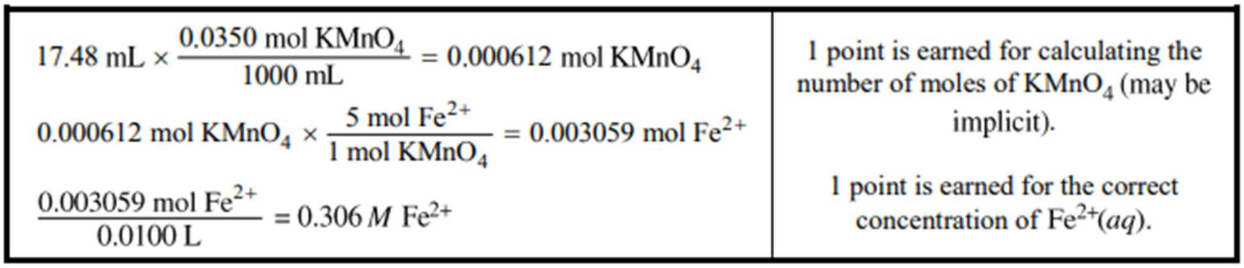
   d. Calculate the percent by mass of Fe in the original sample of powdered Fe (s) with the inert impurity.

   e. If the oxidation of the Fe (s) in the original sample was incomplete so that some of the 7.531 g of product was FeO (s) instead of $Fe_2O_3$ (s), would the calculated mass percent of Fe (s) in the original sample be higher, lower, or the same as the actual mass percent of Fe (s)? Justify your answer.

10. (2018, #3) A student obtains a solution that contains an unknown concentration fo $Fe^{2+}$ (aq). To determine the concentration of $Fe^{2+}$ (aq) in the solution, the student titrates a sample of the solution with $MnO_4^-$ (aq), which converts $Fe^{2+}$ (aq) to $Fe^{3+}$ (aq), as represented by the following equation.

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

a. The student titrates a 10.0 mL sample of the $Fe^{2+}$ (aq) solution. Calculate the value of $[Fe^{2+}]$ in the solution if it takes 17.48 mL of added 0.0350 M $KMnO_4$ (aq) to reach the equivalence point of the titration.

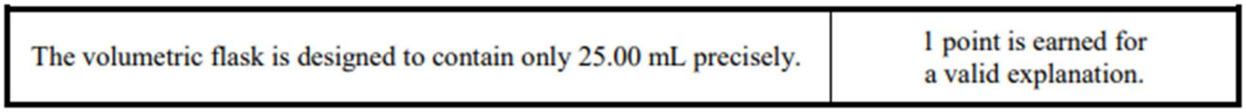


| | |
|---|---|
| $17.48\text{ mL} \times \frac{0.0350\text{ mol KMnO}_4}{1000\text{ mL}} = 0.000612\text{ mol KMnO}_4$<br>$0.000612\text{ mol KMnO}_4 \times \frac{5\text{ mol Fe}^{2+}}{1\text{ mol KMnO}_4} = 0.003059\text{ mol Fe}^{2+}$<br>$\frac{0.003059\text{ mol Fe}^{2+}}{0.0100\text{ L}} = 0.306\ M\ \text{Fe}^{2+}$ | 1 point is earned for calculating the number of moles of $KMnO_4$ (may be implicit).<br>1 point is earned for the correct concentration of $Fe^{2+}(aq)$. |

To deliver the 10.0 mL sample of the $Fe^{2+}$ (aq) solution in part (a), the student has the choice of using one of the pieces of glassware listed below.

25 mL buret 25 mL beaker 25 mL graduated cylinder 25 mL volumetric flask

b. Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of $Fe^{2+}$ (aq) solution.

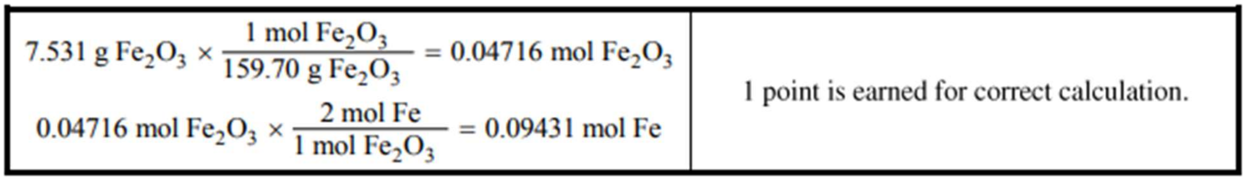


| | |
|---|---|
| The volumetric flask is designed to contain only 25.00 mL precisely. | 1 point is earned for a valid explanation. |

In a separate experiment, the student is given a sample of powdered Fe (s) that contains an inert impurity. The student uses a procedure to oxidize the Fe (s) in the sample to $Fe_2O_3$ (s). The student collects the following data during the experiment.

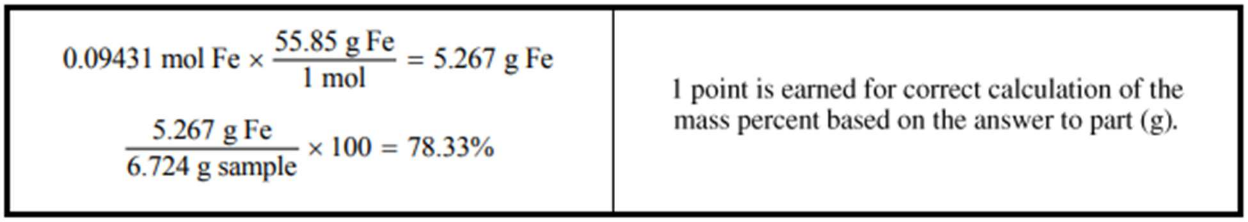
| | |
|---|---|
| Mass of Fe (s) with inert impurity | 6.724 g |
| Mass of $Fe_2O_3$ (s) produced | 7.531 g |

c. Calculate the number of moles of Fe in the $Fe_2O_3$ (s) produced.



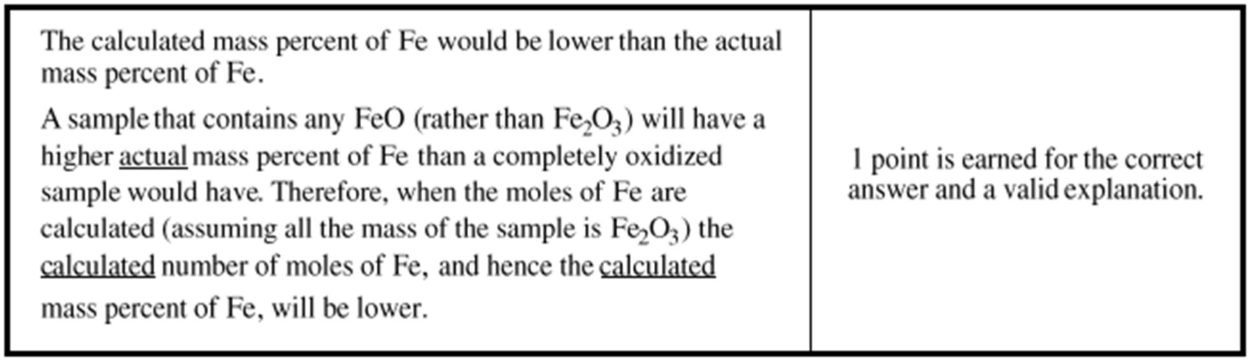
| | |
|---|---|
| $7.531\text{ g Fe}_2\text{O}_3 \times \frac{1\text{ mol Fe}_2\text{O}_3}{159.70\text{ g Fe}_2\text{O}_3} = 0.04716\text{ mol Fe}_2\text{O}_3$<br>$0.04716\text{ mol Fe}_2\text{O}_3 \times \frac{2\text{ mol Fe}}{1\text{ mol Fe}_2\text{O}_3} = 0.09431\text{ mol Fe}$ | 1 point is earned for correct calculation. |

d. Calculate the percent by mass of Fe in the original sample of powdered Fe (s) with the inert impurity.



| | |
|---|---|
| $0.09431 \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol}} = 5.267 \text{ g Fe}$<br>$\frac{5.267 \text{ g Fe}}{6.724 \text{ g sample}} \times 100 = 78.33\%$ | 1 point is earned for correct calculation of the mass percent based on the answer to part (g). |

e. If the oxidation of the Fe (s) in the original sample was incomplete so that some of the 7.531 g of product was FeO (s) instead of $Fe_2O_3$ (s), would the calculated mass percent of Fe (s) in the original sample be higher, lower, or the same as the actual mass percent of Fe (s)? Justify your answer.



| | |
|---|---|
| The calculated mass percent of Fe would be lower than the actual mass percent of Fe.<br>A sample that contains any FeO (rather than $Fe_2O_3$) will have a higher actual mass percent of Fe than a completely oxidized sample would have. Therefore, when the moles of Fe are calculated (assuming all the mass of the sample is $Fe_2O_3$) the calculated number of moles of Fe, and hence the calculated mass percent of Fe, will be lower. | 1 point is earned for the correct answer and a valid explanation. |

11. The ionization of HF (aq) in water is represented by the equation below. In a 0.0350 M HF (aq) solution, the percent ionization of HF is 13.0 percent.

$$HF\ (aq) + H_2O\ (l) \rightleftharpoons F^-\ (aq) + H_3O^+\ (aq)$$

a. Two particulate representations of the ionization of HF molecules in the 0.0350 M HF (aq) solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. The key below identifies the particles in the representations.

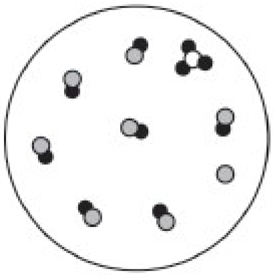


Figure 1

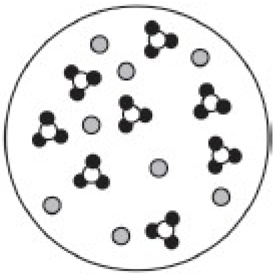


Figure 2

b. Use the percent ionization data above to calculate the value of $K_a$ for HF.

c. If 50.0 mL of distilled water is added to 50.0 mL of 0.035 M HF (aq), will the percent ionization of HF (aq) in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.

11. (2018, #5) The ionization of HF (aq) in water is represented by the equation below. In a 0.0350 M HF (aq) solution, the percent ionization of HF is 13.0 percent.

$$HF\ (aq) + H_2O\ (l) \rightleftharpoons F^-\ (aq) + H_3O^+\ (aq)$$

   a. Two particulate representations of the ionization of HF molecules in the 0.0350 M HF (aq) solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. The key below identifies the particles in the representations.

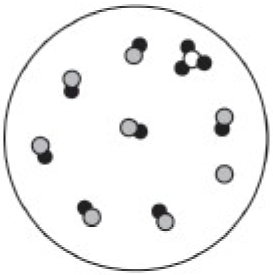


Figure 1

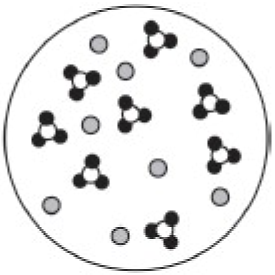


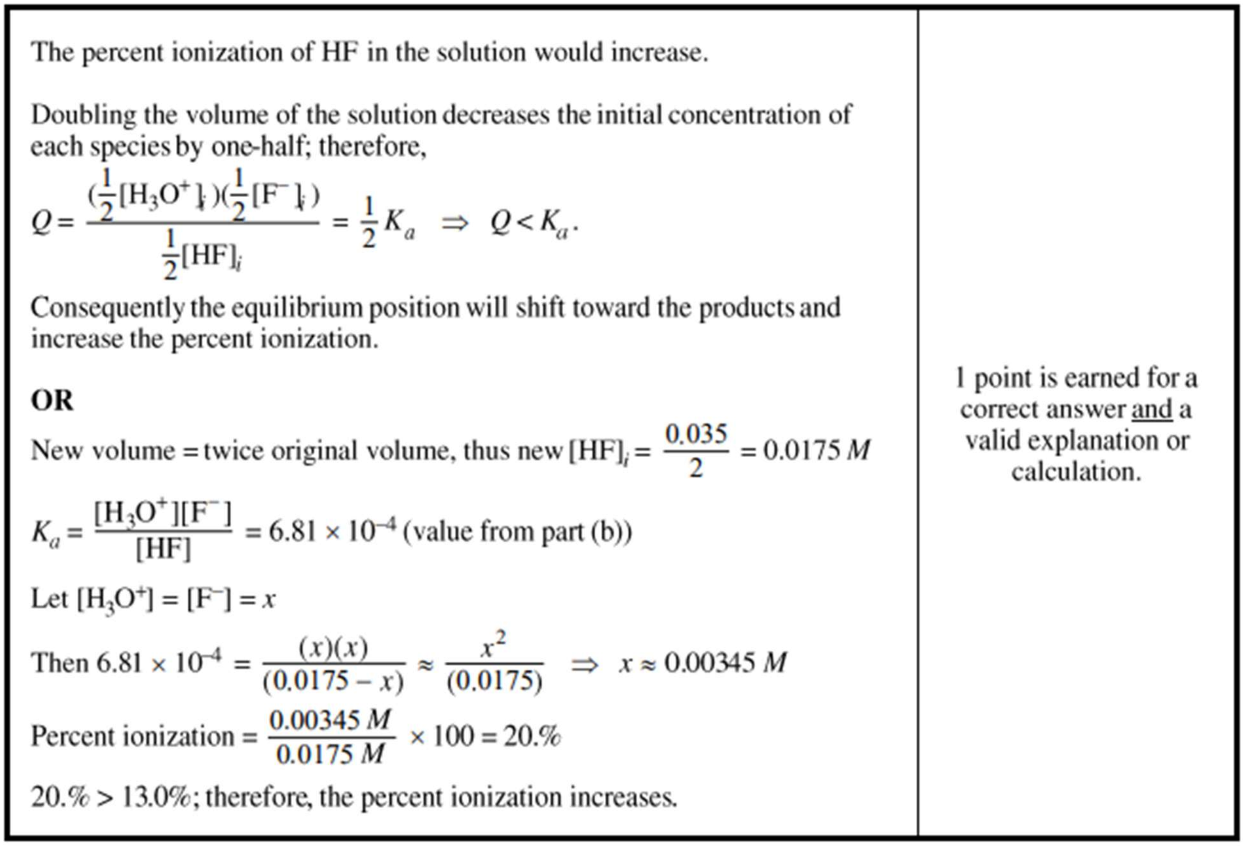
Figure 2

| | |
|---|---|
| HF is a weak acid and is only partially ionized. This fact is consistent with Figure 1, which shows that one out of eight (~13%) HF molecules is ionized (to form one $H_3O^+$ and one $F^-$).<br>OR<br>Figure 2 cannot represent HF because it represents 100% ionization of the acid. | 1 point is earned for a valid explanation. |

   b. Use the percent ionization data above to calculate the value of $K_a$ for HF.

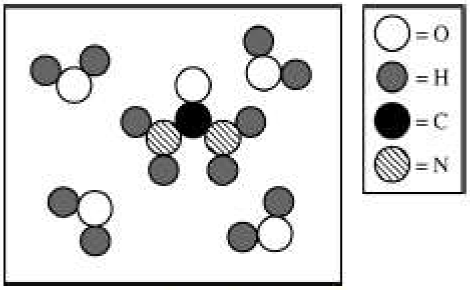
| | |
|---|---|
| Assume $[H_3O^+] = [F^-]$ in HF(*aq*).<br>$\frac{[H_3O^+]}{0.0350\ M} = 0.130 \Rightarrow [H_3O^+] = 0.00455\ M$<br>$HF(aq) + H_2O(l) \rightleftarrows F^-(aq) + H_3O^+(aq)$<br>I 0.0350 0 ~0<br>C −0.00455 +0.00455 +0.00455<br>E 0.0304 0.00455 0.00455<br>$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(0.00455)^2}{(0.0304)} = 6.81 \times 10^{-4}$ | 1 point is earned for the correct calculation of $[H_3O^+]$.<br>1 point is earned for a value of $K_a$ consistent with the calculated value of $[H_3O^+]$. |

c. If 50.0 mL of distilled water is added to 50.0 mL of 0.035 M HF (aq), will the percent ionization of HF (aq) in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.



| | |
|---|---|
| The percent ionization of HF in the solution would increase.<br>Doubling the volume of the solution decreases the initial concentration of each species by one-half; therefore,<br>$Q = \frac{(\frac{1}{2}[H_3O^+]_i)(\frac{1}{2}[F^-]_i)}{\frac{1}{2}[HF]_i} = \frac{1}{2}K_a \Rightarrow Q < K_a$.<br>Consequently the equilibrium position will shift toward the products and increase the percent ionization.<br>**OR**<br>New volume = twice original volume, thus new $[HF]_i = \frac{0.035}{2} = 0.0175\ M$<br>$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.81 \times 10^{-4}$ (value from part (b))<br>Let $[H_3O^+] = [F^-] = x$<br>Then $6.81 \times 10^{-4} = \frac{(x)(x)}{(0.0175 - x)} \approx \frac{x^2}{(0.0175)} \Rightarrow x \approx 0.00345\ M$<br>Percent ionization $= \frac{0.00345\ M}{0.0175\ M} \times 100 = 20.\%$<br>20.% > 13.0%; therefore, the percent ionization increases. | 1 point is earned for a correct answer <u>and</u> a valid explanation or calculation. |

12. The dissolution of urea is represented by the equation below. A student determines that 5.39 grams of $H_2NCONH_2$ (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20. °C.



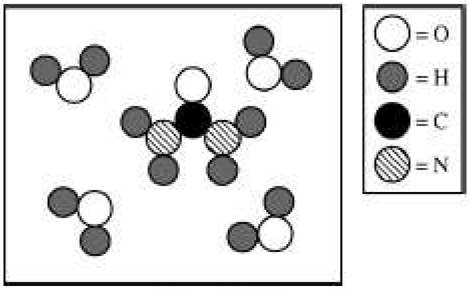
$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

a. Calculate the concentration of urea, in mol/L, in the saturated solution at 20. °C.

b. The student also determines that the concentration of urea in a saturated solution at 25 °C is 19.8 M. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.

c. The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

12. (2019, #1) The dissolution of urea is represented by the equation below. A student determines that 5.39 grams of $H_2NCONH_2$ (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20. °C.



$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$

a. Calculate the concentration of urea, in mol/L, in the saturated solution at 20. °C.

| | |
|---|---|
| $5.39\text{ g } H_2NCONH_2 \times \frac{1\text{ mol}}{60.06\text{ g}} = 0.0897\text{ mol}$<br>$\frac{0.0897\text{ mol}}{0.00500\text{ L}} = 17.9\ M$ | 1 point is earned for the correct number of moles of urea (may be implicit).<br>1 point is earned for the correct molarity. |

b. The student also determines that the concentration of urea in a saturated solution at 25 °C is 19.8 M. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.

| | |
|---|---|
| The increased solubility at the higher temperature implies that the dissolution of urea is endothermic. If a saturated solution of urea is heated, then the equilibrium system is stressed. The stress is counteracted by the endothermic dissolution of more urea. | 1 point is earned for the correct answer with an appropriate justification. |

c. The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

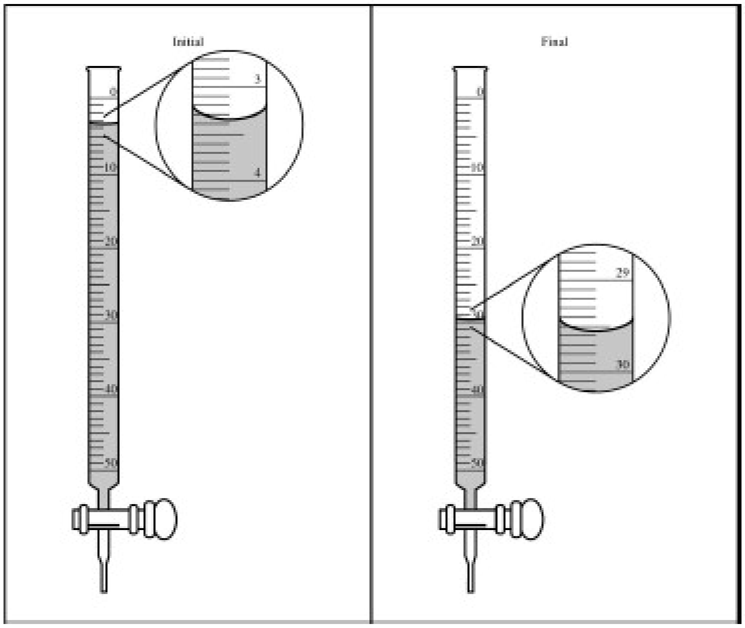
| | |
|---|---|
| mass of urea, mass of water, initial temperature of water, final temperature of solution | 1 point is earned for the masses.<br>1 point is earned for the temperatures. |

13. A student dissolved a 0.139 g sample of oxalic acid, $H_2C_2O_4$, in water in an Erlenmeyer flask. Then the student titrated the $H_2C_2O_4$ solution in the flask with a solution of $KMnO_4$, which has a dark purple color. The balanced chemical equation for the reaction that occurred during the titration is shown below.

$$6\ H^+\ (aq) + 2\ MnO_4^-\ (aq) + 5\ H_2C_2O_4\ (aq) \rightarrow 10\ CO_2\ (g) + 8\ H_2O\ (l) + 2\ Mn^{2+}\ (aq)$$

   a. Identify the species that was reduced in the titration reaction. Justify your answer in terms of oxidation numbers.

   b. The student used a 50.0 mL buret to add the $KMnO_4$ (aq) to the $H_2C_2O_4$ (aq) until a faint lavender color was observed in the flask, an indication that the end point of the titration had been reached. The initial and final volume readings of the solution in the buret are shown below. Write down the initial reading and the final reading and use them to determine the volume of $KMnO_4$ (aq) that was added during the titration.



   c. Given that the concentration of $KMnO_4$ (aq) was 0.0235 M, calculate the number of moles of $MnO_4^-$ ions that completely reacted with the $H_2C_2O_4$.

   d. The student proposes to perform another titration using a 0.139 g sample of $H_2C_2O_4$, but this time using 0.00143 M $KMnO_4$ (aq) in the buret. Would this titrant concentration be a reasonable choice to use if the student followed the same procedure and used the same equipment as before? Justify your response.

