

INORGANIC CHEMISTRY

Bioinformatics 2019

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2019:

Test 1 includes chapters 1-8 on November 13th
Test 2 focuses on chapter 9-11 on December 12th
Test 3 focuses on chapters 12-14 on January 15th

Information from lectures, and 8th edition of Zumbdahls chemistry textbook

If something is missing or needs more, email me jepolitsch@gmail.com and ill add it.

Chapter 1:

Scientific method is a functional process to test observed phenomenon in the world. First, make an observation, formulate a hypothesis and then perform experiments. From this, a theory, or model explains why nature performs in a certain way. Quantitative observations are called measurements and are described by a **number and a unit**. Measurements always have some uncertainty, and this uncertainty is shown by the number of **significant figures**. Significant figures are determined by the accuracy of your lowest observation. Calculations rely on the accuracy of the lowest significant figure, therefore never round until the final answer. Preferred system is the SI system.

Density is described as mass/volume

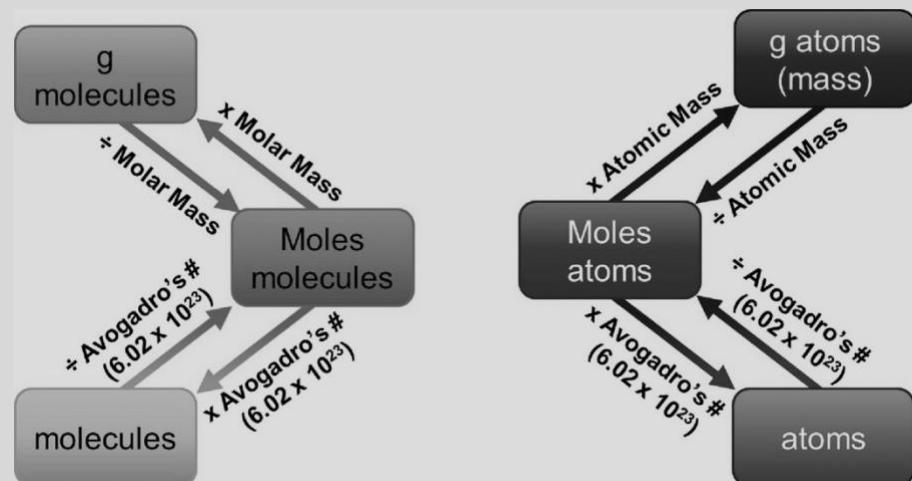
Matter exists in three states:

- solid-no movement. Defined shape and volume
- Liquid- some movement. Defined volume but not shape

-Gas- No shape. Indefinite

volume and shape

Homogeneous mixtures cannot be differentiated into part while heterogeneous mixtures can be distinguished. However, mixtures can be separated by physical means of distillation, filtration, and chromatography which do not change their chemistry. Compounds can be decomposed to elements through chemical changes.



Chapter 2:

Conservation of mass tells us that mass cannot be created or destroyed, this is important in balancing chemical equations and finding expected yield. The law of definite proportions states that a given compound will always contain exactly the same proportion of elements by mass. The law of multiple proportions states that when a compound is created, the proportion of elements in that compound can be reduced to a small whole number ratio.