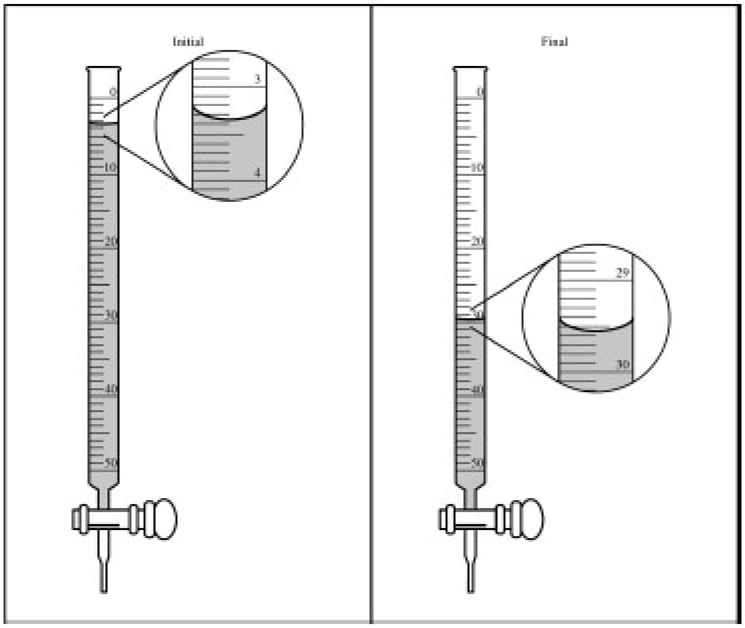
13. (2019, #7) A student dissolved a 0.139 g sample of oxalic acid, $H_2C_2O_4$, in water in an Erlenmeyer flask. Then the student titrated the $H_2C_2O_4$ solution in the flask with a solution of $KMnO_4$, which has a dark purple color. The balanced chemical equation for the reaction that occurred during the titration is shown below.

$$6\ H^+\ (aq) + 2\ MnO_4^-\ (aq) + 5\ H_2C_2O_4\ (aq) \rightarrow 10\ CO_2\ (g) + 8\ H_2O\ (l) + 2\ Mn^{2+}\ (aq)$$

a. Identify the species that was reduced in the titration reaction. Justify your answer in terms of oxidation numbers.

| | |
|---|---|
| $MnO_4^-$ is reduced to $Mn^{2+}$ as the oxidation number of Mn changes from +7 to +2, indicating a gain of 5 electrons. | 1 point is earned for the correct answer with justification. |

b. The student used a 50.0 mL buret to add the $KMnO_4$ (aq) to the $H_2C_2O_4$ (aq) until a faint lavender color was observed in the flask, an indication that the end point of the titration had been reached. The initial and final volume readings of the solution in the buret are shown below. Write down the initial reading and the final reading and use them to determine the volume of $KMnO_4$ (aq) that was added during the titration.

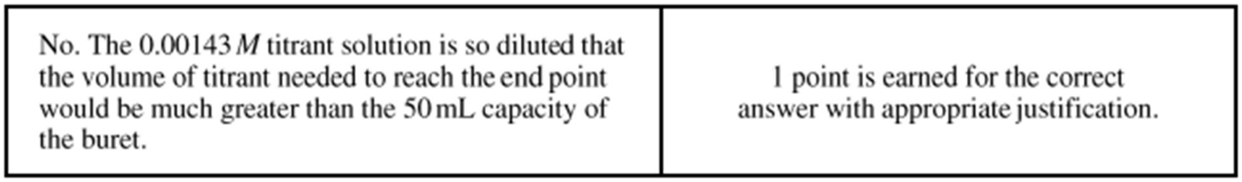


| | |
|---|---|
| 29.55 mL – 3.35 mL = 26.20 mL | 1 point is earned for the correct answer. |

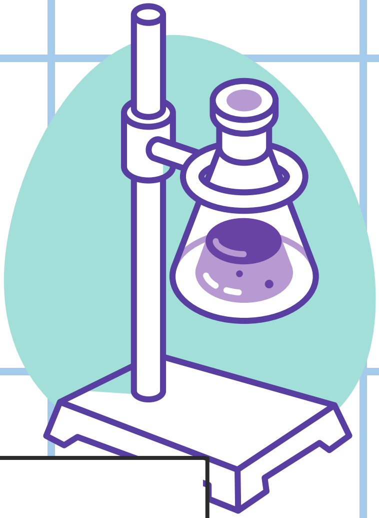
c. Given that the concentration of $KMnO_4$ (aq) was 0.0235 M, calculate the number of moles of $MnO_4^-$ ions that completely reacted with the $H_2C_2O_4$.

| | |
|---|---|
| (0.02620 L)(0.0235 mol/L) = 0.000616 mol | 1 point is earned for the correct answer. |

d. The student proposes to perform another titration using a 0.139 g sample of $H_2C_2O_4$, but this time using 0.00143 M $KMnO_4$ (aq) in the buret. Would this titrant concentration be a reasonable choice to use if the student followed the same procedure and used the same equipment as before? Justify your response.

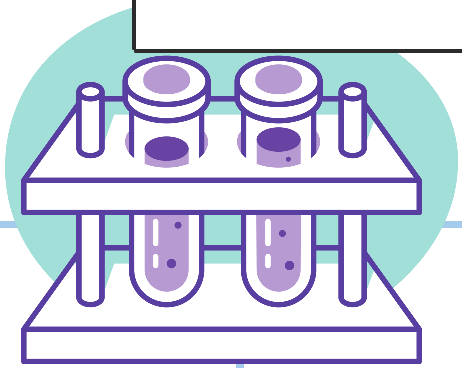


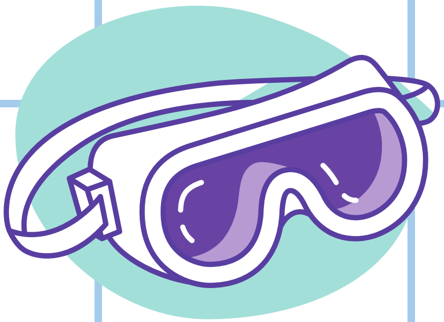
| | |
|---|---|
| No. The 0.00143 *M* titrant solution is so diluted that the volume of titrant needed to reach the end point would be much greater than the 50 mL capacity of the buret. | 1 point is earned for the correct answer with appropriate justification. |

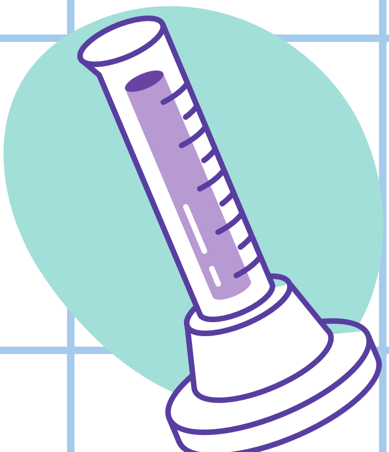


# WRITE THIS, NOT THAT!

2022 AP Chemistry Review Mr. Nackers







# Write This, Not That!

Compiled by: Nora Walsh FJ Reitz High School, Evansville, IN

Sources:
Released Free-Response Questions with Samples and Commentary/Chief Reader’s Reports
Adrian Dingle’s Blog Posts on Writing Good Answers
(https://www.adriandingleschemistrypages.com/)
AACT Webinar: Teaching Students How to Better Answer Non-Calculator Problems
AACT Webinars: Lessons Learned from AP Chemistry Exam (2017, 2018 and 2019)
AP Teacher Community
AP Teachers in the National AP Chemistry Teachers Facebook Group

All practice problems are taken from previous AP Chemistry Exams and are property of the College Board.

*IPE stands for International Practice Exam.

*FRQ stands for free response question and are the questions publicly released from the exam.

# For All Questions

| Write This… | …Not That! | Rationale |
|---|---|---|
| Handwriting that is clear, legible, dark enough and large enough to be read by someone who doesn't know you | Messy, illegible, light, tiny writing that cannot be read | Answers deemed illegible by a reader and the table leader will earn no points on corresponding parts/questions |
| Variables that are clearly denoted and appropriately used | Variables that are incorrectly represented | Variables have specific meaning and must be correctly denoted/abbreviated; case matters for many variables:<br>• M (not m) for molarity,<br>• K (equilibrium constant) vs k (rate constant)<br>• m is meters, not minutes, moles or molarity, etc. |
| Abbreviations that are generally accepted (M, min, s, IMF, LDF, etc.) | Abbreviations that are not generally accepted/ are incorrect/ change the meaning (ex: mol for molecule, CL instead of Coulomb's Law, etc) | Abbreviations still must convey the correct information; if in doubt, avoid them – don't create ambiguity in an answer by using an abbreviation |
| Answer the specific question first, then "justify", "explain" etc. | Burying the answer in the text of the response | Make it easy to follow your answer and give you points |
| Answers that are concise and direct | Burying the answer in a long response | Make it easy to follow your answer and give you points |
| Names of specific elements and compounds, "reactants", "products", etc. | "it" | Ambiguous |
| "Species" | "It", "stuff", etc. | Be formal in language |

# For All Questions (cont.)

| Write This… | …Not That! | Rationale |
|---|---|---|
| A justification or explanation when it is part of the question | Only the answer without supporting it | Justification/explanation required to earn point |
| “mass”, “volume”, etc. | “size” | Be specific to indicate understanding |
| References to specific data or graphs when prompted to “explain how the data…”, “using the table below…” or something similar | Generalizations about the data without specifically citing provided data or trials | Required to earn point |
| Particle view diagrams with ions and polar molecules orientated in the correct direction relative to each other | Incorrectly oriented dipoles | Drawings must demonstrate understanding of interactions at the molecular level<br>(ex. 2015 #4) |
| An answer with units if “include units” is stated in the problem | An answer without units | If “include units” is written in the prompt, a unit is required to earn full points |
| Complete dimensional analysis/work with units | Incomplete dimensional analysis without units | Including units clearly shows intended work, and allows points for “implied” calculations to be earned |
| Values with units that match constants and that are the same throughout the equation | Values with units that do not match other values/constants | Values must be the same unit through an equation, for both constants and variables |
| Answers expressed to the correct number of significant figures, based on data given in the problem | Answers with an incorrect number of significant figures or significant figures limited by molar mass, constants, etc. | 1 pt traditionally is assessed somewhere in the FR for significant figures (typically found in a laboratory data question) |

# For All Questions (cont.)

| Write This… | …Not That! | Rationale |
|---|---|---|
| Answers that only refer to substances/data included in the prompt | Answers with justifications based on situations or data that are not indicated in the prompt | Do not claim something happened that was not present in prompt– any valid assumptions would be stated |
| Analysis of given data in a thoughtful way that is based on chemical principals | Saying that data is wrong, that the data is impossible, calling the test writers liars, etc. | The AP Exam is never going to try to trick you- it will not give false or impossible data |
| Answers that refer to specific and correct glassware and interpret figures correctly | Answers that use incorrect glassware for the task, particularly with regard to precision and/or misread figures of glassware | Glassware has different specialized uses, and should be appropriately referenced/used/read based on the task |
| Explanation of an application of usage of a term | Definition of a term | A definition is not required on the exam – an explanation of how this term applies is needed |
| An explanation of the reason behind an observation of phenomena. | Stating a law/rule or observation without explaining the chemical principles or phenomena behind the law/rule/trend. | Simply stating the end result without discussing the reason for that result does not fully answer the question. Evidence and reasoning must both be included. (ex. 2019 #4) |
| Using deductive reasoning to make conclusions or approximate values when the terms “estimate” or “justify” are in the prompt | Using long, time-intensive math reasoning when “calculate” is not indicated in the prompt | While correct calculations will earn credit, the loss in this type of answer is the amount of time spent on the calculations when an assessment without lengthy calculations can be done instead (ex: 2018 #2e-f, 2019 #3g) |
| Answers that pay attention to the relative scale on graphs | Answers that make assumptions on the scale without examining data | Don’t assume that marked lines automatically are increments of 1, 10, etc. – use the data to determine the scale (ex. 2019 #5a) |

# Unit 1: Atomic Structure and Properties

| Write This… | …Not That! | Rationale |
|---|---|---|
| “period” | “shell” when referring to elements and their location on the Periodic Table | Elements are in a period, electrons are in a shell |
| Ion electron configurations that show electrons were removed from valence shell orbitals | Ion electron configurations that show electrons were removed from inner orbitals | Ions form by electrons being lost from the outermost shell; this may or may not be the electrons that were filled last in the electron configuration (ref. 2018 #3a) |
| Reference reasons for periodic trends (i.e. effective nuclear charge, Coulomb’s law, polarizability, etc.) | Stating the trend as the reason (“because it is to the left”, “because it is further down the periodic table”, etc.) | State the actual reason not the memory aid |
| “Effective nuclear charge increases” | “It wants to have a full octet”; “it’s close to having a full octet” | State the actual reason not the memory aid |
| “It has a more polarizable cloud of electrons” | “It has more electrons”, “it has more mass”, “it has more surface area”, “it is bigger”, “it has more protons” | State the actual reason not the memory aid |
| “Electrons in higher energy levels are farther from the nucleus, resulting in a larger atom/ion.” | “More electrons/more energy levels makes the atom/ion bigger.” | Explanation of reason, not just statement of fact, required for point<br>(Ref 2016 #1) |

# Unit 1 Practice Problem – 2018 FRQ #3

Answer the following questions relating to Fe and its ions, $Fe^{2+}$ and $Fe^{3+}$.

(a) Write the ground-state electron configuration of the $Fe^{2+}$ ion.

| Ion | Ionic Radius (pm) |
|---|---|
| $Fe^{2+}$ | 92 |
| $Fe^{3+}$ | 79 |

(b) The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the $Fe^{2+}$ ion is larger than the radius of the $Fe^{3+}$ ion.

(c) $Fe^{3+}$ ions interact more strongly with water molecules in aqueous solution than $Fe^{2+}$ ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

Parts d-f pertain to different units and were removed for this example

In a separate experiment, the student is given a sample of powdered $Fe(s)$ that contains an inert impurity. The student uses a procedure to oxidize the $Fe(s)$ in the sample to $Fe_2O_3(s)$. The student collects the following data during the experiment.

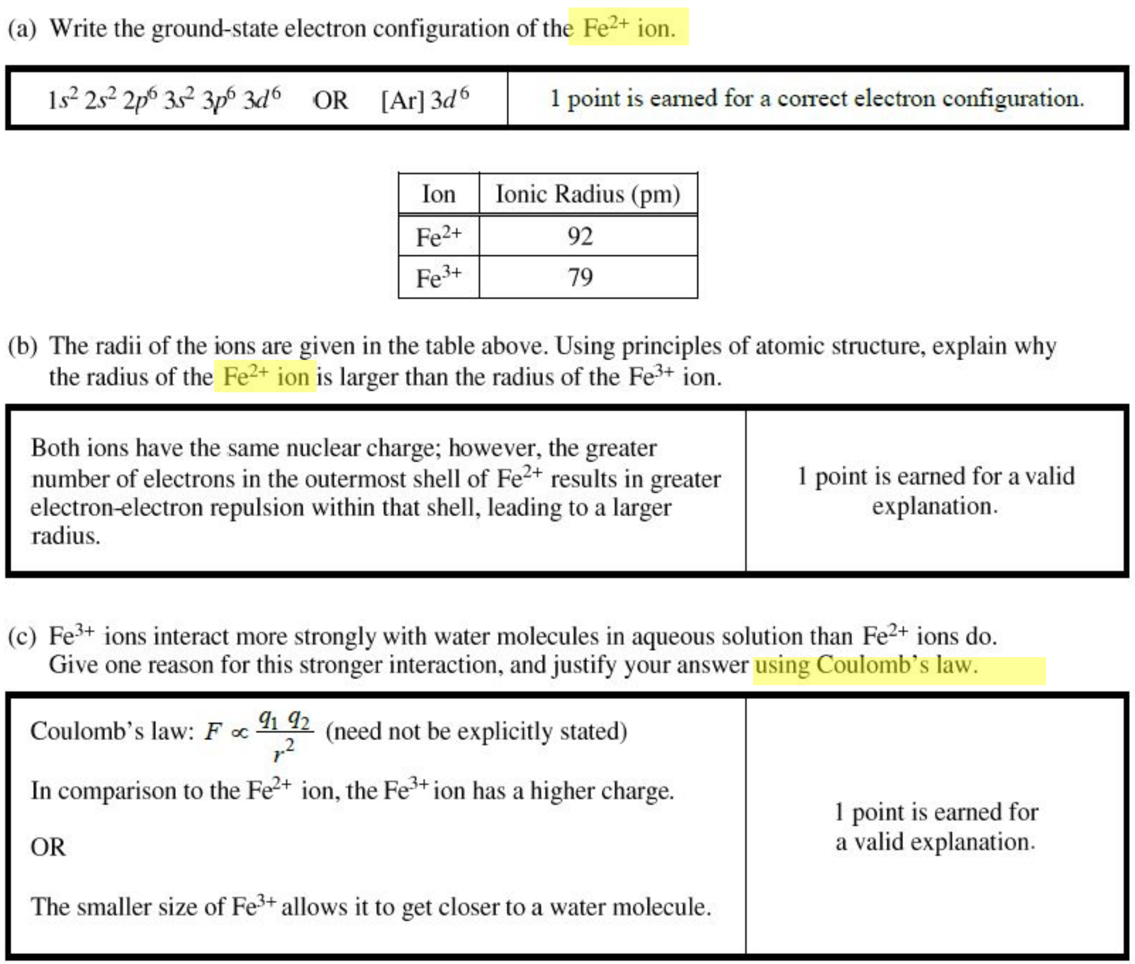
| | |
|---|---|
| Mass of $Fe(s)$ with inert impurity | 6.724 g |
| Mass of $Fe_2O_3(s)$ produced | 7.531 g |

(g) Calculate the number of moles of Fe in the $Fe_2O_3(s)$ produced.

(h) Calculate the percent by mass of Fe in the original sample of powdered $Fe(s)$ with the inert impurity.

(i) If the oxidation of the $Fe(s)$ in the original sample was incomplete so that some of the 7.531 g of product was $FeO(s)$ instead of $Fe_2O_3(s)$, would the calculated mass percent of $Fe(s)$ in the original sample be higher, lower, or the same as the actual mass percent of $Fe(s)$? Justify your answer.

# 2018 FRQ #3 Scoring Guidelines and Things to Notice



(a) Write the ground-state electron configuration of the $Fe^{2+}$ ion.

| | |
|---|---|
| $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ OR $[Ar] 3d^6$ | 1 point is earned for a correct electron configuration. |

| Ion | Ionic Radius (pm) |
|---|---|
| $Fe^{2+}$ | 92 |
| $Fe^{3+}$ | 79 |

(b) The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the $Fe^{2+}$ ion is larger than the radius of the $Fe^{3+}$ ion.

| | |
|---|---|
| Both ions have the same nuclear charge; however, the greater number of electrons in the outermost shell of $Fe^{2+}$ results in greater electron-electron repulsion within that shell, leading to a larger radius. | 1 point is earned for a valid explanation. |

(c) $Fe^{3+}$ ions interact more strongly with water molecules in aqueous solution than $Fe^{2+}$ ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

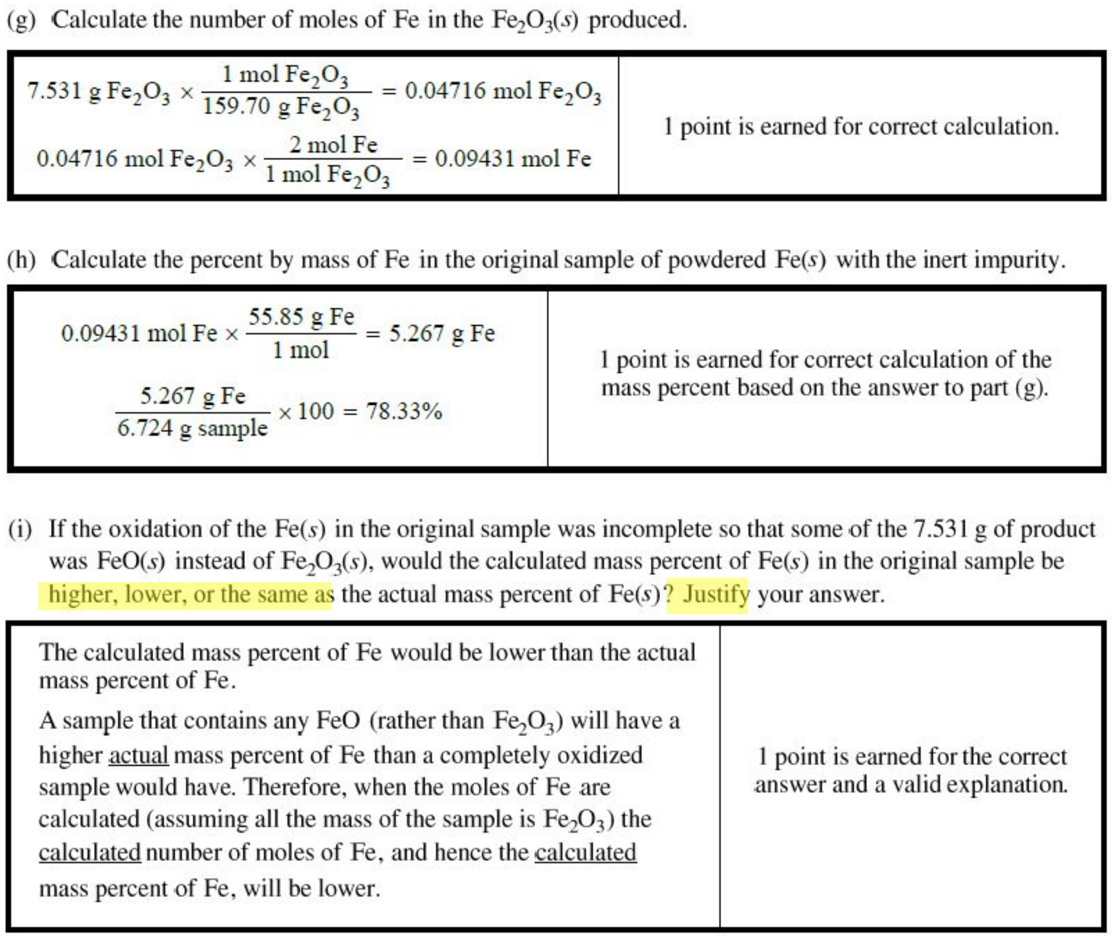
| | |
|---|---|
| Coulomb's law: $F \propto \frac{q_1 q_2}{r^2}$ (need not be explicitly stated)<br>In comparison to the $Fe^{2+}$ ion, the $Fe^{3+}$ ion has a higher charge.<br>OR<br>The smaller size of $Fe^{3+}$ allows it to get closer to a water molecule. | 1 point is earned for a valid explanation. |

- Notice that this electron configuration is for an ion, and that the two electrons were lost from the valence shell (not the last filled shell)

- Notice that the response references both ions but then the justification is in terms of the $Fe^{2+}$ (because the prompt asks why the $Fe^{2+}$ is larger)

- Because you are told to justify using Coulomb's law, the explanation will not be correct without referencing features of the law at play

# 2018 FRQ #3 Scoring Guidelines and Things to Notice (cont).



(g) Calculate the number of moles of Fe in the $Fe_2O_3(s)$ produced.

| | |
|---|---|
| $7.531\ g\ Fe_2O_3 \times \frac{1\ mol\ Fe_2O_3}{159.70\ g\ Fe_2O_3} = 0.04716\ mol\ Fe_2O_3$<br>$0.04716\ mol\ Fe_2O_3 \times \frac{2\ mol\ Fe}{1\ mol\ Fe_2O_3} = 0.09431\ mol\ Fe$ | 1 point is earned for correct calculation. |

(h) Calculate the percent by mass of Fe in the original sample of powdered Fe(*s*) with the inert impurity.

| | |
|---|---|
| $0.09431\ mol\ Fe \times \frac{55.85\ g\ Fe}{1\ mol} = 5.267\ g\ Fe$<br>$\frac{5.267\ g\ Fe}{6.724\ g\ sample} \times 100 = 78.33\%$ | 1 point is earned for correct calculation of the mass percent based on the answer to part (g). |

(i) If the oxidation of the Fe(*s*) in the original sample was incomplete so that some of the 7.531 g of product was FeO(*s*) instead of $Fe_2O_3(s)$, would the calculated mass percent of Fe(*s*) in the original sample be higher, lower, or the same as the actual mass percent of Fe(*s*)? Justify your answer.

| | |
|---|---|
| The calculated mass percent of Fe would be lower than the actual mass percent of Fe.<br>A sample that contains any FeO (rather than $Fe_2O_3$) will have a higher actual mass percent of Fe than a completely oxidized sample would have. Therefore, when the moles of Fe are calculated (assuming all the mass of the sample is $Fe_2O_3$) the calculated number of moles of Fe, and hence the calculated mass percent of Fe, will be lower. | 1 point is earned for the correct answer and a valid explanation. |

- Show all work and make it easy to follow by using units and math that has a logical progression on the page

- Remember: no double jeopardy; using an incorrect answer from part g will still give the point here if this part is done correctly

- Answer the question first: “lower”
- Justify second. Notice that the point is not earned without the justification – it must be included.
- Don’t let wording through you off – you don’t need to do anything with oxidation here, it’s all thinking about the impact of an leftover reactant on calculations in an experiment

# Unit 2: Molecular and Ionic Compound Structure and Properties

| Write This… | …Not That! | Rationale |
|---|---|---|
| “ionic compound” | “molecule” when discussing an ionic compound | A molecule is a covalent compound |
| “ions” | “atoms” when discussing ionic compounds | Ionic compounds contain ions – this shows the understanding that it is the charges that form the bond |
| “atoms” | “ions” when discussing covalent compounds | Covalent compounds do not contain ions |
| “Coulombic attraction” | “Opposites attract” | State the actual reason not the memory aid |
| Lewis structures that are complete with necessary lone pairs and/or resonance | Lewis structures that are missing lone pairs and/or resonance (if needed for correct structures) | Lewis structures are incorrect without necessary lone pairs/resonance |
| Multiple bonds when there are not enough valence electrons to satisfy the octet rule | Multiple bonds when the octet rule for the structure would have been satisfied without them | Multiple bonds are only needed when there are not enough valence electrons to satisfy the octet rule |
| Stating a VSEPR geometry/hybridization that thinks about the 3D arrangement of atoms in a molecule | State a VSEPR geometry/hybridization that thinks about a molecule based on its 2D representation | VSEPR/hybridization are used to describe the 3D arrangement of atoms in a molecule; failing to recognize the difference between the way a Lewis structure is drawn and the way the actual molecule is arranged may lead to an incorrect analysis of structure (ref. 2018 #2d) |

# Unit 2 Practice Problem - 2014 IPE #5

| Nonmetal | C | N | O | Ne | Si | P | S | Ar |
|---|---|---|---|---|---|---|---|---|
| Formula of Compound | $CF_4$ | $NF_3$ | $OF_2$ | No compound | $SiF_4$ | $PF_3$ | $SF_2$ | No compound |

Some binary compounds that form between fluorine and various nonmetals are listed in the table above. A student examines the data in the table and poses the following hypothesis: the number of F atoms that will bond to a nonmetal is always equal to 8 minus the number of valence electrons in the nonmetal atom.

(a) Based on the student's hypothesis, what should be the formula of the compound that forms between chlorine and fluorine?

(b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula $ClF_3$. In the box below, draw a complete Lewis electron-dot diagram for a molecule of $ClF_3$.

(c) Two possible geometric shapes for the $ClF_3$ molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the $ClF_3$ molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

In an attempt to resolve the existence of the $ClF_3$ molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list.

| Halogen | Formula(s) |
|---|---|
| F | $F_2$ |
| Cl | |
| Br | $BrF$, $BrF_3$, $BrF_5$ |
| I | $IF$, $IF_3$, $IF_5$, $IF_7$ |

(d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.

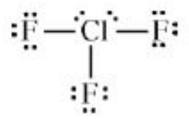
# 2014 IPE #5 Scoring Guidelines and Things to Notice

(a) Based on the student's hypothesis, what should be the formula of the compound that forms between chlorine and fluorine?

| | |
|---|---|
| ClF | 1 point is earned for the correct formula. |

- Be sure that your handwriting shows clearly that this is ClF with correct capitalization and order of the atoms

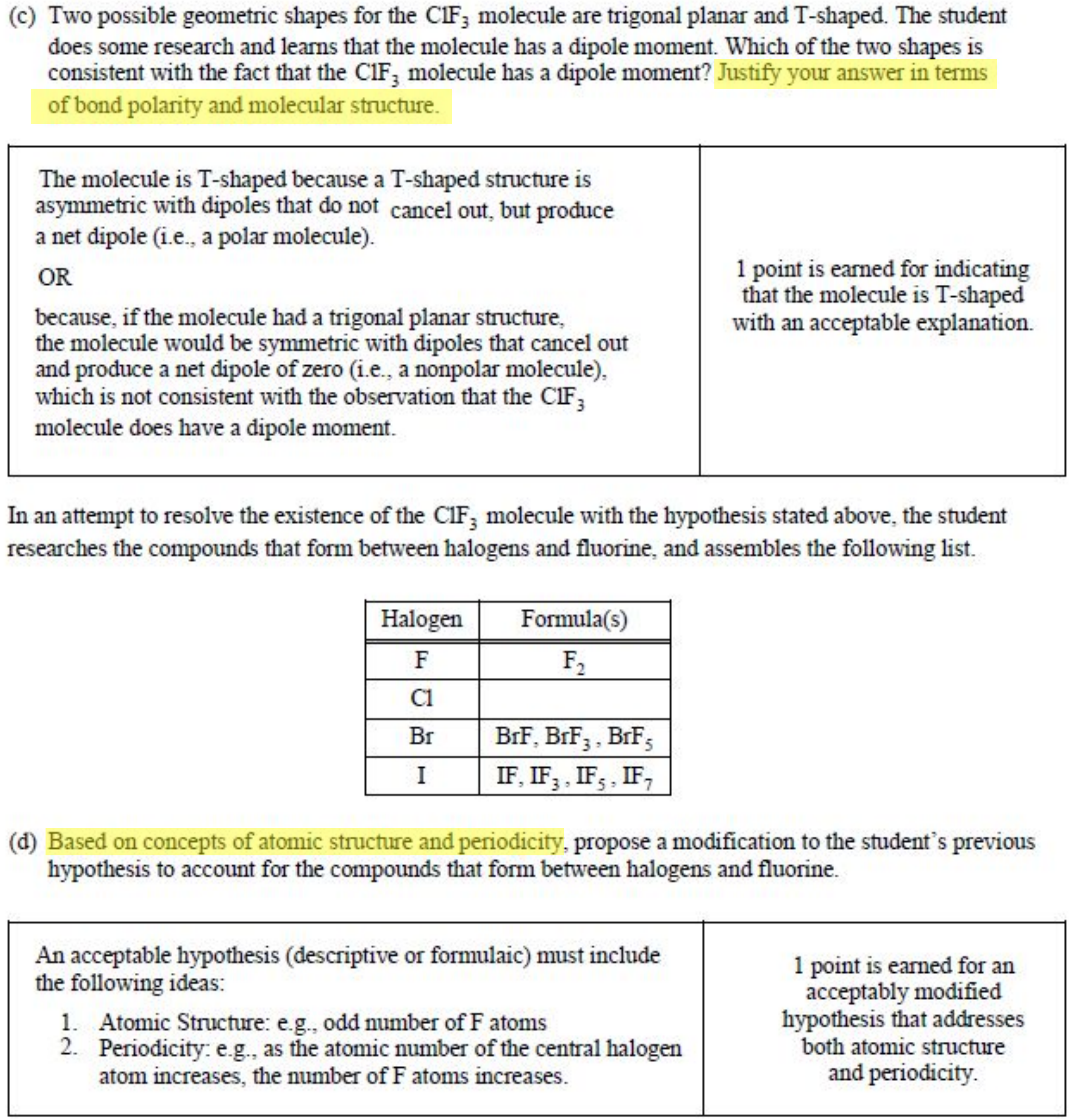
(b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula $ClF_3$ In the box below, draw a complete Lewis electron-dot diagram for a molecule of $ClF_3$.



| | |
|---|---|
| See diagram above. | 1 point is earned for a central Cl atom surrounded by three bonding pairs with F atoms and two nonbonding (lone) pairs of electrons. F atoms must have three nonbonding pairs each. Electron pairs can be depicted as dots or line segments. |

- Be sure that you clearly denote the 3 bonds between the Cl and the 3 F atoms and that you fully complete the 3 lone pairs around EACH F atom and the 2 lone pairs on the Cl

# 2014 IPE #5 Scoring Guidelines and Things to Notice (cont.)



(c) Two possible geometric shapes for the $ClF_3$ molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the $ClF_3$ molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

| | |
|---|---|
| The molecule is T-shaped because a T-shaped structure is asymmetric with dipoles that do not cancel out, but produce a net dipole (i.e., a polar molecule).<br>OR<br>because, if the molecule had a trigonal planar structure, the molecule would be symmetric with dipoles that cancel out and produce a net dipole of zero (i.e., a nonpolar molecule), which is not consistent with the observation that the $ClF_3$ molecule does have a dipole moment. | 1 point is earned for indicating that the molecule is T-shaped with an acceptable explanation. |

In an attempt to resolve the existence of the $ClF_3$ molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list.

| Halogen | Formula(s) |
|---|---|
| F | $F_2$ |
| Cl | |
| Br | $BrF$, $BrF_3$, $BrF_5$ |
| I | $IF$, $IF_3$, $IF_5$, $IF_7$ |

(d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.

| | |
|---|---|
| An acceptable hypothesis (descriptive or formulaic) must include the following ideas:<br>1. Atomic Structure: e.g., odd number of F atoms<br>2. Periodicity: e.g., as the atomic number of the central halogen atom increases, the number of F atoms increases. | 1 point is earned for an acceptably modified hypothesis that addresses both atomic structure and periodicity. |

- Note that just saying "T Shaped" would not earn the point here – the correct geometry AND the justification are both needed
- The prompt says "in terms of bond polarity and molecular structure" – in addition to the geometry, the dipoles must be referenced

- The prompt says "based on concepts of atomic structure and periodicity" – both must be referenced to earn this point

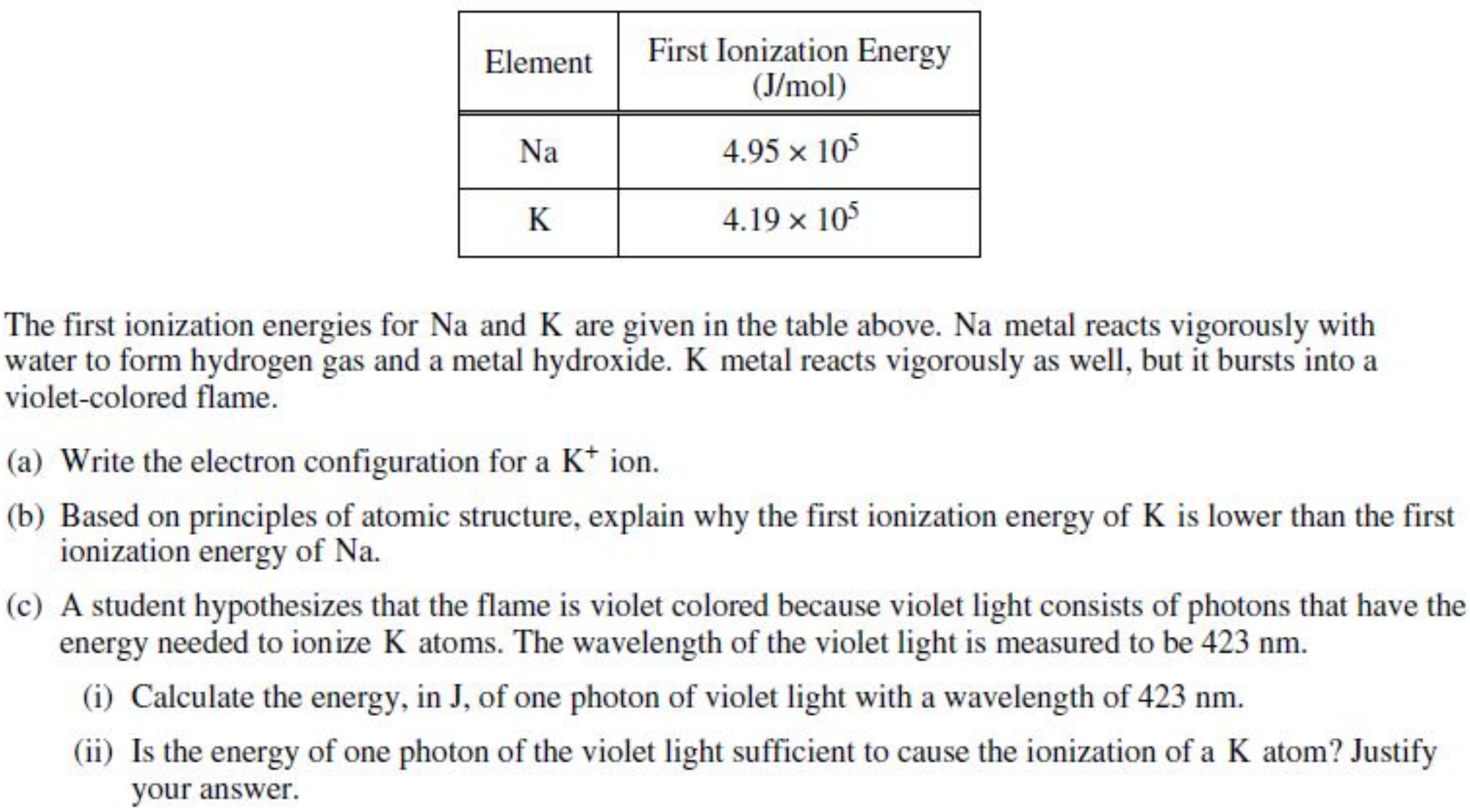
# Unit 3: Intermolecular Forces and Properties

| Write This… | …Not That! | Rationale |
|---|---|---|
| Hydrogen bonding, dipole-dipole, London dispersion forces, etc. when asked to identify intermolecular forces | Ionic bonds, covalent bonds, metallic bonds when asked to identify intermolecular forces | Intermolecular forces are attractions between molecules; bonds are intramolecular forces (within molecules) |
| Discussion of ALL intermolecular forces when prompted to do so | Neglecting IMFs that may be weaker | If asked to state all IMFs, all points will not be earned if some of the IMFs are not stated (ref. 2018 #4a and 2019 #2c) |
| “Has hydrogen bonds between the molecules” | “Has hydrogen bonds” | Is unambiguous - Shows that you understand hydrogen bonds are not actually bonds |
| Electrical conductivity is a property of an ionic solution due to the charges on the dissociated ions | Electrical conductivity is due to the ionic precipitate, electrical conductivity is due to the water | Conductivity is due to the ability of a ion to carry charge; precipitate would not influence in solid form; pure water is non-conductive, (ref. 2019 #3e) |
| “Overcome intermolecular forces” | “break up” a solid/liquid, break covalent bonds | IMFs should be used to justify phase changes |
| “Stronger intermolecular forces increase boiling point” | “Stronger covalent bonds increase boiling point” | IMF’s, not bonds, are what must be overcome during phase changes |
| Ion interactions when discussing ionic compounds | LDF’s when discussing ionic compounds | Ionic compounds have ions with whole charges, which dominate interactions |
| “Coulombic attraction” | “Opposites attract” | State the actual reason not the memory aid |
| Describe the process of overcoming intermolecular forces/polarity | “Like dissolves like” | State the actual reason not the memory aid |

# Unit 3: Intermolecular Forces and Properties (cont.)

| Write This… | …Not That! | Rationale |
|---|---|---|
| Identify specific intermolecular forces at play | “stronger intermolecular forces” | Shows your understanding of the particulate-level chemistry |
| LDFs increase with an increasing number of electrons and therefore polarizability | LDFs increase with increasing size/mass | Increased number of electrons in an atom is what increases LDF; increased size is not the reason for increased strength of LDF |
| Intermolecular forces in discussing physical properties (MP, BP, etc) | Intramolecular forces (“bonds”) in discussing physical properties | Bonds are not broken and so intramolecular forces are not the determining factors (ref. 2018 #4a and 2019 #2c) |
| Pressure is caused by the collision of gas particles with the walls of a container. | Pressure is caused by the collision of gas particles. | Unclear wording – implies pressure is caused by gas particles colliding with each other not with the container (ref. 2019 #4c) |
| Use R with corresponding units to those used in work (and correctly report final unit) | R value with mismatched units | Units used in Ideal Gas Law must match units on the R value (ref. 2018 #4b and 2019 #2d) |
| Comparison of $R_f$ values in chromatography | Comparison of absolute height of spots on chromatograms | Take into account a difference in the distance the solvent front travelled between different chromatograms (ref. 2017 #4) |
| Discussion of intermolecular forces between analyte molecules and stationary/mobile phases | Repulsions between analyte molecules and stationary/mobile phases | The movement in chromatography is determined by the attraction for the stationary/mobile phase (ref. 2017 #4) |
| “Solution” when an ionic compound is dissolved in water | “Liquid” instead of solution | An ionic compound dissolved in water is a solution, not a liquid (the word liquid indicates a molten compound) (ref. 2019 #3e) |

# Unit 3 Practice - 2016 IPE #5



| Element | First Ionization Energy (J/mol) |
|---|---|
| Na | $4.95 \times 10^5$ |
| K | $4.19 \times 10^5$ |

The first ionization energies for Na and K are given in the table above. Na metal reacts vigorously with water to form hydrogen gas and a metal hydroxide. K metal reacts vigorously as well, but it bursts into a violet-colored flame.

(a) Write the electron configuration for a $K^+$ ion.