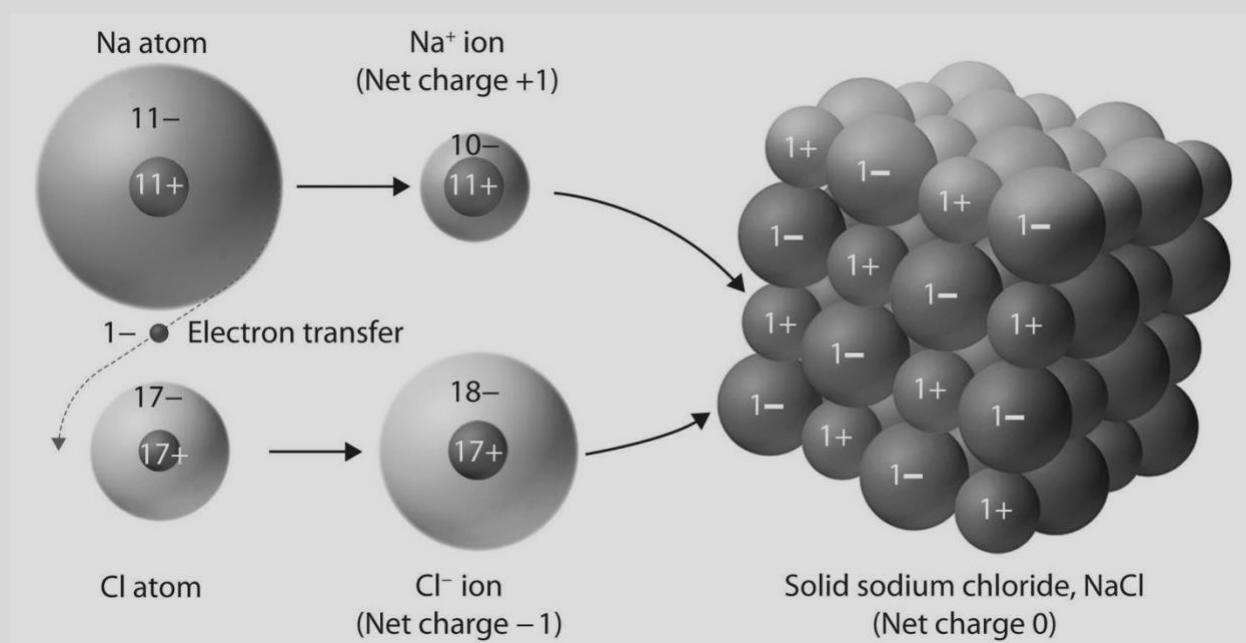
The Bohr Model was the earliest ideas of atomic structure. Stated that when electrons are brought closer to the center of the atom, energy is released. Bohr model fails because it does not account for intermolecular electric charges, thus works for hydrogen and nothing else.

Dalton's atomic theory states that all elements are composed of atoms, and all atoms of a given element are identical. Chemical compounds are formed when atoms are combined. Atoms are never changed in chemical reactions, but the way they bond together does.

Atomic structure is made of three main parts. In the center, is a small, extremely dense nucleus containing protons and neutrons. Protons hold a positive charge, and neutrons do not hold any charge. Together, protons + neutrons are the mass number, or atomic weight. Electrons reside in a cloud outside the nucleus and hold a negative charge but have an extremely small mass. Isotopes have the same atomic number but different mass numbers, due to the difference in neutrons. If number of electrons changed, the element would no longer be itself.

Atoms combine to form molecules by sharing electrons to form covalent bonds. Covalent bonds can be polar or non-polar based on the element's electronegativity. Molecules are described by their chemical formulas. Chemical formulas show number and type of atom.

Ions are created when an element gains or loses an electron. Cations are formed by the loss of an electron and have a positive charge. Anions are formed by gaining an electron and are negatively charged. An anion and a cation form an Ionic bond, because of their opposite charges. These ions form a crystal lattice. No molecular formula can be determined, only an empirical formula. Polyatomic ions contain more than 2 elements.



The periodic table is organized in order of increasing mass. Elements with similar properties are organized into columns (same number of valence electrons) and groups (similar reactive properties). The most common category is Metals, which form Cations. Nonmetals form anions.

Chapter 3:

Stoichiometry deals with the amount of substance consumed and produced in a chemical reaction. We count atoms by measuring mass, then using the atomic mass to convert to molecules. Average atomic mass is calculated by multiplying the mass of all known isotopes - measured in a mass spectrometer- of an element by their relative abundance (0-1). A mole is a number used to scale activity on an atomic level to a scale we can comprehend. A mole is 6.022×10^{23} units, which is exactly the number of carbon atoms in 12g of pure carbon-12. Therefore, the mass of 1 mole of an element = the atomic mass in grams. $m = g/\text{amu}$. Molar mass is the mass of 1 mole of a compound or element. For a compound, the molar mass can be calculated by summing the molar mass of each element, times that elements frequency.