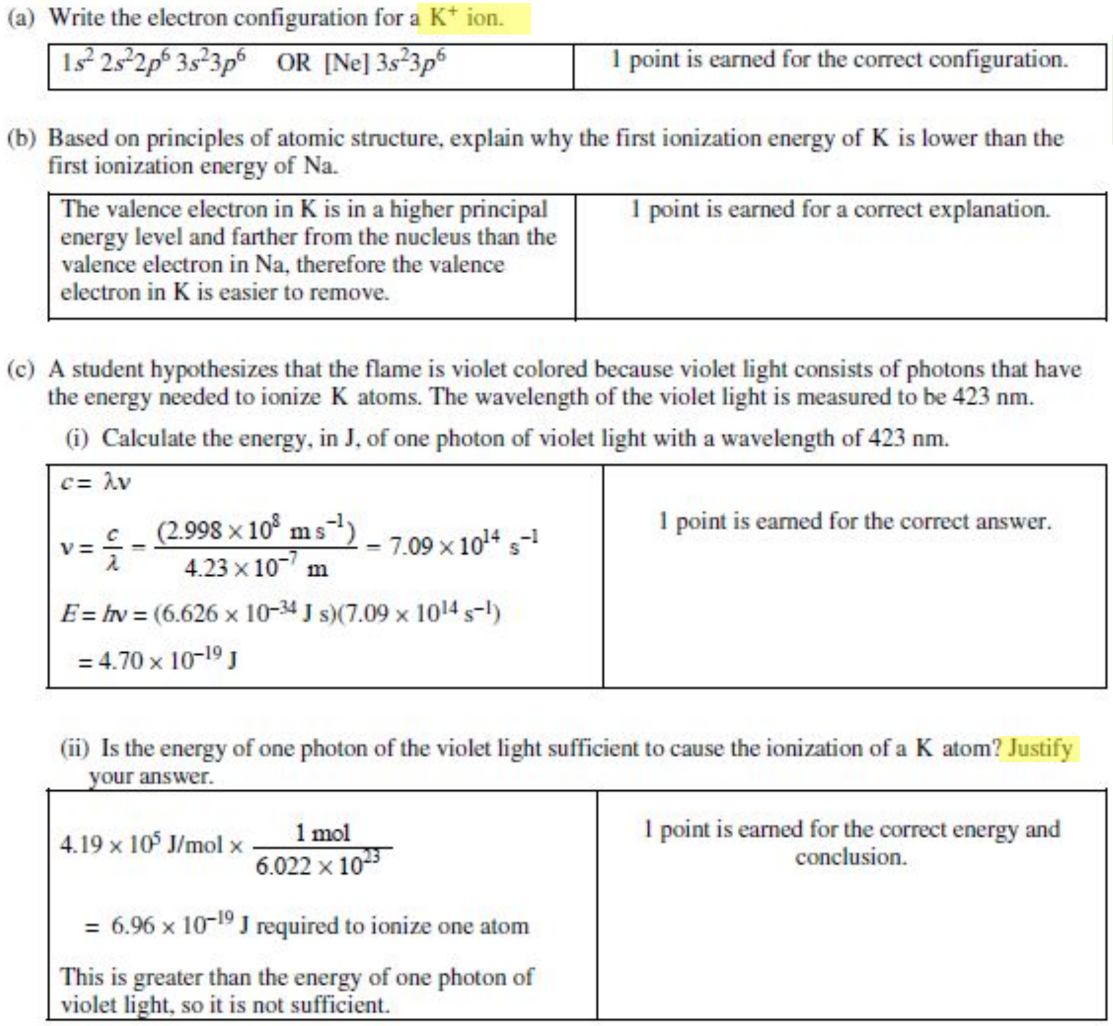
(b) Based on principles of atomic structure, explain why the first ionization energy of K is lower than the first ionization energy of Na.

(c) A student hypothesizes that the flame is violet colored because violet light consists of photons that have the energy needed to ionize K atoms. The wavelength of the violet light is measured to be 423 nm.

(i) Calculate the energy, in J, of one photon of violet light with a wavelength of 423 nm.

(ii) Is the energy of one photon of the violet light sufficient to cause the ionization of a K atom? Justify your answer.

# 2016 IPE #5 Scoring Guidelines and things to notice



(a) Write the electron configuration for a $K^+$ ion.

| | |
|---|---|
| $1s^2\,2s^22p^6\,3s^23p^6$ OR $[Ne]\,3s^23p^6$ | 1 point is earned for the correct configuration. |

(b) Based on principles of atomic structure, explain why the first ionization energy of K is lower than the first ionization energy of Na.

| | |
|---|---|
| The valence electron in K is in a higher principal energy level and farther from the nucleus than the valence electron in Na, therefore the valence electron in K is easier to remove. | 1 point is earned for a correct explanation. |

(c) A student hypothesizes that the flame is violet colored because violet light consists of photons that have the energy needed to ionize K atoms. The wavelength of the violet light is measured to be 423 nm.

(i) Calculate the energy, in J, of one photon of violet light with a wavelength of 423 nm.

| | |
|---|---|
| $c = \lambda\nu$<br>$\nu = \frac{c}{\lambda} = \frac{(2.998 \times 10^8\ \mathrm{m\,s^{-1}})}{4.23 \times 10^{-7}\ \mathrm{m}} = 7.09 \times 10^{14}\ \mathrm{s^{-1}}$<br>$E = h\nu = (6.626 \times 10^{-34}\ \mathrm{J\,s})(7.09 \times 10^{14}\ \mathrm{s^{-1}})$<br>$= 4.70 \times 10^{-19}\ \mathrm{J}$ | 1 point is earned for the correct answer. |

(ii) Is the energy of one photon of the violet light sufficient to cause the ionization of a K atom? Justify your answer.

| | |
|---|---|
| $4.19 \times 10^5\ \mathrm{J/mol} \times \frac{1\ \mathrm{mol}}{6.022 \times 10^{23}}$<br>$= 6.96 \times 10^{-19}$ J required to ionize one atom<br>This is greater than the energy of one photon of violet light, so it is not sufficient. | 1 point is earned for the correct energy and conclusion. |

- Because this is K+, the valence electron is absent

- Both K and Na are mentioned, by using their symbol/name, and a comparison between the two is made

- Units are noted in the work so that it is easy to follow
- Correct units and sig figs are used – while not required to earn this particular point, they are often required

- Units are noted in the work so that it is easy to follow
- Notice that the math alone would not earn the point – the correct energy AND the application of the calculation to the conclusion are necessary

# Unit 4: Chemical Reactions

| Write This… | …Not That! | Rationale |
|---|---|---|
| Net ionic equations only containing species that change | Aqueous ionic compounds in their undissociated form, spectator ions | Including these is not a net ionic, it's a molecular or complete ionic |
| Polyatomic ions that are shown as a compound with the correct charge in solution | Polyatomic ions that are broken down into elemental ions in solution | Polyatomic ions themselves do not dissociate in solution, they only dissociate from the other ion in an ionic compound |
| Net ionic equations with correct species, ionic charges and stoichiometric coefficients | Net ionic equations that contain incorrect formulas or ions without associated charges or that are not stoichiometrically balanced | Net ionic equations must correctly represent the ions and other species (ref. 2018 #6a and 2019 #3a) |
| Determination of the concentration of an analyte in a titration that takes into account the stoichiometry of the reaction | Applying $M_1V_1=M_2V_2$ as a blanket method for determining concentration at an end point if the stoichiometry is not 1:1 | While acid-base titrations are often 1:1, not all titrations (especially REDOX titrations) follow this stoichiometry; in situations that are not 1:1, the stoichiometric ratios must be accounted for in calculations (ref. 2018 #3e) |
| Justification of whether a species is oxidized/reduced by referencing oxidation numbers | A justification of oxidation/reduction that uses charge on an ion | Oxidation numbers are assigned to individual atoms in the reaction, and they are not automatically the same as the charge in a polyatomic ion (ref. 2019 #7a) |

# Unit 3-4 Practice – 2018 FRQ #4

Sulfur atom = ◍ Carbon atom = ● Oxygen atom = ○

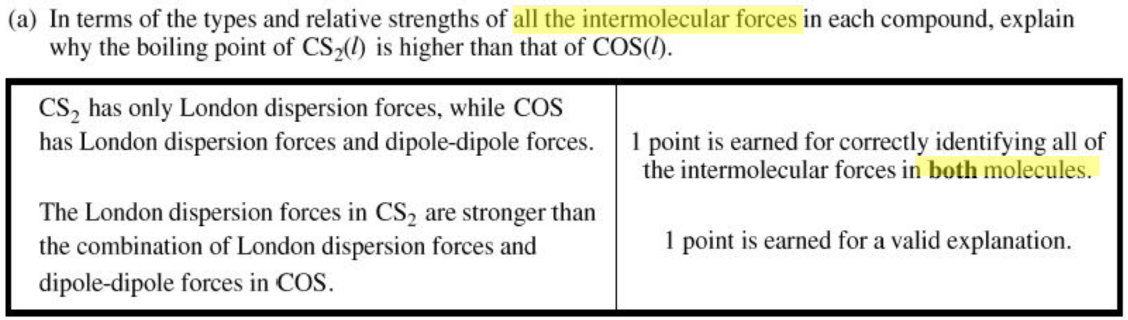
| Compound | Molecular Structure | Boiling Point at 1 atm (K) |
|---|---|---|
| $CS_2$ |  | 319 |
| $COS$ |  | 223 |

The table above gives the molecular structures and boiling points for the compounds $CS_2$ and $COS$.

(a) In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of $CS_2(l)$ is higher than that of $COS(l)$.

(b) A 10.0 g sample of $CS_2(l)$ is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the $CS_2(l)$ has vaporized. What is the pressure in the container once all of the $CS_2(l)$ has vaporized?

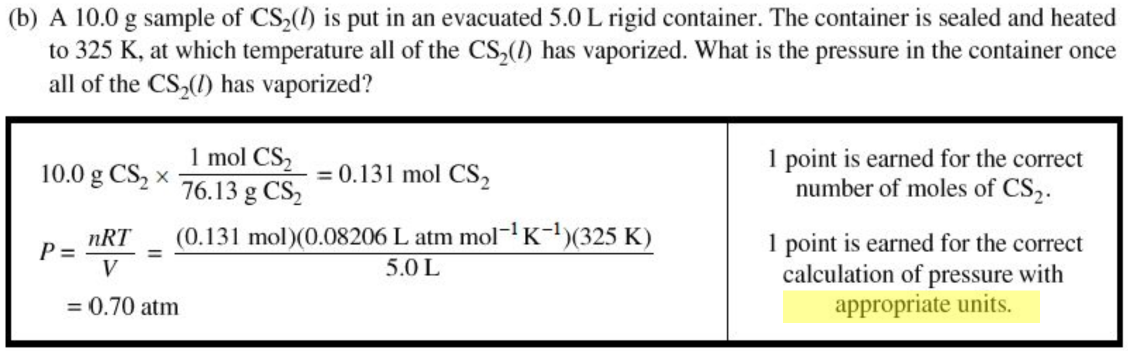
# 2018 FRQ #4 Scoring Guidelines and Things to Notice



(a) In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of $CS_2(l)$ is higher than that of $COS(l)$.

| | |
|---|---|
| $CS_2$ has only London dispersion forces, while COS has London dispersion forces and dipole-dipole forces. | 1 point is earned for correctly identifying all of the intermolecular forces in **both** molecules. |
| The London dispersion forces in $CS_2$ are stronger than the combination of London dispersion forces and dipole-dipole forces in COS. | 1 point is earned for a valid explanation. |

- Prompt states ALL intermolecular forces; first point is not earned without saying all IMFs for both molecules
- In the explanation discuss the $CS_2$ relative to the COS – your answer should match the prompt



(b) A 10.0 g sample of $CS_2(l)$ is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the $CS_2(l)$ has vaporized. What is the pressure in the container once all of the $CS_2(l)$ has vaporized?

| | |
|---|---|
| $10.0\text{ g }CS_2 \times \frac{1\text{ mol }CS_2}{76.13\text{ g }CS_2} = 0.131\text{ mol }CS_2$ | 1 point is earned for the correct number of moles of $CS_2$. |
| $P = \frac{nRT}{V} = \frac{(0.131\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})(325\text{ K})}{5.0\text{ L}}$<br>$= 0.70\text{ atm}$ | 1 point is earned for the correct calculation of pressure with appropriate units. |

- The point could be earned even if you combined the math into one entry in your calculator – units and labels are important so the reader can award you this implicit point
- The answer must include units to be awarded the second point

# Unit 5: Kinetics

| Write This… | …Not That! | Rationale |
|---|---|---|
| A rate law based only on reactants | A rate law that includes products | Rate laws are based only on reactants |
| A rate law that includes the rate constant k as part of it | A rate law without k being included | Incomplete rate law if k is not included |
| Value of k with units | Value of k without units | Units required to earn point |
| Specific parts of the molecules that must collide in order for the reaction to occur | “Collision must occur in the correct orientation” | Show your understanding of the chemistry at play |
| A validation of a proposed mechanism by showing that the rate law matches the slow (rate-determining step) and the mechanism matching the overall stoichiometry for the reaction. | A justification of a mechanism just by saying “it matches the rate law” or “the intermediates cancel to give the overall process”. | The rate law must be discussed as matching the rate-determining step, and the overall stoichiometry should always match for any proposed mechanism – an understanding of the rate determining step must be demonstrated. (ref. 2019 #6b) |

# Unit 5 Practice – 2014 IPE #7


*cis*-2-butene *trans*-2-butene

The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

| Trial Number | Initial $P_{cis\text{-}2\text{-butene}}$ (torr) | $V$ (L) | $T$ (K) | $t_{1/2}$ (s) |
|---|---|---|---|---|
| 1 | 300. | 2.00 | 350. | 100. |
| 2 | 600. | 2.00 | 350. | 100. |
| 3 | 300. | 4.00 | 350. | 100. |
| 4 | 300. | 2.00 | 365 | 50. |

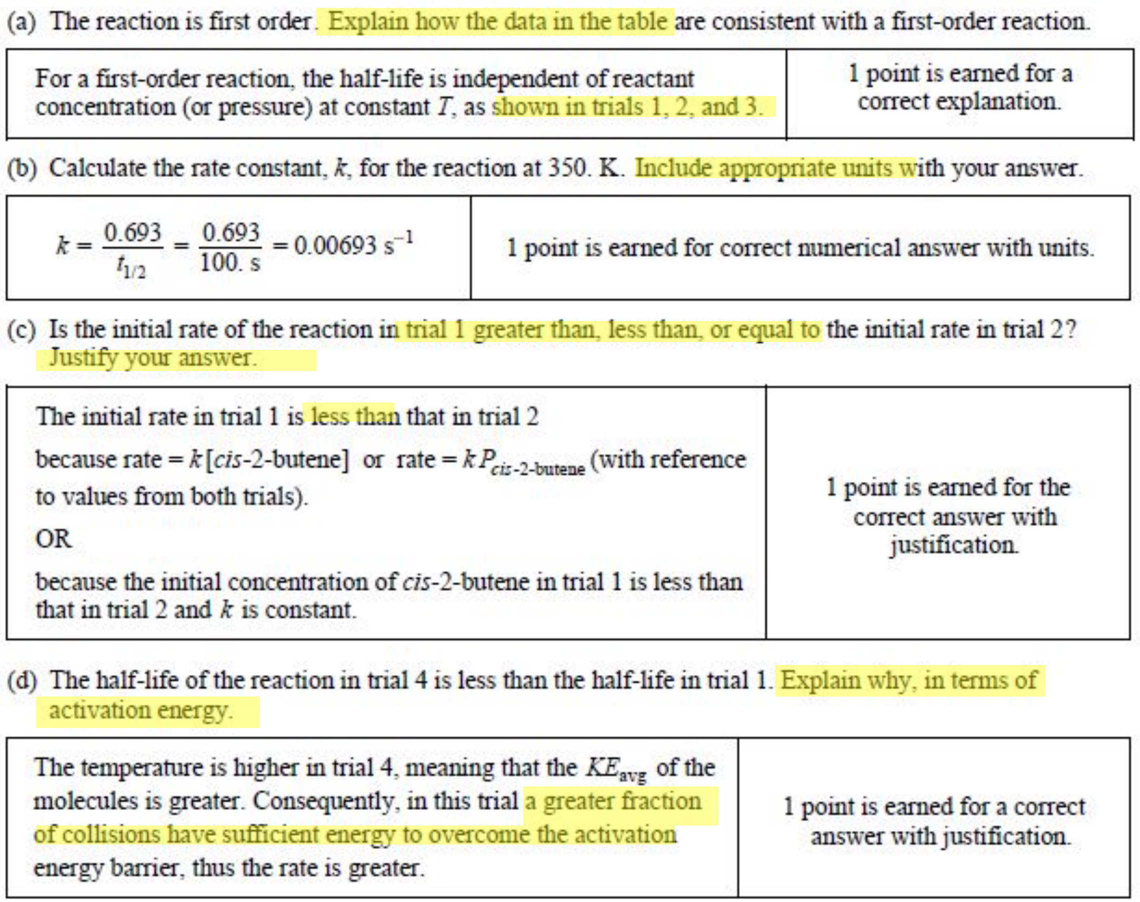
(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, $k$, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

# 2014 IPE #7 Scoring Guidelines and Things to Notice



(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

| | |
|---|---|
| For a first-order reaction, the half-life is independent of reactant concentration (or pressure) at constant $T$, as shown in trials 1, 2, and 3. | 1 point is earned for a correct explanation. |

(b) Calculate the rate constant, $k$, for the reaction at 350. K. Include appropriate units with your answer.

| | |
|---|---|
| $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100.\ \text{s}} = 0.00693\ \text{s}^{-1}$ | 1 point is earned for correct numerical answer with units. |

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

| | |
|---|---|
| The initial rate in trial 1 is less than that in trial 2<br>because rate = $k$[*cis*-2-butene] or rate = $k P_{cis\text{-2-butene}}$ (with reference to values from both trials).<br>OR<br>because the initial concentration of *cis*-2-butene in trial 1 is less than that in trial 2 and $k$ is constant. | 1 point is earned for the correct answer with justification. |

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

| | |
|---|---|
| The temperature is higher in trial 4, meaning that the $KE_{avg}$ of the molecules is greater. Consequently, in this trial a greater fraction of collisions have sufficient energy to overcome the activation energy barrier, thus the rate is greater. | 1 point is earned for a correct answer with justification. |

- The answer needs to reference the data table so that it meets the requirements in the prompt.

- The answer must include units to be awarded the point.

- First answer the question by choosing one of the listed options (for trial 1).
- Then justify
- Both parts must be included in order for the point to be earned

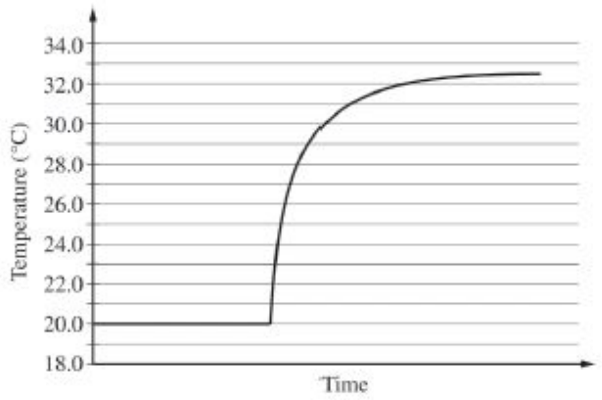
- The answer must be justified relative to activation energy – just stating the KE is greater will not be enough.

# Unit 6: Thermodynamics

| Write This… | …Not That! | Rationale |
|---|---|---|
| “Thermodynamically favorable”, “thermodynamically feasible” | “Spontaneous” | Preferred AP language |
| Values with correct signs | Values with incorrect signs | Necessary for correct calculations and determinations – watch signs based on bonds breaking/forming, heat flow in calorimetry indicated by temperature changes, signs that may change in application of Hess’ Law, etc. |
| Using values of q recognizing that it is the amount of energy absorbed/released during a thermodynamic change | Using values of q interchangeably as values of ΔH without taking the entire situation into account. | ΔH and q do not have identical meaning; ΔH is the enthalpy change for a reaction, q is the overall amount of heat exchanged ; Stoichiometric relationships, the component of the system being examined, etc. may influence how q should be manipulated to determine ΔH (ref. 2018 #1) |
| In using $q=mc\Delta T$ for solutions, using mass of ENTIRE solution for m | Using mass of only one component of solution | When using $q=mc\Delta T$, the mass of the entire system being examined must be used |
| Use a thermometer to measure temperature values, and then subtract to find ΔT | Use a thermometer to measure ΔT | A thermometer doesn’t measure ΔT, it measures T values that can then be used to calculate ΔT (ref. 2019 #1e) |
| $\Delta H^\circ = \Sigma$(enthalpies of bonds broken) $-\Sigma$(enthalpies of bonds formed) when calculating $\Delta H^\circ_{rxn}$ from bond energies | $\Delta H^\circ_{rxn} = \Delta H_{products} - \Delta H_{reactants}$ when calculating $\Delta H^\circ_{rxn}$ from bond energies | Applying the wrong formula will give an incorrect sign for the $\Delta H^\circ_{rxn}$ (ref. 2017 #2b) |
| Multiplying bond energy values by stoichiometric factors as well as number of bonds in a molecule when calculating ΔH from bond energies | Only using number of bonds in a single molecule without taking stoichiometric factors into account | Stoichiometry factors represent the number of molecules taking part in the reaction, so number of bonds in a single molecule must be multiplied by this coefficient (ref. 2019 #2g) |

# Unit 6 Practice – 2018 FRQ #1 (parts d-g)

The solutions, all originally at 20.0°C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



(d) According to the graph, what is the temperature change of the reaction mixture?

(e) The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is 3.94 J/(g·°C) and that the heat absorbed by the calorimeter is negligible.

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction, $\Delta H^\circ_{rxn}$, in kJ/mol$_{rxn}$. Include the appropriate algebraic sign with your answer.

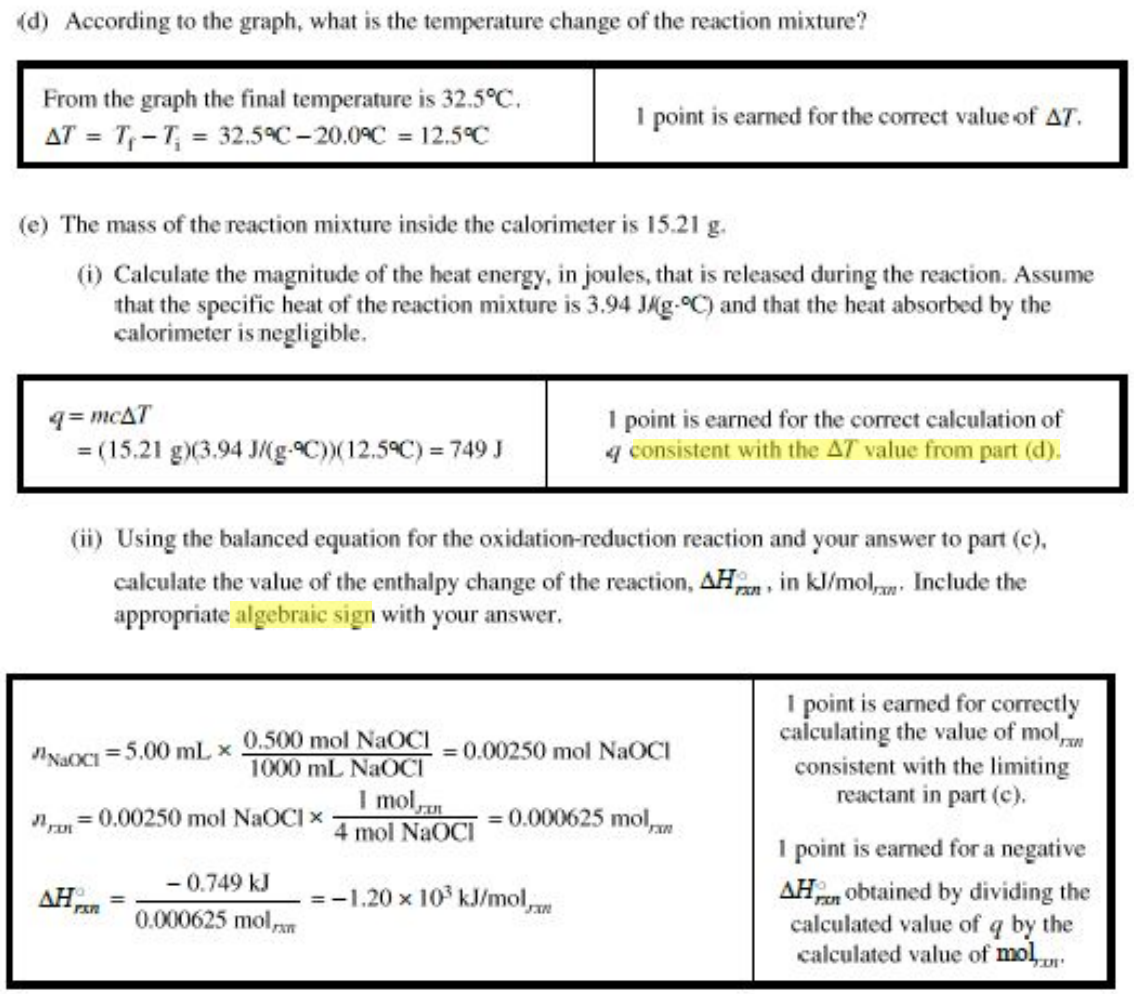
The student repeats the experiment, but this time doubling the volume of each of the reactants, as shown in the table below.

| Solution | Concentration ($M$) | Volume (mL) |
|---|---|---|
| $Na_2S_2O_3(aq)$ | 0.500 | 10.0 |
| $NaOCl(aq)$ | 0.500 | 10.0 |
| $NaOH(aq)$ | 0.500 | 10.0 |

(f) The magnitude of the enthalpy change, $\Delta H^\circ_{rxn}$, in kJ/mol$_{rxn}$, calculated from the results of the second experiment is the same as the result calculated in part (e)(ii). Explain this result.

(g) Write the balanced net ionic equation for the given reaction.

# 2018 FRQ #1 Scoring Guidelines and Things to Notice



(d) According to the graph, what is the temperature change of the reaction mixture?

| | |
|---|---|
| From the graph the final temperature is 32.5°C.<br>$\Delta T = T_f - T_i = 32.5°C - 20.0°C = 12.5°C$ | 1 point is earned for the correct value of $\Delta T$. |

(e) The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is 3.94 J/(g·°C) and that the heat absorbed by the calorimeter is negligible.

| | |
|---|---|
| $q = mc\Delta T$<br>$= (15.21\ g)(3.94\ J/(g{\cdot}°C))(12.5°C) = 749\ J$ | 1 point is earned for the correct calculation of $q$ consistent with the $\Delta T$ value from part (d). |

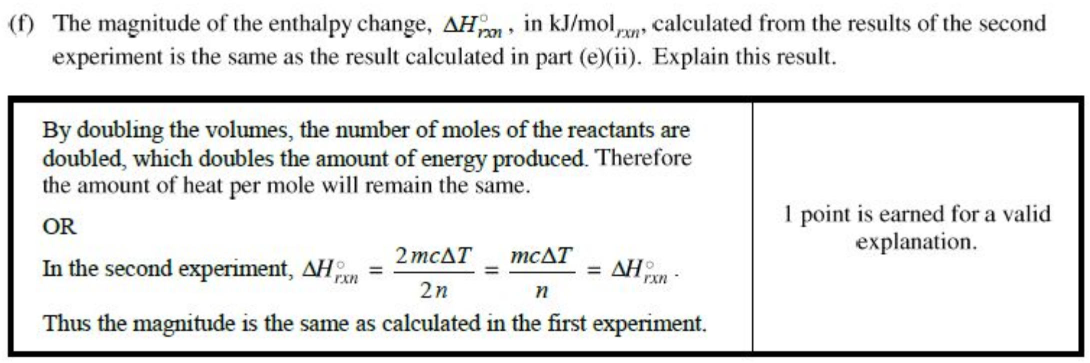
(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction, $\Delta H^\circ_{rxn}$, in kJ/mol$_{rxn}$. Include the appropriate algebraic sign with your answer.

| | |
|---|---|
| $n_{NaOCl} = 5.00\ mL \times \frac{0.500\ mol\ NaOCl}{1000\ mL\ NaOCl} = 0.00250\ mol\ NaOCl$<br>$n_{rxn} = 0.00250\ mol\ NaOCl \times \frac{1\ mol_{rxn}}{4\ mol\ NaOCl} = 0.000625\ mol_{rxn}$<br>$\Delta H^\circ_{rxn} = \frac{-0.749\ kJ}{0.000625\ mol_{rxn}} = -1.20 \times 10^3\ kJ/mol_{rxn}$ | 1 point is earned for correctly calculating the value of mol$_{rxn}$ consistent with the limiting reactant in part (c).<br>1 point is earned for a negative $\Delta H^\circ_{rxn}$ obtained by dividing the calculated value of $q$ by the calculated value of mol$_{rxn}$. |

- Notice that there is no double-jeopardy – a wrong value from part (d) used correctly here earns point

- Be sure work is represented so that all intermediate work can be recognized -even if you don’t stop to get an answer – so you can earn full points
- Missing negative sign would not earn the point
- Show work so that maximum points can be earned

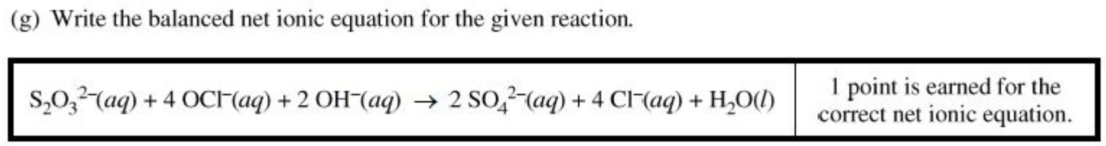
# 2018 FRQ #1 Scoring Guidelines and Things to Notice



(f) The magnitude of the enthalpy change, $\Delta H^\circ_{rxn}$, in kJ/mol$_{rxn}$, calculated from the results of the second experiment is the same as the result calculated in part (e)(ii). Explain this result.

| | |
|---|---|
| By doubling the volumes, the number of moles of the reactants are doubled, which doubles the amount of energy produced. Therefore the amount of heat per mole will remain the same.<br>OR<br>In the second experiment, $\Delta H^\circ_{rxn} = \frac{2mc\Delta T}{2n} = \frac{mc\Delta T}{n} = \Delta H^\circ_{rxn}$ .<br>Thus the magnitude is the same as calculated in the first experiment. | 1 point is earned for a valid explanation. |

- Answer must be clear and easy to follow; also, both cause and effect are noted



(g) Write the balanced net ionic equation for the given reaction.

| | |
|---|---|
| $S_2O_3^{2-}(aq) + 4\ OCl^-(aq) + 2\ OH^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + 4\ Cl^-(aq) + H_2O(l)$ | 1 point is earned for the correct net ionic equation. |

- Correct charges and stoichiometric factors must be included

# Unit 7: Equilibrium

| Write This… | …Not That! | Rationale |
|---|---|---|
| Correct formulas (including charges!) for all species in equilibrium expressions | Substitutions, abbreviations, chargeless ions, other shorthand that may work out in calculations but does not represent the correct species | Equilibrium expressions must be written formally when requested |
| In $K_p$ expressions: $P_{species}$ | In $K_p$ expressions: [species] | Concentration (which is indicated by brackets around the species) is not used in $K_p$ - partial pressures are |
| K expressions with EITHER concentration "[ ]" or partial pressures "P" | K expressions that include both concentration "[ ]" and partial pressures "P" in the same expression | Equilibrium expressions are written for either concentration values or partial pressure values, not both at the same time in a single expression (ref. 2019 #2e) |
| K without units | K with units | K is a unitless constant |
| "K is greater than 1, indicating that the products are present in a higher concentration and therefore equilibrium lies to the right" | "K is large" | Use specific values to demonstrate understanding about the meaning of K relative to the equilibrium position (ref. 2017 #2d) |
| "Proceeds" | "Shift" – if equilibrium has not yet been established (i.e. a precipitate has not yet been formed when evaluating $K_{sp}$) | If equilibrium is not yet established, then it cannot "shift" – rxn will proceed in a certain direction until equilibrium is established |

# Unit 7: Equilibrium (cont.)

| Write This… | …Not That! | Rationale |
|---|---|---|
| Calculations of K expressions that use concentrations/partial pressures at equilibrium | Calculations of K expressions that use initial concentrations/partial pressures | K values can only be calculated using equilibrium values; if initial values are given, an ICE table (or similar method) should be used to determine equilibrium values before calculating the K value (ref. 2018 #5b) |
| Using stoichiometric factors in ICE tables | Neglecting stoichiometry when calculating change in equilibrium scenarios | Stoichiometry ratios impact how much an initial value is changed during the establishment of equilibrium (ref. 2019 #2f) |
| “x has been assumed to be so small relative to the original concentrations that it can be ignored” | Nothing about why you ignore x to avoid quadratics | Show you understand why you are making the decision |
| Discussion of Q vs. K | “reduce the stress”, or “due to Le Châtelier’s Principle” | Preferred AP language-shows a deeper understanding of chemical principals (ref. 2018 #5c) |
| $K_{sp}$ expressions that only contain the ions | $K_{sp}$ expressions that contain or imply a species in the denominator | Solids and liquids are not included in equilibrium expressions |

# Unit 7 Practice – 2015 FRQ #4

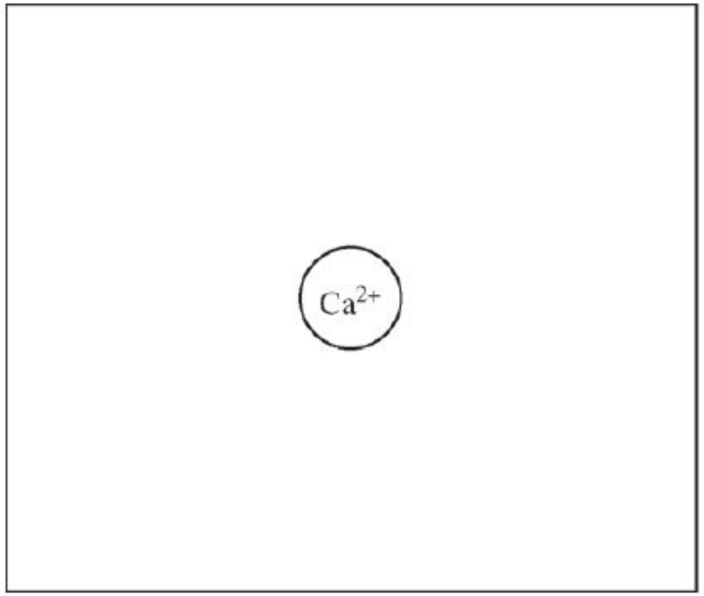
Answer the following questions about the solubility of $Ca(OH)_2$ ($K_{sp} = 1.3 \times 10^{-6}$).

(a) Write a balanced chemical equation for the dissolution of $Ca(OH)_2(s)$ in pure water.

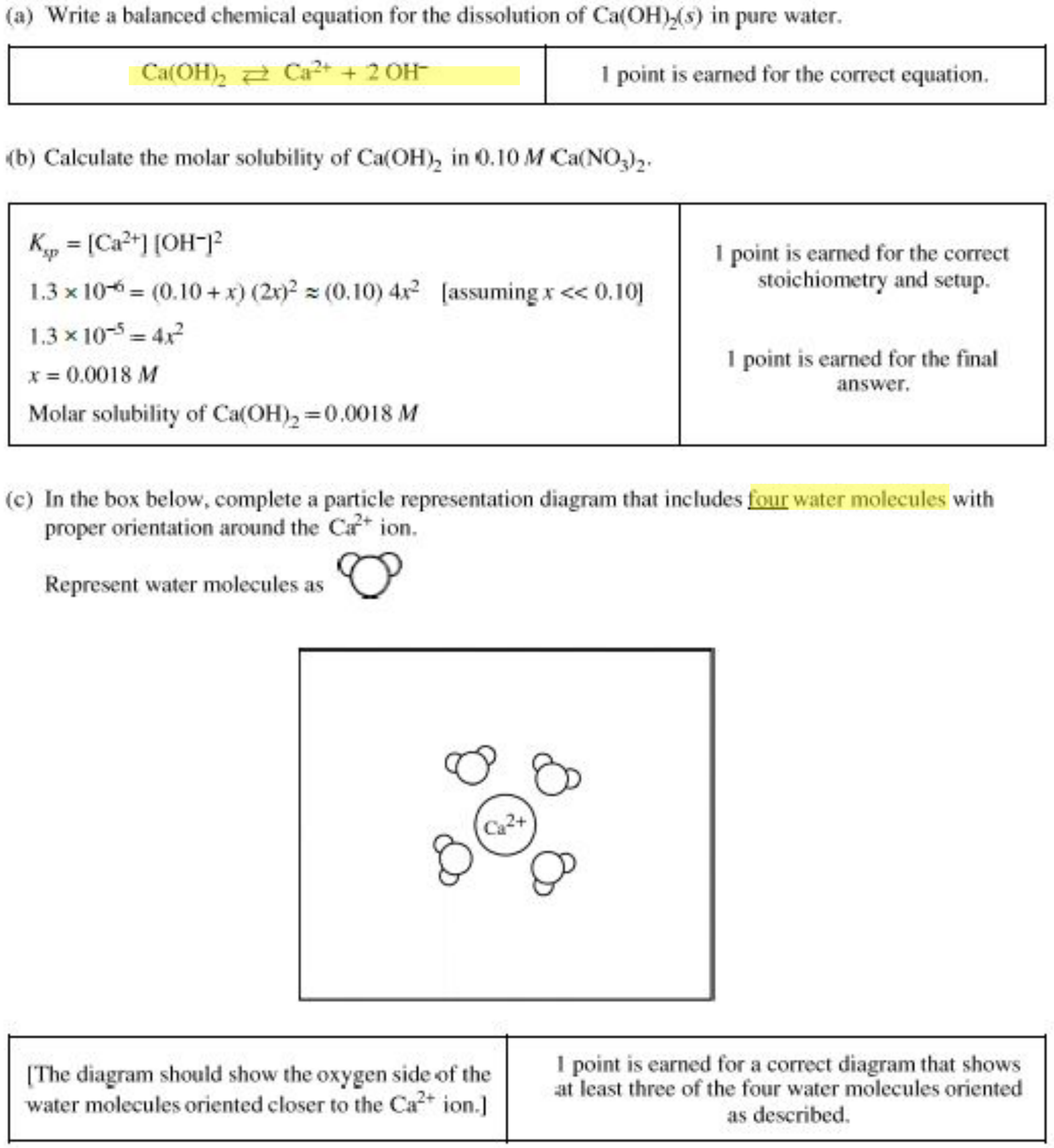
(b) Calculate the molar solubility of $Ca(OH)_2$ in 0.10 $M$ $Ca(NO_3)_2$.

(c) In the box below, complete a particle representation diagram that includes <u>four</u> water molecules with proper orientation around the $Ca^{2+}$ ion.

Represent water molecules as .



# 2015 FRQ #4 Scoring Guidelines and Things to Notice



(a) Write a balanced chemical equation for the dissolution of $Ca(OH)_2(s)$ in pure water.

| | |
|---|---|
| $Ca(OH)_2 \rightleftarrows Ca^{2+} + 2\,OH^-$ | 1 point is earned for the correct equation. |

(b) Calculate the molar solubility of $Ca(OH)_2$ in 0.10 *M* $Ca(NO_3)_2$.

| | |
|---|---|
| $K_{sp} = [Ca^{2+}]\,[OH^-]^2$<br>$1.3 \times 10^{-6} = (0.10 + x)\,(2x)^2 \approx (0.10)\,4x^2$ [assuming $x << 0.10$]<br>$1.3 \times 10^{-5} = 4x^2$<br>$x = 0.0018\ M$<br>Molar solubility of $Ca(OH)_2 = 0.0018\ M$ | 1 point is earned for the correct stoichiometry and setup.<br>1 point is earned for the final answer. |

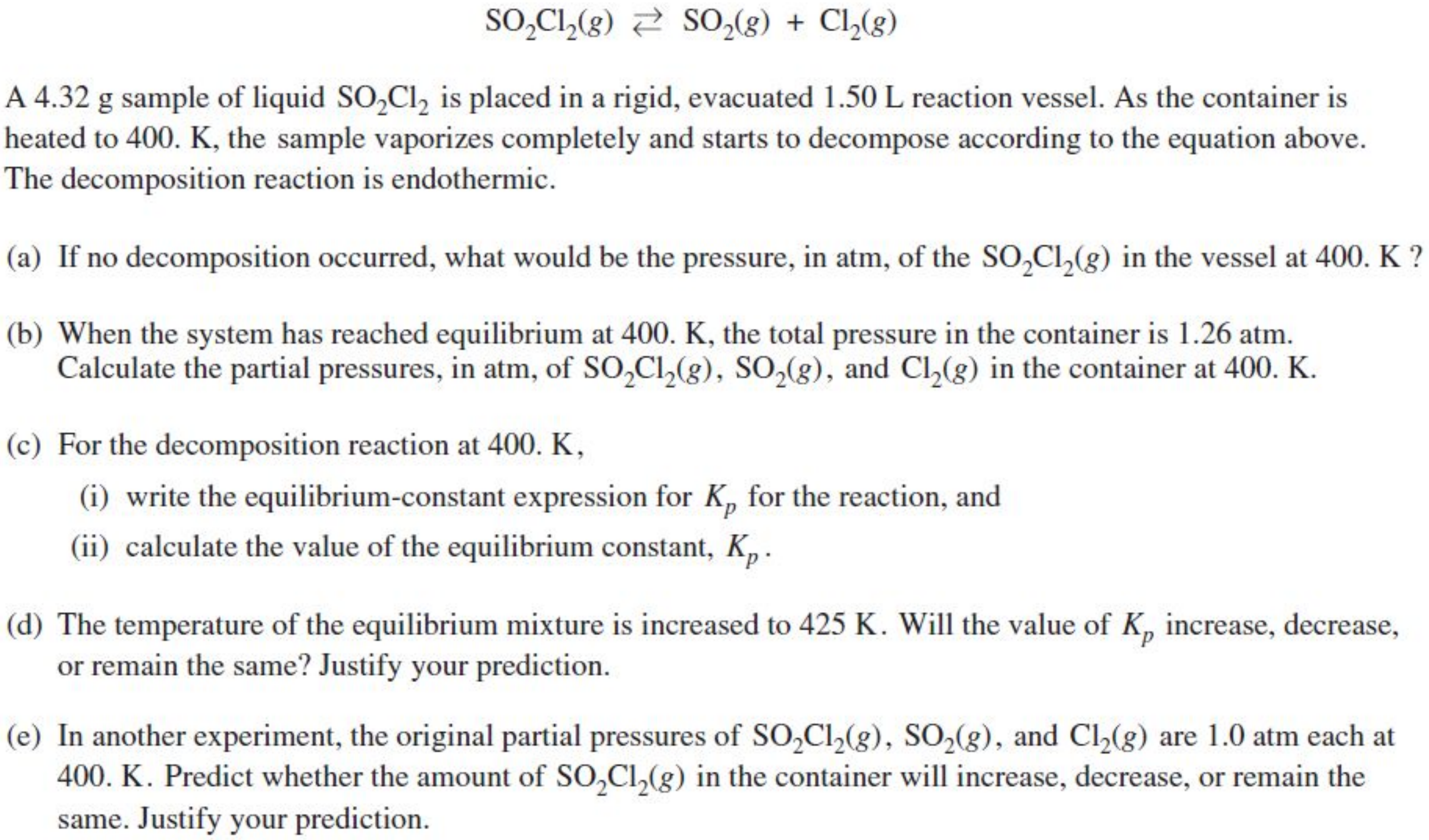
(c) In the box below, complete a particle representation diagram that includes four water molecules with proper orientation around the $Ca^{2+}$ ion.

Represent water molecules as

| | |
|---|---|
| [The diagram should show the oxygen side of the water molecules oriented closer to the $Ca^{2+}$ ion.] | 1 point is earned for a correct diagram that shows at least three of the four water molecules oriented as described. |

- Correct stoichiometry and charges must be included to earn the point
- Show work so that maximum points can be earned – no work would not earn the first point
- Be sure to pay attention to direction in prompt

# Unit 7 Practice – 2013 IPE #3



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

A 4.32 g sample of liquid $SO_2Cl_2$ is placed in a rigid, evacuated 1.50 L reaction vessel. As the container is heated to 400. K, the sample vaporizes completely and starts to decompose according to the equation above. The decomposition reaction is endothermic.

(a) If no decomposition occurred, what would be the pressure, in atm, of the $SO_2Cl_2(g)$ in the vessel at 400. K ?

(b) When the system has reached equilibrium at 400. K, the total pressure in the container is 1.26 atm. Calculate the partial pressures, in atm, of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ in the container at 400. K.