Empirical formulas are the simplest whole number ratio of the various types of atoms in a compound. They can be found from the mass percentage. Molecular formulas on the other hand cannot be found only from percent composition without knowing molar mass. Molecular formulas are the actual formulation of the compound and are always an integer multiple of the empirical formula. For ionic substances, however, the empirical formula is the same as the molecular formula, because it's impossible to measure ionic compounds in this way.

In a chemical equation, reactants are turned into products. Atoms are neither created nor destroyed, but often move around. Thus, all the atoms present in the reactants must be present in the products. Chemical equations are used to represent a chemical reaction, with reactants on the left side and products on the right, and when balanced give the relative amount of reactant and product.

Using stoichiometry, we can balance chemical equations so that for each element, the number of atoms in the reactant is the same as the product. With this so-called molar ratio, we can determine exactly how much of a specific substance will be created based on the reactants. The limiting reactant is the reactant consumed first, thus stopping the reaction, while the other

reactants are left in excess. This amount that is produced is called the yield. The theoretical yield is the amount that the reactants could produce in perfect conditions, while the actual yield is what is actually produced. The percent yield is the actual yield/theoretical yield.

Chapter 4:

A solvent breaks ionic bonds while a solute is the ion being broken. Solubility depends on bond strength. Water is an important solvent that dissolves ionic and polar substances. Electrolytes are substances that disassociate in polar solutions, strong electrolytes disassociate 100% while weak electrolytes only partially disassociate. Strong electrolytes also conduct an electric current and produce separate ions, which weak electrolytes do not carry a current. Nonelectrolytes dissolve but produce no ions nor do they conduct a current.

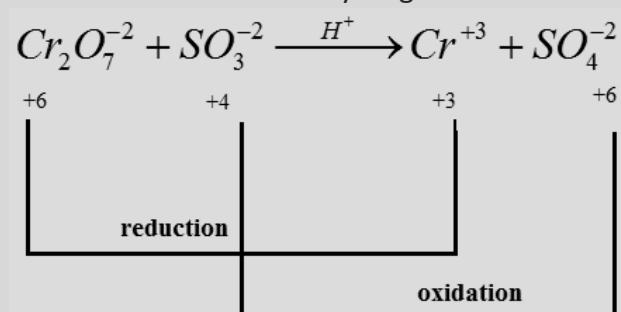
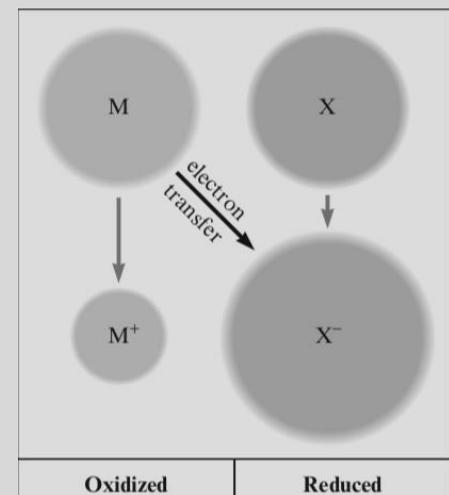
In Oxidation-Reduction reactions the oxidation states of each compound are assigned to keep track of electrons. Oxidation is the loss of electrons, and thus the increase of the oxidation state (OIL). Reduction is the gaining of electrons and thus the decreasing of the oxidation state (RIG). The oxidizing agent gains electrons, and is therefore reduced, while the reducing agent loses electrons and is therefore oxidized. Equations of oxidation reactions can be balanced by the oxidation state method, or the half reaction method.

Balancing Oxidation–Reduction Reactions by Oxidation States:

1. Write the unbalanced equation.
 2. Determine the oxidation states of all atoms in the reactants and products.
 3. Show electrons gained and lost using “tie lines.”
 4. Use coefficients to equalize the electrons gained and lost.
 5. Balance the rest of the equation by inspection.
 6. Add appropriate states.