(c) For the decomposition reaction at 400. K,

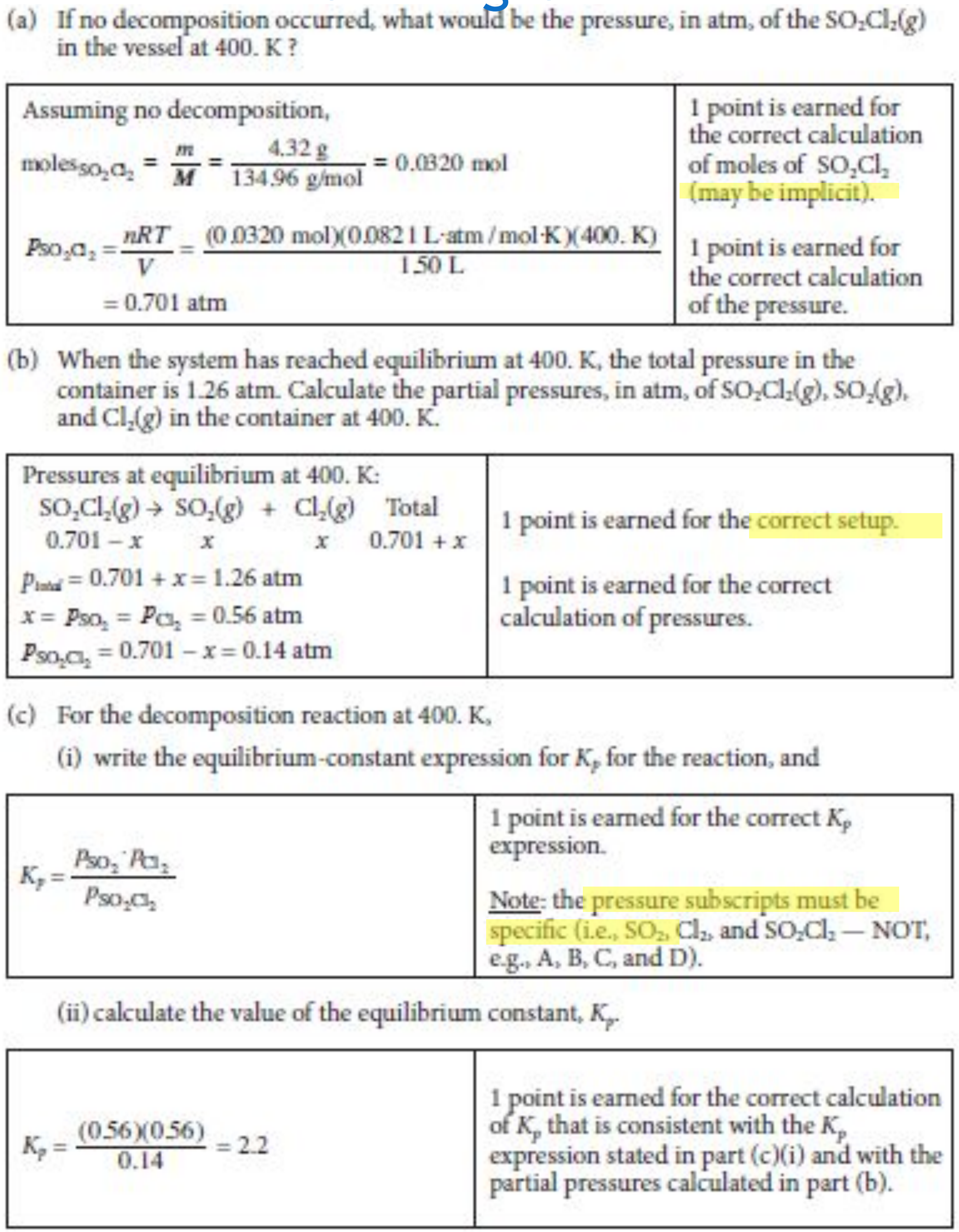
  (i) write the equilibrium-constant expression for $K_p$ for the reaction, and

  (ii) calculate the value of the equilibrium constant, $K_p$.

(d) The temperature of the equilibrium mixture is increased to 425 K. Will the value of $K_p$ increase, decrease, or remain the same? Justify your prediction.

(e) In another experiment, the original partial pressures of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ are 1.0 atm each at 400. K. Predict whether the amount of $SO_2Cl_2(g)$ in the container will increase, decrease, or remain the same. Justify your prediction.

# 2013 IPE #3 Scoring Guidelines and Things to Notice



(a) If no decomposition occurred, what would be the pressure, in atm, of the $SO_2Cl_2(g)$ in the vessel at 400. K ?

| | |
|---|---|
| Assuming no decomposition,<br>$\text{moles}_{SO_2Cl_2} = \frac{m}{M} = \frac{4.32\text{ g}}{134.96\text{ g/mol}} = 0.0320\text{ mol}$<br>$P_{SO_2Cl_2} = \frac{nRT}{V} = \frac{(0.0320\text{ mol})(0.0821\text{ L·atm/mol·K})(400.\text{ K})}{1.50\text{ L}}$<br>$= 0.701\text{ atm}$ | 1 point is earned for the correct calculation of moles of $SO_2Cl_2$ (may be implicit).<br>1 point is earned for the correct calculation of the pressure. |

- Show work so that maximum points can be earned – do not have to stop and show value of moles, but work must demonstrate process to calculate it

(b) When the system has reached equilibrium at 400. K, the total pressure in the container is 1.26 atm. Calculate the partial pressures, in atm, of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ in the container at 400. K.

| | |
|---|---|
| Pressures at equilibrium at 400. K:<br>$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ Total<br>$0.701 - x$ $x$ $x$ $0.701 + x$<br>$P_{total} = 0.701 + x = 1.26\text{ atm}$<br>$x = P_{SO_2} = P_{Cl_2} = 0.56\text{ atm}$<br>$P_{SO_2Cl_2} = 0.701 - x = 0.14\text{ atm}$ | 1 point is earned for the correct setup.<br>1 point is earned for the correct calculation of pressures. |

- Again, SHOW ALL WORK

(c) For the decomposition reaction at 400. K,

(i) write the equilibrium-constant expression for $K_p$ for the reaction, and

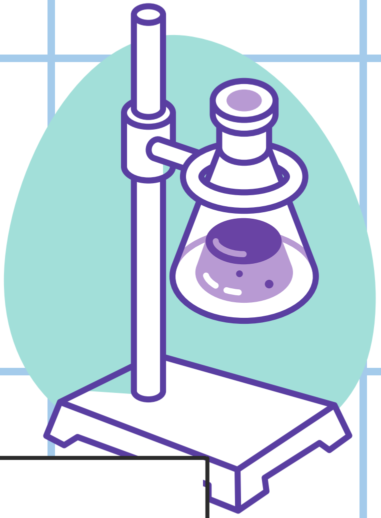
| | |
|---|---|
| $K_p = \frac{P_{SO_2} \cdot P_{Cl_2}}{P_{SO_2Cl_2}}$ | 1 point is earned for the correct $K_p$ expression.<br>Note: the pressure subscripts must be specific (i.e., $SO_2$, $Cl_2$, and $SO_2Cl_2$ — NOT, e.g., A, B, C, and D). |

(ii) calculate the value of the equilibrium constant, $K_p$.

| | |
|---|---|
| $K_p = \frac{(0.56)(0.56)}{0.14} = 2.2$ | 1 point is earned for the correct calculation of $K_p$ that is consistent with the $K_p$ expression stated in part (c)(i) and with the partial pressures calculated in part (b). |

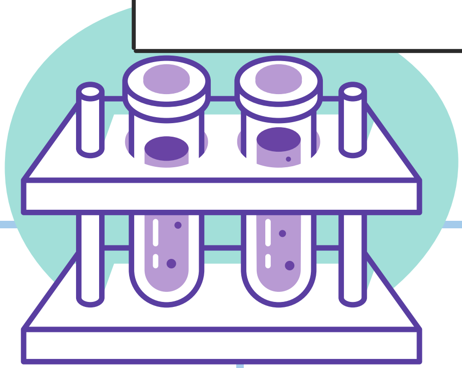
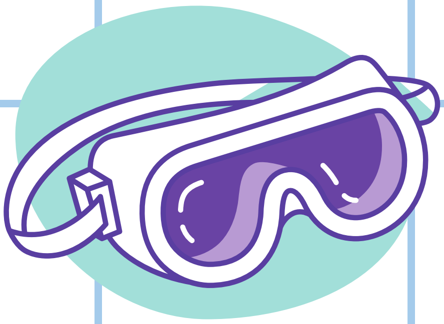
- Be specific in responses, using proper names/formulas
- Must use P notation here, NOT [ ]

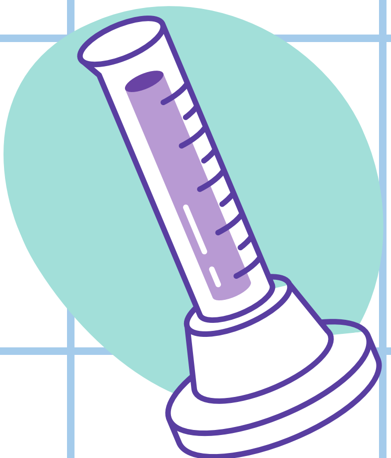




# UNIT 1-7 PRACTICE PROBLEMS

2022 AP Chemistry Review Mr. Nackers



# AP CHEMISTRY PRACTICE Unit 1

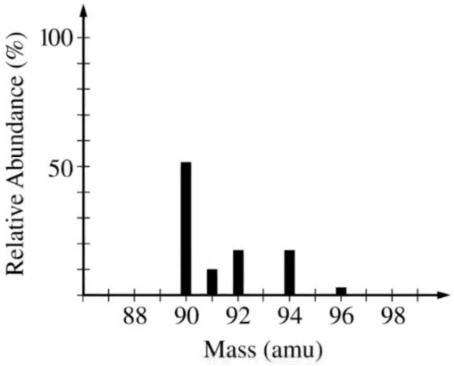
1. A student is given 50.0 mL of a solution of $Na_2CO_3$ of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $Ca(NO_3)_2$ (*aq*), causing a precipitate to form. The balanced equation for the reaction is shown below

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \longrightarrow 2\,NaNO_3(aq) + CaCO_3(s)$$

The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below. Determine the number of moles of $Na_2CO_3$ in the original 50.0 mL of solution.

| | |
|---|---|
| Volume of $Na_2CO_3$ solution | 50.0 mL |
| Volume of 1.0 M $Ca(NO_3)_2$ added | 100.0 mL |
| Mass of $CaCO_3$ precipitate collected | 0.93 g |

2. The mass spectrum of element X is presented in the diagram below. Based on the spectrum, what is the identity of element X? Explain.



3. The average atomic mass of naturally occurring neon is 20.18 amu. There are two common isotopes of naturally occurring neon as indicated in the table below

| Isotope | Mass (amu) |
|---|---|
| Ne-20 | 19.99 |
| Ne-22 | 21.99 |

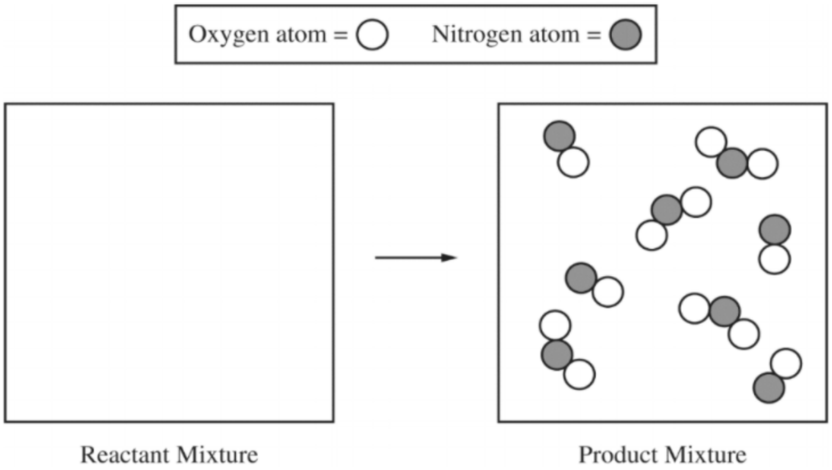
Using the information above, calculate the percent abundance of each isotope.

4. A 31 g sample of a compound that contains only the elements C,H and N is completely burned in $O_2$ to produce 44.0 g of $CO_2$, 45.0 g of $H_2O$, and 92.0 g of $NO_2$. Determine the empirical formula of the compound.

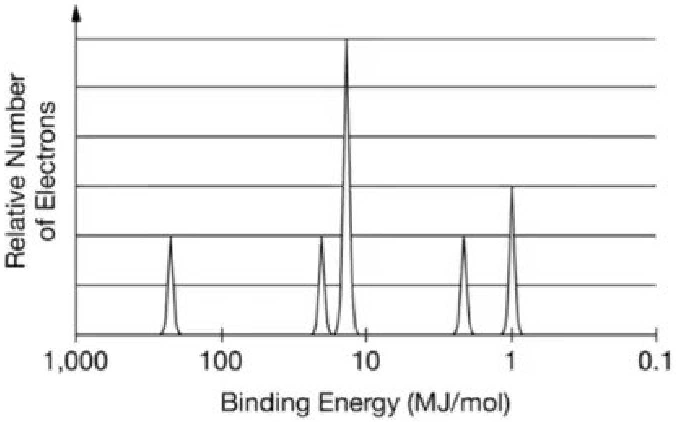
5. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of NO(*g*) and $NO_2$(*g*), which the student produces by using the reaction represented above. The particle-level representation of the equimolar mixture of NO(*g*) and $NO_2$(*g*) in the flask at the completion of the reaction between NO(*g*) and $O_2$(*g*) is shown below in the box on the right. In the box below on the left , draw the particle-level representation of the <u>reactant</u> mixture NO(*g*)

and $O_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.

$$\mathbf{2NO}(g) + \mathbf{O_2}(g) \longrightarrow \mathbf{2\ NO_2}(g)$$



**6.** The complete photoelectron spectrum of an element is given below. What is the electron configuration of the element with this spectrum?



**7**. The elements in which of the following have most nearly the same atomic radius? Explain your choice.

A. Be, B, C, N
B. Ne, Ar, Kr, Xe
C. Mg, Ca, Sr, Ba
D. C, P, Se, I
E. Cr, Mn, Fe, Co

**8.** Using the following elements from the periodic table, select which one that best fits each statement:

**A.** Se
**B.** Br
**C.** Ag
**D.** Cs
**E.** Pb

a) Has the highest electronegativity _________
b) Has the largest atomic radius _______
c) Has the lowest first-ionization energy ________

**9.** Atoms of Mg combine with atoms of F to form a compound. Identify another element that you would expect to combine with atoms of F in the same ratio? Explain.

**10.** The only common oxide of zinc has the formula ZnO

(a) Write the electron configuration for a Zn atom in the ground state.

(b) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?

**11.** Answer the following questions related to Fe and its ions, $Fe^{2+}$ and $Fe^{3+}$.

(a) Write the ground-state electron configuration of the $Fe^{2+}$ ion.

| Ion | Ionic Radius (pm) |
|---|---|
| $Fe^{2+}$ | 92 |
| $Fe^{3+}$ | 79 |

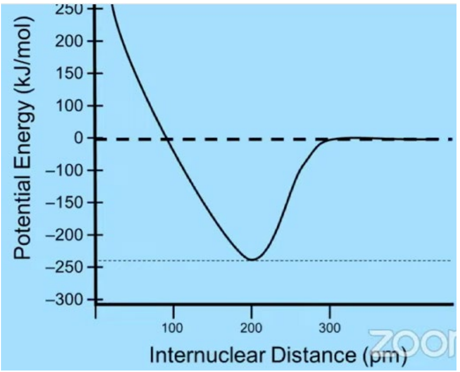
(b) The radii of the ions are given in the table above. Using the principles of atomic structure, explain why the radius of the $Fe^{2+}$ ion is larger than the radius of the $Fe^{3+}$ ion.

## AP CHEMISTRY PRACTICE Unit 2

**1.** Consider the following information for the Cl—Cl bond:

| Bond | Cl—Cl | Br—Br |
|---|---|---|
| Bond Length (pm) | 200 | **?** |
| Bond Energy (kJ/mol) | 243 | **?** |

Make a prediction about the Br—Br bond, in terms of bond length and bond energy. Draw on the graph below the Br-Br bond



**2.** Data for the lattice energy of NaF is given in the table below. Make predictions about the lattice energy of MgO. Do you predict that the lattice energy of each compound is less than 930 kJ/mol or greater than 930 kJ/mol? Justify your answer in terms of periodic properties and Coulomb's law.

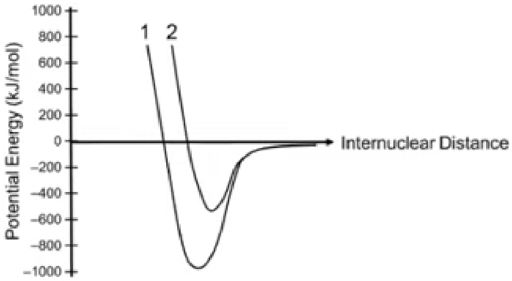
| **Reaction** | **Lattice Energy (kJ/mol)** |
|---|---|
| $NaF(s) \longrightarrow Na^+(g) + F^-(g)$ | 930 |
| $MgO(s) \longrightarrow Mg^{2+}(g) + O^{2-}(g)$ | |

**3.** Brass is an alloy that contains copper and zinc. The atomic radii of the elements are given in the table below. Should brass be classified as an interstitial alloy or a substitutional alloy? Justify your answer.

| **Element** | **Atomic radius (pm)** |
|---|---|
| Cu | 130 |
| Zn | 125 |

**4.** Answer the following questions about nitrogen and oxygen.

(a) Draw the Lewis structure for the diatomic molecules $N_2$ and $O_2$.



(b) The potential energy as a function of internuclear distance for the diatomic molecules $N_2$ and $O_2$ is shown in the graph above. Based on the data in the graph and the Lewis structures that you drew in part (a), which curve, 1 or 2, is the better representation of the $N_2$ molecule? Justify your answer.

**5.** Answer the following questions related to Mg and Sr.

(a) Write the complete ground state electron configuration for the ions $Mg^{2+}$ and $Sr^{2+}$.

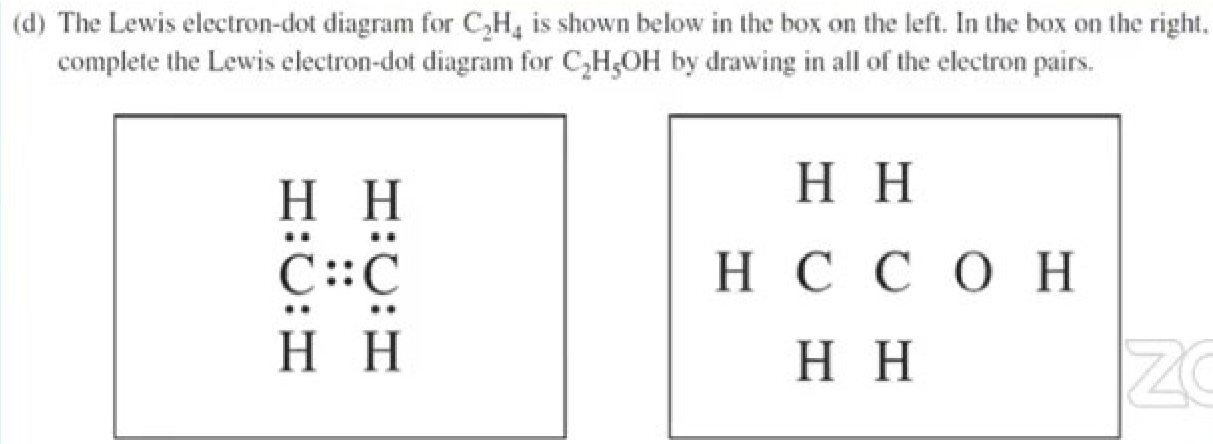
(b) The lattice energy of $MgCl_2(s)$ is equal to 2300 kJ/mol. Do you predict that the lattice energy of $SrCl_2$ should be less than or greater than 2300 kJ/mol? Justify your answer in terms of Coulomb's law.

**6**. Draw the following Lewis structures in the space provided.

| **$CH_4$** | **$NH_3$** | **$H_2O$** | **$CH_2Cl_2$** |
|---|---|---|---|
| | | | |

| **$C_2H_6$** | **$C_2H_4$** | **$C_2H_2$** |
|---|---|---|
| | | |

**7.**



(d) The Lewis electron-dot diagram for $C_2H_4$ is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for $C_2H_5OH$ by drawing in all of the electron pairs.

**8.**More than one equivalent Lewis structure can be drawn for the molecule **$O_3$.** Draw all the resonance structures and estimate the bond order for the O-O bonds.

**9.** Determine the Formal charge on each structure and determine which is the best structure based upon formal charge

**10.** $S_2Cl_2$ is a product of a reaction.

(a) In the box below, complete the Lewis electron-dot diagram for the $S_2Cl_2$ molecule by drawing in all of the electron pairs.

Cl S S Cl

(b) What is the approximate value of the Cl—S—S bond angle in the $S_2Cl_2$ molecule that you drew in part (a) ? (If the two Cl—S—S bond angles are not equal, include both angles.)

**11.** The skeletal structure of the $HNO_2$ molecule is shown in the box below.

(a) Complete the Lewis electron-dot diagram of the $HNO_2$ molecule in the box below, including any lone pairs of electrons.

H O N O

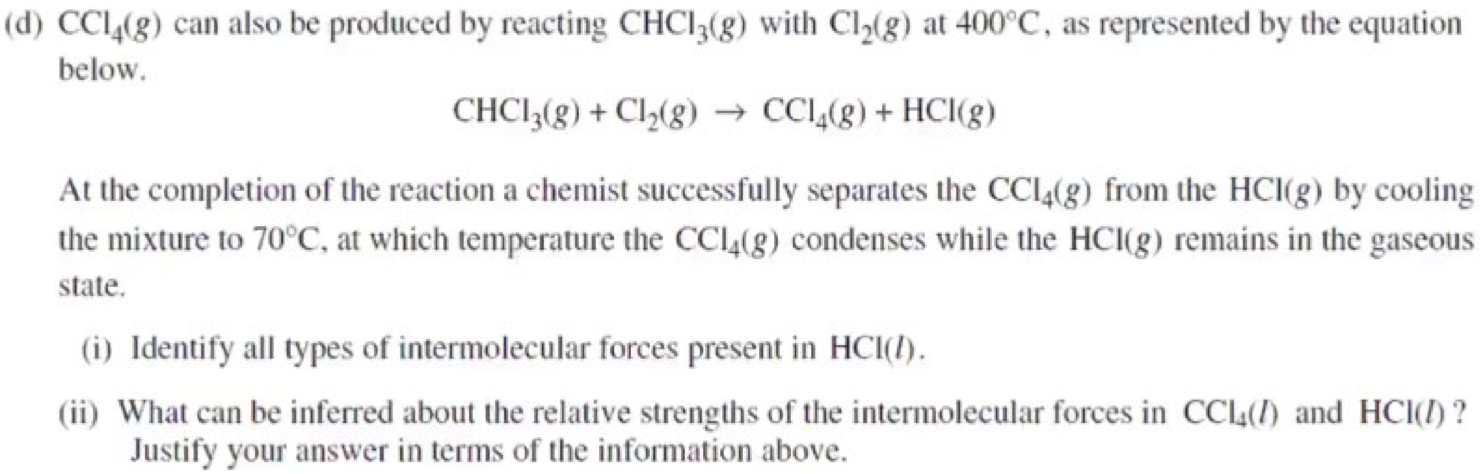
(b) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the $HNO_2$ molecule.

## Unit 3 Review

1. Substances # 1 and # 2 represent two different elements located in Group 18 (noble gases). Which substance, #1 or # 2, has stronger attractive forces between particles? How can you tell?

| Substance | Boiling Point (K) |
|---|---|
| # 1 | 87 |
| #2 | 165 |

**2.**



(d) $CCl_4(g)$ can also be produced by reacting $CHCl_3(g)$ with $Cl_2(g)$ at 400°C, as represented by the equation below.

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

At the completion of the reaction a chemist successfully separates the $CCl_4(g)$ from the $HCl(g)$ by cooling the mixture to 70°C, at which temperature the $CCl_4(g)$ condenses while the $HCl(g)$ remains in the gaseous state.

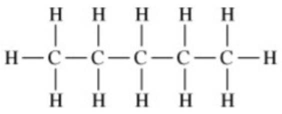
(i) Identify all types of intermolecular forces present in $HCl(l)$.

(ii) What can be inferred about the relative strengths of the intermolecular forces in $CCl_4(l)$ and $HCl(l)$? Justify your answer in terms of the information above.

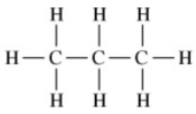
**3.** Using the boiling point data given below, which liquid, $C_5H_{12}$ or $H_2O$, has a higher vapor pressure at 300 K? Justify your answer.

$C_5H_{12}$ Boiling Point= 309K
$H_2O$ Boiling Point = 373K

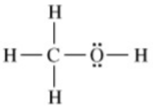
**4.** Answer the following questions in terms of principles of chemical bonding and intermolecular forces. In each explanation where a comparison is to be made, a complete answer must include a discussion of both substances. The following complete Lewis electron-dot diagrams may be useful in answering parts of this question.



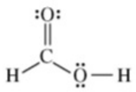
Pentane



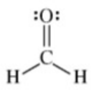
Propane



Methanol



Methanoic (formic) acid



Methanal (formaldehyde)

(a) At 1 atm and 298 K, pentane is a liquid whereas propane is a gas. Explain.

(b) At 1 atm and 298 K, methanol is a liquid whereas propane is a gas. Explain.

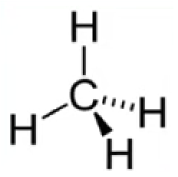
(c) Indicate the hybridization of the carbon atom in methanol and Methanoic acid

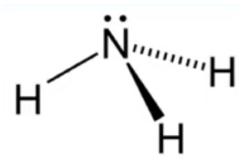
**5**. A gas mixture at O°C and 1.15 atm contains 0.010 mol of $H_2$, 0.015 mol of $O_2$, and 0.025 mol of $N_2$. Assuming ideal behavior, what are the partial pressures of hydrogen gas($H_2$), oxygen gas ($O_2$) and nitrogen gas ($N_2$) in the mixture?

**6.** Explain the following statements about gases. Be sure to mention specific information about both gases.

a) Ar(*g*) deviates more from ideal behavior at extremely high pressures than Ne(*g*) does.

b) The pressure of a sample of $CH_4$ (*g*) (molar mass = 16 g/mol) is closer to the pressure predicted by the ideal gas law than a sample of $NH_3$(*g*) (molar mass = 17 g/mol)





$$Mg(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$$

**7.** A student performs an experiment to determine the volume of hydrogen gas produced when a given mass of magnesium reacts with excess HCl(*aq*), as represented by the net ionic equation above. The student begins with a 0.0360 g sample of pure magnesium and a solution of 2.0 *M* HCl(*aq*).

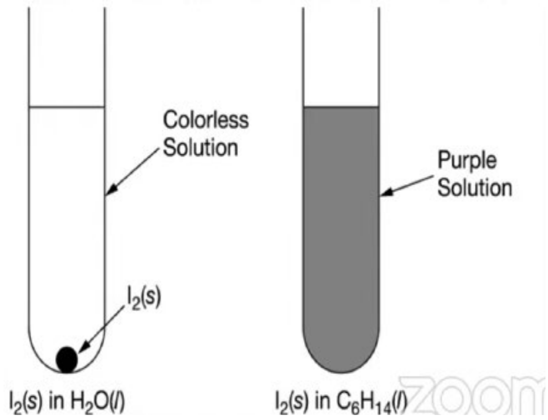
(a) Calculate the number of moles of magnesium in the 0.0360 g sample.

(b) Calculate the number of molecules of HCl(*aq*) needed to react completely with the sample of magnesium.

As the magnesium reacts, the hydrogen gas produced is collected by water displacement at 23.0°C. The pressure of the gas in the collection tube is measured to be 749 torr.

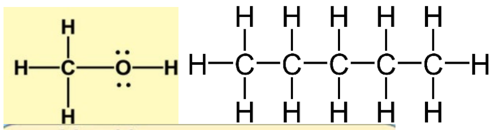
(c) Given that the equilibrium vapor pressure of water is 21 torr at 23.0°C, calculate the pressure that the $H_2$(*g*) produced in the reaction would have if it were dry.

**8.** What does this image indicate about the intermolecular interactions of the substances?

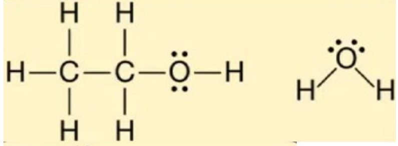


**9.** Which of these pairs of molecules would you expect to mix together? Explain.

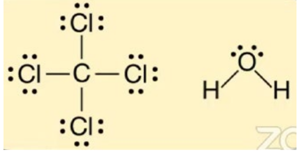
A.



B.

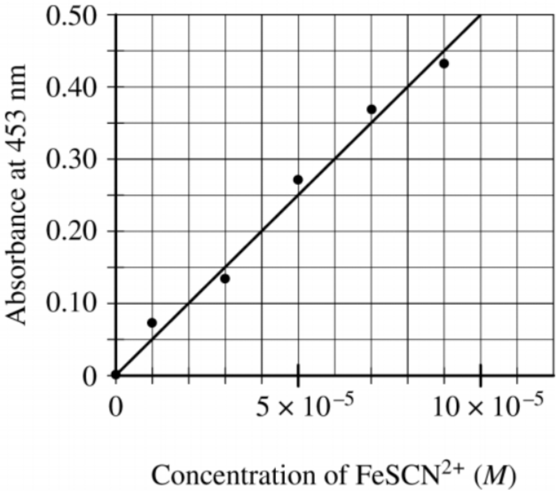


C.



**10.** $Fe^{3+}(aq) + KSCN(s) \rightarrow FeSCN^{2+}(aq) + K^{+}(aq)$

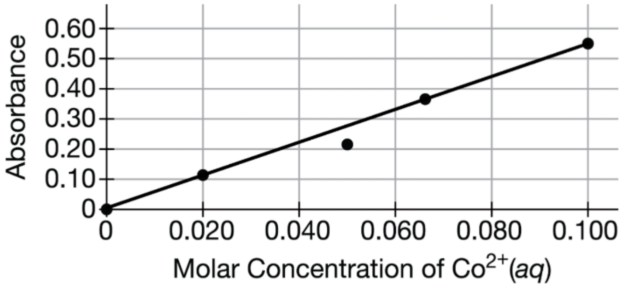
To determine the moles of $Fe^{3+}$*(aq)* in a 100. mL sample of an unknown solution, excess KSCN*(s)* is added to convert all the $Fe^{3+}$*(aq)* into the dark red species $FeSCN^{2+}$(aq), as represented by the equation above. The absorbance of $FeSCN^{2+}$*(aq)* at different concentrations is shown in the graph to the right.The absorbance of the mixture is 0.20 at 453 nm.



a) What is the concentration of $FeSCN^{2+}$(aq)?

b) How many moles of $Fe^{3+}$(*aq*) were present in the 125 mL sample?

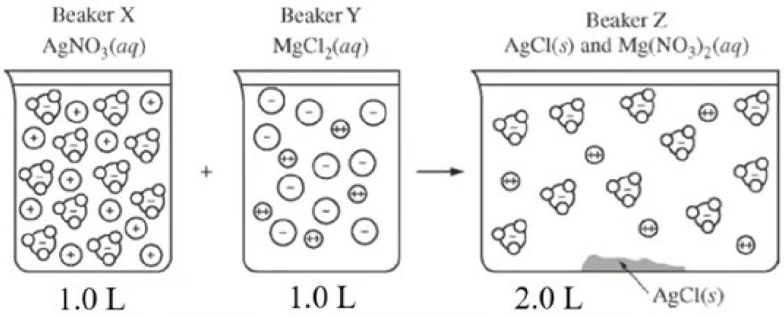
**11.** A student uses visible spectrophotometry to determine the concentration of $CoCl_2$*(aq)* in a sample solution. First the student prepares a set of $CoCl_2$*(aq)* solutions of known concentration. Then the student uses a spectrophotometer to determine the absorbance of each of the standard solutions at a wavelength of 510 nm and constructs a standard curve. Finally, the student determines the absorbance of the sample of unknown concentration. The student made the standard curve. What is a possible experimental error which could have caused the error in the point the student plotted at 0.050M$Co^{2+}$*(aq)* ?



## Unit 4 Review

1. Solutions of $Hg(NO_3)_2$ and NaI are combined. Write the net ionic equation.

**2.** After examining the particle diagram shown, a student made the claim that the concentration of $AgNO_3(aq)$ is the same as the concentration of $MgCl_2(aq)$. Do you agree with the student's claim? Justify your answer based on the information in the particle diagram.



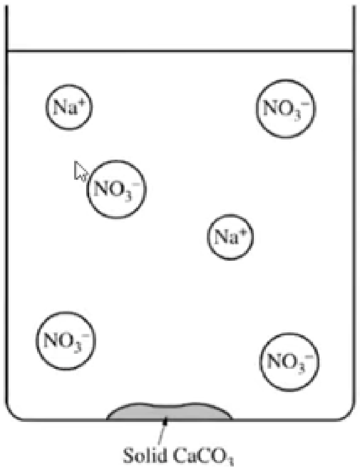
**$2\ AgNO_3(aq) + MgCl_2(aq) \longrightarrow 2\ AgCl(s) + Mg(NO_3)_2(aq)$**

**3.** A student is given 50.0 mL of a solution of $Na_2CO_3$ of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $Ca(NO_3)_2\ (aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below

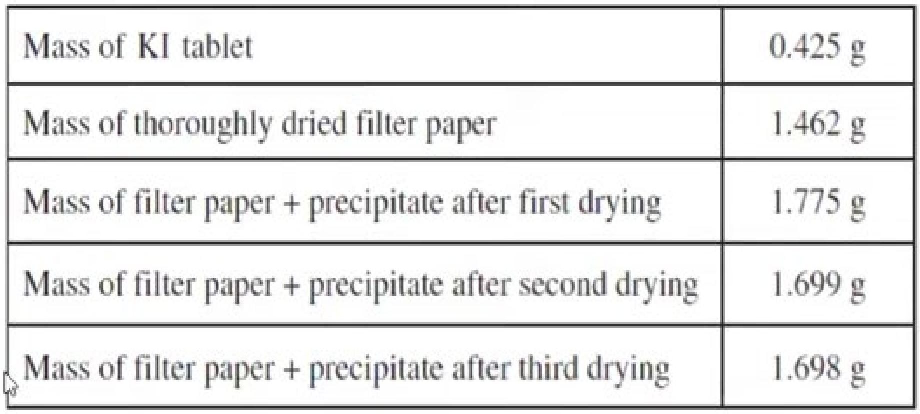
$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \longrightarrow 2\ NaNO_3\ (aq) + CaCO_3(s)$$

(a) Write the net ionic equation for the reaction that occurs when the solutions of $Na_2CO_3$ and $Ca(NO_3)_2$ are mixed.

(b) The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



**4.** A student is given the task of determining the $I^-$ content of tablets that contain KI and an inert, water-soluble sugar as a filler. A tablet is dissolved in 50.0 mL of distilled water, and an excess of 0.20 *M* $Pb(NO_3)_2(aq)$ is added to the solution. A yellow precipitate forms, which is then filtered, washed, and dried. The data from the experiment are shown in the table below.



| | |
|---|---|
| Mass of KI tablet | 0.425 g |
| Mass of thoroughly dried filter paper | 1.462 g |
| Mass of filter paper + precipitate after first drying | 1.775 g |
| Mass of filter paper + precipitate after second drying | 1.699 g |
| Mass of filter paper + precipitate after third drying | 1.698 g |

(a) For the chemical reaction that occurs when the precipitate forms, write a balanced, net-ionic equation for the reaction.

(b) Explain the purpose of drying and weighing the filter paper with the precipitate three times.

(c) In the filtrate solution, is $[K^+]$ greater than, less than, or equal to $[NO_3^-]$? Justify your answer.

(d) Calculate the number of moles of precipitate that is produced in the experiment.

(e) Calculate the mass percent of $I^-$ in the tablet.

**5.** **___Al(*s*) + ___HCl(*aq*) ⟶ ___$AlCl_3$ (*aq*) + ___$H_2$(*g*)**

a)Balance the equation above.

b)Al(*s*) and HCl(*aq*) react together according to the unbalanced chemical equation shown above. If 0.36 mol of $AlCl_3$ is produced in this reaction, how many moles of $H_2$ are also produced?

c) Al(*s*) and HCl(*aq*) react together according to the chemical equation shown above. How many grams of Al are required to produce 75 grams of $H_2$? Assume that HCl is added in excess.

d) Al(*s*) and HCl(*aq*) react together according to the chemical equation shown above. How many mL of 5.0 *M* HCl are required to react completely with 4.25 grams of Al?

*e) Note: Connection to ideal gas law (PV = nRT)*
35 g Al(*s*) reacts with excess HCl(*aq*) according to the chemical equation shown above. What is the volume (in L) of $H_2$ gas produced at a temperature of 345 K and a pressure of 1.12 atm?

f)125 g of Al(*s*) reacts with 2.50 L of 3.20*M of HCl*(*aq*) according to the chemical equation shown above. Which chemical, Al or HCl, is the limiting reactant? What is the theoretical yield of $H_2$ in units of grams?

**6.** A student made the claim that the reaction shown below is a redox reaction. Do you agree with the student's claim? Justify your answer in terms of the oxidation numbers.

$$FeS + HNO_3 \longrightarrow Fe(NO_3)_2 + H_2S$$

**7**. Add the electrons to the half reactions and label as oxidation or reduction

$Fe^{3+} \longrightarrow Fe^{2+}$

$Sn^{2+} \longrightarrow Sn^{4+}$

**8**. For the following reaction, write the oxidation and reduction half reactions.

$$6H^+(aq) + 2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) \rightarrow 10\ CO_2(g) + 8\ H_2O(l) + 2\ Mn^{2+}(aq)$$

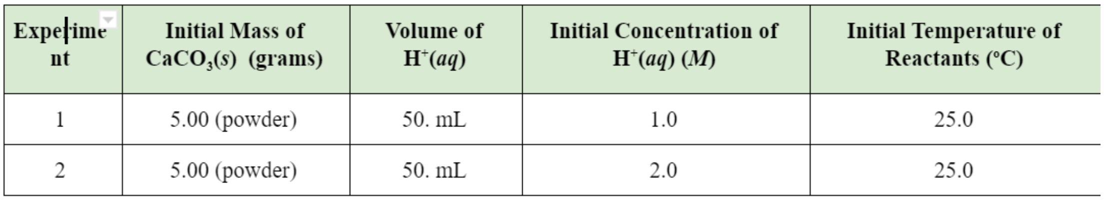
# Unit 5 Review

**1.** For the following equation, the rate of disappearance of $Br^-(aq)$ at a moment during the reaction is $3.5 \times 10^{-4}$ mol $L^{-1}s^{-1}$. **$5\ Br^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \longrightarrow 3\ Br_2(aq) + 3\ H_2O(l)$**

a. What is the rate of appearance of $Br_2(aq)$ at that moment?

b. What is the rate of disappearance of $H^+(aq)$ at that moment?

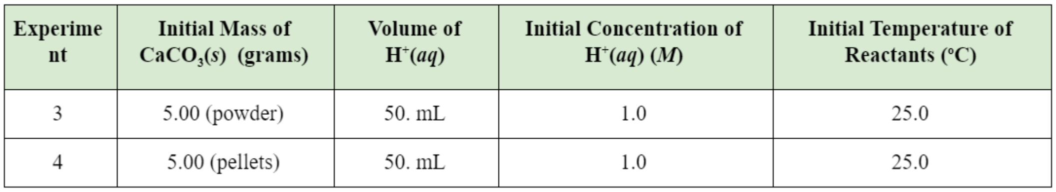
**2.** $CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$



| Experiment | Initial Mass of $CaCO_3(s)$ (grams) | Volume of $H^+(aq)$ | Initial Concentration of $H^+(aq)$ (*M*) | Initial Temperature of Reactants (°C) |
|---|---|---|---|---|
| 1 | 5.00 (powder) | 50. mL | 1.0 | 25.0 |
| 2 | 5.00 (powder) | 50. mL | 2.0 | 25.0 |

The initial rate of formation of $CO_2(g)$ from the chemical reaction represented by the equation above was studied in two separate experiments. Which experiment, if any, will have the faster initial rate of formation of $CO_2(g)$? Justify

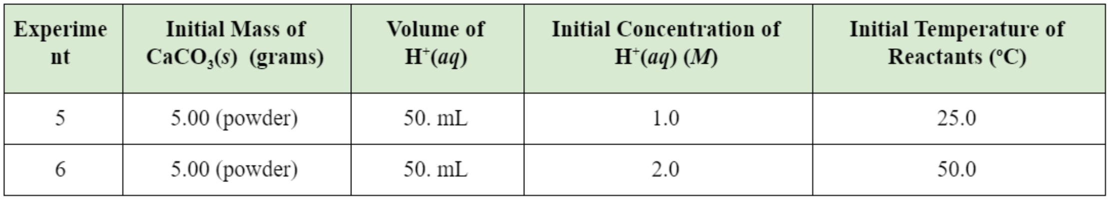
**3.** $CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$



| Experiment | Initial Mass of $CaCO_3(s)$ (grams) | Volume of $H^+(aq)$ | Initial Concentration of $H^+(aq)$ (*M*) | Initial Temperature of Reactants (°C) |
|---|---|---|---|---|
| 3 | 5.00 (powder) | 50. mL | 1.0 | 25.0 |
| 4 | 5.00 (pellets) | 50. mL | 1.0 | 25.0 |

The initial rate of formation of $CO_2(g)$ from the chemical reaction represented by the equation above was studied in two separate experiments. Which experiment, if any, will have the faster initial rate of formation of $CO_2(g)$? Justify

**4.** $CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$



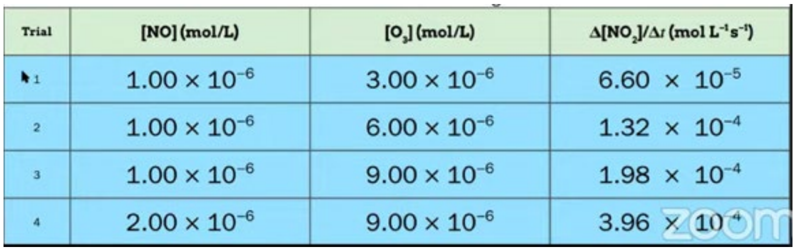
| Experiment | Initial Mass of $CaCO_3(s)$ (grams) | Volume of $H^+(aq)$ | Initial Concentration of $H^+(aq)$ (*M*) | Initial Temperature of Reactants (°C) |
|---|---|---|---|---|
| 5 | 5.00 (powder) | 50. mL | 1.0 | 25.0 |
| 6 | 5.00 (powder) | 50. mL | 2.0 | 50.0 |

The initial rate of formation of $CO_2(g)$ from the chemical reaction represented by the equation above was studied in two separate experiments. Which experiment, if any, will have the faster initial rate of formation of $CO_2(g)$? Justify

**5.** Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica. One such reaction is the combination of nitric oxide, NO, with ozone, $O_3$:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

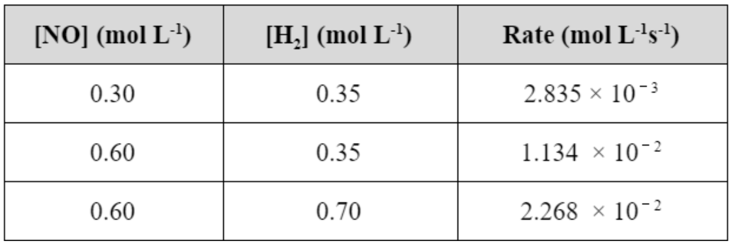
Use the data to determine the rate law and the rate constant for the reaction at 25°C.



| Trial | [NO] (mol/L) | $[O_3]$ (mol/L) | $\Delta[NO_2]/\Delta t$ (mol $L^{-1}s^{-1}$) |
|---|---|---|---|
| 1 | $1.00 \times 10^{-6}$ | $3.00 \times 10^{-6}$ | $6.60 \times 10^{-5}$ |
| 2 | $1.00 \times 10^{-6}$ | $6.00 \times 10^{-6}$ | $1.32 \times 10^{-4}$ |
| 3 | $1.00 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | $1.98 \times 10^{-4}$ |
| 4 | $2.00 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | $3.96 \times 10^{-4}$ |

**6.** Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation: $H_2(g) + 2\ NO(g) \longrightarrow N_2O(g) + H_2O(g)$

Determine the rate law, the rate constant, and the orders with respect to each reactant from the following data:

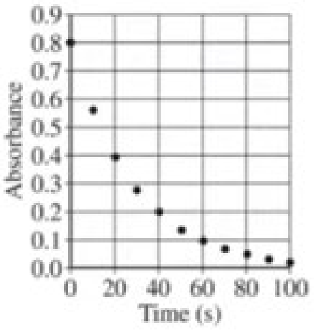


| [NO] (mol $L^{-1}$) | $[H_2]$ (mol $L^{-1}$) | Rate (mol $L^{-1}s^{-1}$) |
|---|---|---|
| 0.30 | 0.35 | $2.835 \times 10^{-3}$ |
| 0.60 | 0.35 | $1.134 \times 10^{-2}$ |
| 0.60 | 0.70 | $2.268 \times 10^{-2}$ |

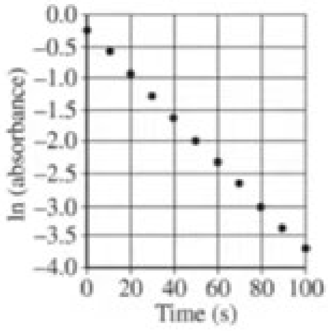
**7.**

$$\underset{blue}{Na_2C_{37}H_{34}N_2S_3O_9} + OCl^- \longrightarrow \underset{colorless}{\text{products}}$$

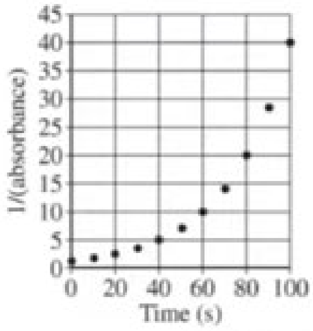
Blue food coloring can be oxidized by household bleach (which contains $OCl^-$) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of $OCl^-$ is essentially constant throughout the reaction. The students use data from the study to generate the graphs below.



Graph I



Graph II



Graph III

Based on the graphs above, what is the order of the reaction with respect to the blue food coloring? Explain.

**8.** What is the rate law for the overall reaction that is consistent with the proposed mechanism?

**Step 1:** $HBr(g) + O_2(g) \longrightarrow HOBr_2(g)$ **(SLOW)**
**Step 2:** $HOBr_2(g) + HBr(g) \longrightarrow 2\ HOBr(g)$ **(FAST)**
**Step 3:** $2\ HOBr(g) \longrightarrow H_2O_2(g) + Br_2(g)$ **(FAST)**

$$2 \quad NO_2(g) + F_2(g) \longrightarrow NO_2F(g)$$

**9.** $NO_2$ and $F_2$ can react to produce $NO_2F$ as represented above. A proposed mechanism for this reaction has two elementary steps, as shown below. Write a rate law for the overall reaction that is consistent with the proposed mechanism.

**Step 1:** $NO_2 + F_2 \longrightarrow NO_2F + F$ (*slow*)
**Step 2:** $NO_2 + F \longrightarrow NO_2F$ (*fast*)

**10.** What is the expected rate law for the overall reaction shown below?

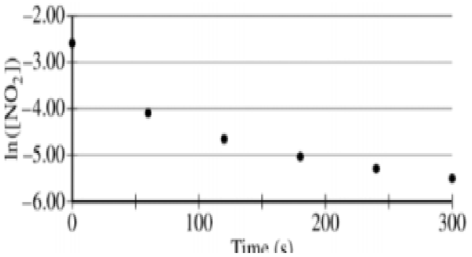
Step 1: $NO(g) + Br_2(g) \rightleftarrows NOBr_2(g)$ (*fast*)

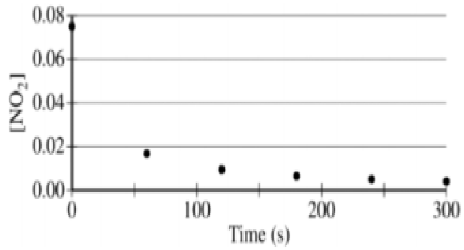
Step 2: $NOBr_2(g) + NO \longrightarrow 2\ NO(g) + 2\ Br(g)$ (*slow*)

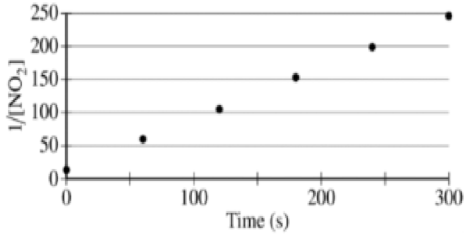
**11**. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \longrightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) What order is the following reaction?

(b) Write the rate law for the decomposition of $NO_2(g)$.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by the mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I

Step 1: $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ *slow*

Step 2: $NO_3(g) \longrightarrow NO(g) + O_2(g)$ *fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism II

Step 1: $NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$ *fast equilibrium*

Step 2: $N_2O_4(g) \longrightarrow 2\ NO(g) + O_2(g)$ *slow*

**12.** Consider the four reaction-energy diagrams below:

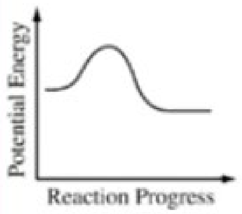


Diagram 1

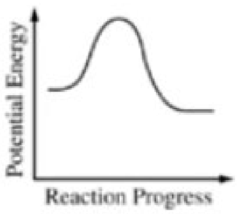


Diagram 2

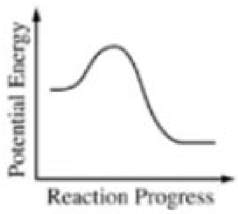


Diagram 3

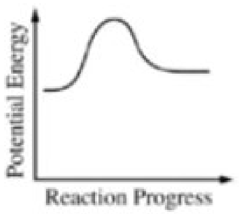
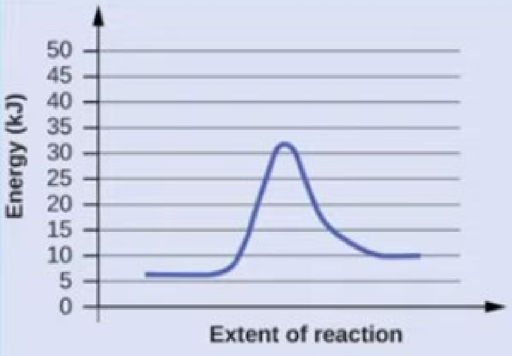


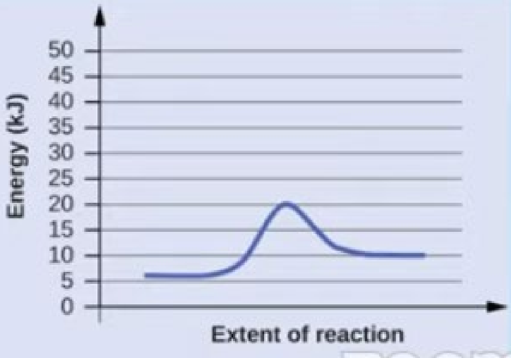
Diagram 4

Identify the **two diagrams** that could represent a **catalyzed** and an **uncatalyzed** reaction pathway for the same reaction. Indicate which of the two diagrams represents the catalyzed reaction pathway for the reaction.

**13.** The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



(a)



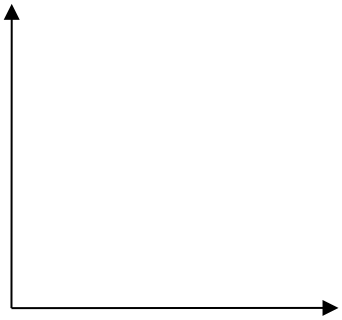
(b)

**14.** The formation of $C_2H_5Cl(g)$ is an exothermic reaction ($\Delta H° = -72.6\ kJ/mol_{rxn}$). The following two step reaction mechanism is proposed:

Step 1: $C_2H_4(g) + HCl(g) \longrightarrow C_2H_5^+(g) + Cl^-(g)$ *Slow step*

Step 2: $C_2H_5^+(g) + Cl^-(g) \longrightarrow C_2H_5Cl(g)$ *Fast step*

(a) Write the rate law for the reaction that is consistent with the reaction mechanism above.



(b) Identify an intermediate in the reaction mechanism above. Using the axes provided, draw a curve that shows energy changes that occur during the progress of the reaction. The curve should illustrate both proposed two-step mechanisms and the enthalpy change of the reaction.

# Unit 6 Review

**1.** This is the chemical equation for the process of evaporation

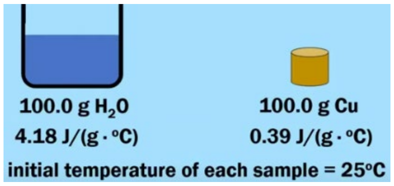
$$H_2O(l) \longrightarrow H_2O(g)$$

a) Evaporation is an (exothermic / endothermic) process.
b) Heat flows from the (surroundings to the system / system to the surrounding)

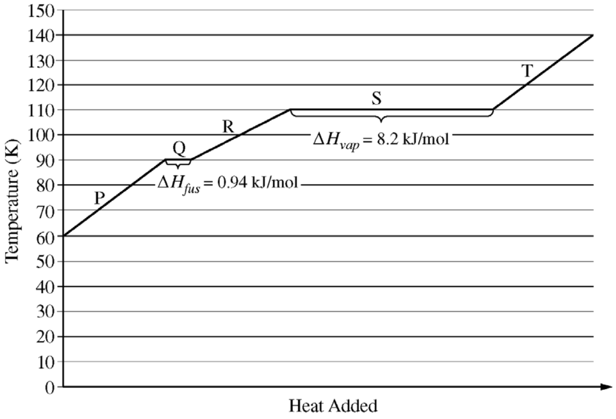
**2.** A student collects the data presented in the table and claims that, since the magnitude of ΔT for the copper is greater than that of water, it means that the magnitude of heat (*q*) lost by the copper is greater than the magnitude of (*q*) gained by the water. Do you agree with this claim? *Explain.*

| | |
|---|---|
| Mass of Copper | 50.00 g |
| Initial Temperature of Copper | 100.0 °C |
| Mass of Water | 100.0 °C |
| Initial Temperature of Water | 20.0 °C |
| Final Temperature of System (Copper + Water) | 23.6°C |

**3.** Suppose that each of these samples absorbs 500 J of heat. Which sample, $H_2O$ or Cu, will reach a higher final temperature? Justify your answer.



**4**. The following question refers to the graph below, which shows the heating curve for methane, $CH_4$.



In terms of intermolecular attractive forces, explain why line segment S is much longer than line segment Q.

**5.** In terms of intermolecular attractive forces, explain why the value of $\Delta H_{vap}$ for $H_2O$ is much greater than the value of $\Delta H_{vap}$ for $CH_4$.

| **Substance** | **$\Delta H_{vap}$ (kJ/mol)** |
|---|---|
| $CH_4$ | 8.2 |
| $H_2O$ | 40.7 |

**6.**The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

**7**. The combustion of methane gas is represented by the equation shown below.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H^\circ = -802 \text{ kJ/mol}_{rxn}$$

When this reaction occurs, is energy absorbed or released by the system? Explain.

**8**. The combustion of methane gas is represented by the equation shown below.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H^\circ = -802 \text{ kJ/mol}_{rxn}$$

Suppose that 7.50 g of $CH_4(g)$ reacts completely with excess $O_2(g)$ according to the equation shown above. How many kJ of thermal energy would be released?

**9**. Fulminic acid can convert to isocyanic acid according to the equation below.

$HCNO(g) \rightleftarrows HNCO(g)$

*Fulminic acid*     *isocyanic acid*

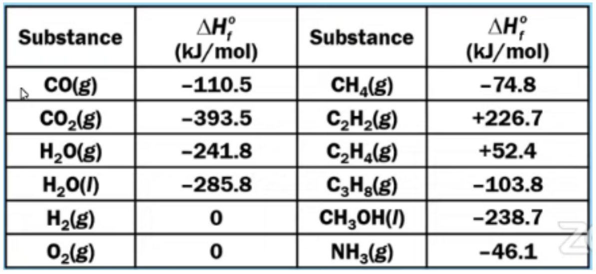
| Fulminic Acid | Isocyanic Acid |
|---|---|
| $H-C\equiv N-\ddot{\underset{..}{O}}:$ | $H-\ddot{N}=C=\ddot{O}:$ |

Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H^o$ for the reaction of HCNO(*g*) to form HNCO(*g*) .

| Bond | Enthalpy (kJ/mol) | Bond | Enthalpy (kJ/mol) | Bond | Enthalpy (kJ/mol) |
|---|---|---|---|---|---|
| N–O | 201 | C=N | 615 | H–C | 413 |
| C=O | 745 | C≡N | 891 | H–N | 391 |

**10.** Calculate the $\Delta H_{rxn}$ for the following chemical equation. Use the $\Delta H_f^o$ *given.*

$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O$



| Substance | $\Delta H_f^\circ$ (kJ/mol) | Substance | $\Delta H_f^\circ$ (kJ/mol) |
|---|---|---|---|
| CO(*g*) | –110.5 | $CH_4(g)$ | –74.8 |
| $CO_2(g)$ | –393.5 | $C_2H_2(g)$ | +226.7 |
| $H_2O(g)$ | –241.8 | $C_2H_4(g)$ | +52.4 |
| $H_2O(l)$ | –285.8 | $C_3H_8(g)$ | –103.8 |
| $H_2(g)$ | 0 | $CH_3OH(l)$ | –238.7 |
| $O_2(g)$ | 0 | $NH_3(g)$ | –46.1 |

**11.** $Na_2S_2O_3(aq) + 4\,NaOCl(aq) + 2\,NaOH(aq) \longrightarrow 2\,Na_2SO_4(aq) + 4\,NaCl(aq) + H_2O(l)$

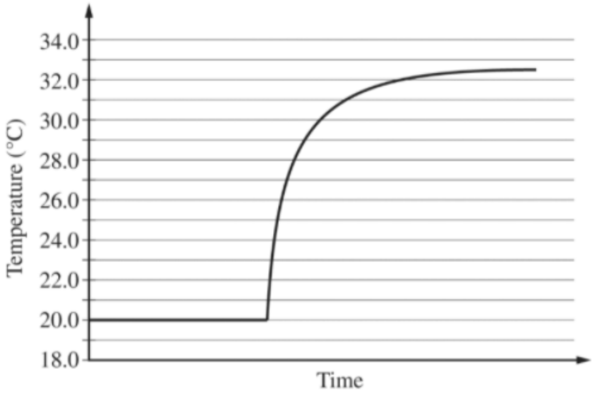
A student performs an experiment to determine the value of the enthalpy change, $\Delta H^o_{rxn}$, for the oxidation-reduction reaction represented by the balanced equation above.

In the experiment, the student uses the solutions shown in the table below.

| Solution | Concentration (*M*) | Volume (mL) |
|---|---|---|
| $Na_2S_2O_3(aq)$ | 0.500 | 5.00 |
| NaOCl(*aq*) | 0.500 | 5.00 |
| NaOH(*aq*) | 0.500 | 5.00 |

Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

**12.** Three solutions, all originally at 20.0°C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



According to the graph, what is the temperature change of the reaction mixture?

# Unit 7 Review

**1.** The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

| | | | | | |
|---|---|---|---|---|---|
| (a) | $2\ NH_3(g) \rightleftarrows N_2(g) + 3\ H_2(g)$ | $K_c = 17$ | **$[NH_3]$** = 0.20 *M* | **$[N_2]$** = 1.00 *M* | **$[H_2]$** = 1.00 *M* |

| | | | | | |
|---|---|---|---|---|---|
| (b) | $2\ NH_3(g) \rightleftarrows N_2(g) + 3\ H_2(g)$ | $K_P = 6.8 \times 10^4$ | **$NH_3$**= 3.0 atm | **$N_2$** = 2.0 atm | **$H_2$** = 1.0 atm |

**2.** $2\ A(g) + B(g) \rightleftarrows 2\ C(g)$

A(*g*) and B(*g*) react to form C(*g*), according to the balanced equation above. In an experiment, a previously evacuated rigid vessel is charged with A(*g*), B(*g*), and C(*g*), each with a concentration of 0.0100 M. The following table shows the concentrations of the gases at equilibrium at a particular temperature.

| **$[A]_{eq}$** | **$[B]_{eq}$** | **$[C]_{eq}$** |
|---|---|---|
| 0.018 | 0.014 | 0.0020 |

a. Calculate the value of $K_c$.

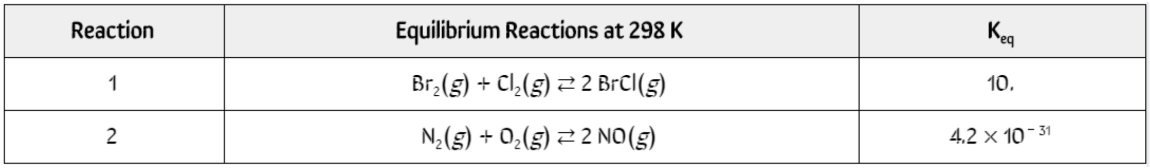
b. If the experiment is repeated at a higher temperature, $K_c$, is found to have a larger value. Describe the effect of the temperature change on the concentrations of the gases at equilibrium.

**3**. Write equilibrium expressions for the following reactions. (Remember, we do not include solids or liquids)

a. $CH_4(g) + 2\ O_2(g) \rightleftarrows CO_2(g) + 2\ H_2O(l)$ K =

b. $2\ Pb(NO_3)_2(s) \rightleftarrows 2\ PbO(s) + 4\ NO_2(g) + O_2(g)$ K =

**4.**



| Reaction | Equilibrium Reactions at 298 K | $K_{eq}$ |
|---|---|---|
| 1 | $Br_2(g) + Cl_2(g) \rightleftarrows 2\ BrCl(g)$ | 10. |
| 2 | $N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$ | $4.2 \times 10^{-31}$ |

The table above shows data for two reactions carried out in two separate experiments. The students started with 2 evacuated 1.0-Liter rigid containers at a constant temperature of 298 K. To each container 0.50 mol of the appropriate reactants was added, and the reaction was allowed to reach equilibrium. Based on this information, how do the relative concentrations of BrCl and NO present inside their respective containers at equilibrium compare to one another?

**5.** $H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$

At Equilibrium, $[H_2] = 0.100\ M$, $[I_2] = 0.100\ M$ *and* $[HI] = 0.714\ M$. **Calculate the value of $K_c$.**

**6.**Given the initial concentrations shown below, find the equilibrium concentrations for A, B, and C.

$K = 9.0 \times 10^{-8}$ $[A] = [B] = 0.300M$ Use a (R )ICE chart to support

$A(g) + B(g) \leftrightarrows 2C(g)$

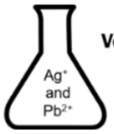
**7**. Find final equilibrium concentration for HA, $H^+$ and $A^-$. Initial [HA] = 0.50M. Use a (R )ICE chart to support.

$HA \leftrightarrows H^+ + A^-$ $K = 2.0 \times 10^{-5}$

**8.**

| Compound | $K_{sp}$ | Which substance, AgCl(s), AgBr(s) orAgI(s) has the greatest solubility? |
|---|---|---|
| AgCl(s) | $1.8 \times 10^{-10}$ | |
| AgBr(s) | $5.4 \times 10^{-13}$ | |
| AgI(s) | $8.5 \times 10^{-17}$ | |

**9.** A 0.0010 mol sample of $K_2SO_4(s)$ is added to the solution in the flask. Will a precipitate occur? Explain.

| Compound | $K_{sp}$ |  Volume of solution = 1 L<br>$[Ag^+] = 0.020\ M$<br>$[Pb^{2+}] = 0.0010\ M$ |
|---|---|---|
| $Ag_2SO_4(s)$ | $1 \times 10^{-5}$ | |
| $PbSO_4(s)$ | $1 \times 10^{-8}$ | |

**10.** For the endothermic reaction below, which change would cause the equilibrium to shift to the right? Justify.

$CH_4(g) + 2H_2S(g) \leftrightarrow CS_2(g) + 4H_2(g)$

(a) Decrease the concentration of dihydrogen sulfide.

(b) Increase the pressure on the system.

(c) Increase the temperature of the system.

(d) Increase the concentration of carbon disulfide.

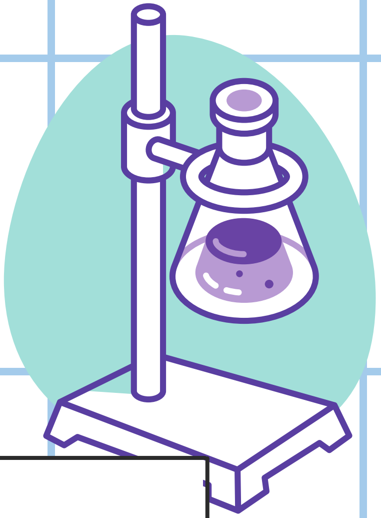
(e) Decrease the concentration of methane.

**11.** Predict the effect of decreasing the temperature on the position of the following equilibria. Justify.

(a) $H_2(g) + Cl_2(g) \leftrightarrow 2HCl(g)$ $\Delta H = +49.7$ kJ/mol

(b) $2NH_3(g) \leftrightarrow N_2(g) + 3H_2(g)$ $\Delta H = 37.2$ kJ/mol

(c) $CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$ $\Delta H = -27.6$ kJ/mol



# FULL PRACTICE TEST

2022 AP Chemistry Review Mr. Nackers