Rules for Assigning Oxidation Numbers

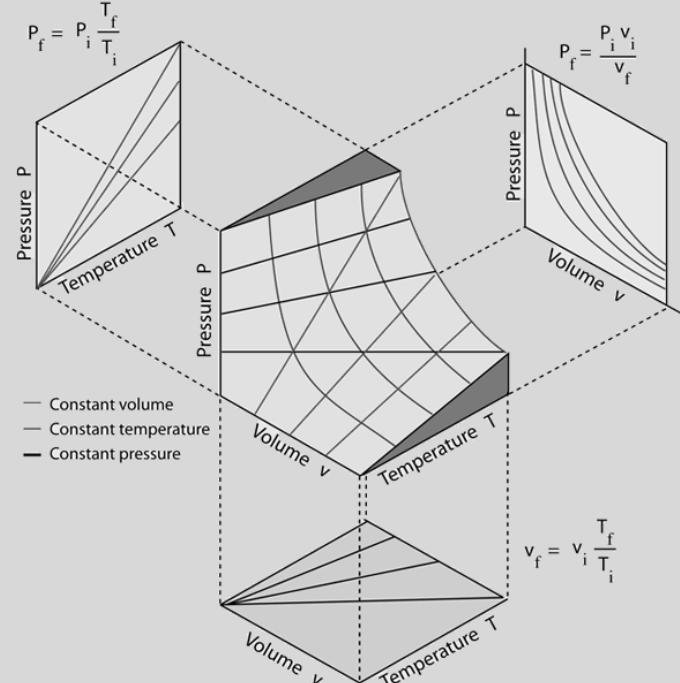
- The convention is that the cation is written first in a formula, followed by the anion. For example, in NaH, the H is H⁻; in HCl, the H is H⁺.
 - The oxidation number of a free element is always 0. The atoms in He and N₂, for example, have oxidation numbers of 0.
 - The oxidation number of a monatomic ion equals the charge of the ion. For example, the oxidation number of Na⁺ is +1; the oxidation number of N³⁻ is -3.
 - The usual oxidation number of hydrogens is +1. The oxidation number of hydrogens is -1 in compounds containing elements that are less electronegative than hydrogen, as in CaH₂.
 - The oxidation number of oxygens in compounds is usually -2. Exceptions include OF₂ because F is more electronegative than O, and BaO₂, due to the structure of the peroxide ion, which is [O-O]²⁻.
 - The oxidation number of a Group IA element in a compound is +1.
 - The oxidation number of a Group IIA element in a compound is +2.
 - The oxidation number of a Group VIIA element in a compound is -1, except when that element is combined with one having a higher electronegativity. The oxidation number of Cl is -1 in HCl, but the oxidation number of Cl is +1 in HOCl.
 - The sum of the oxidation numbers of all of the atoms in a neutral compound is 0.



Chapter 5:

A gas can be completely described by knowing its specific pressure(P), volume(V), and temperature (T) and amount in moles of the gas present(n). Units are Liters, Kelvin, Moles, and atm. 1 torr = 1 mm Hg, 1 atm = 760 torr 1 atm = 101,325 Pa. Gas laws were discovered by observing properties of gases.

Boyle's law relates volume and pressure and works when temp is constant. It tells us that pressure and volume are directly related, so increasing volume increases pressure. The equation is $P_1V_1 = P_2V_2$. Charles law relates volume to temperature, when pressure is fixed. $V_1/T_1 = V_2/T_2$. Avogadro's law states that 1 mole of any gas at the 1 atm and $T = 273$ will equal exactly 22.4 liters. All of these laws combine to give the ideal gas law of $PV=nRT$ where $R=0.0821$. Molar mass of a gas can be found using $M = (g/PV) * RT$.



Ideal gases have four conditions, 1) all of their molecules are point particles 2) there are no intermolecular forces 3) collisions are perfectly elastic, no energy is lost and 4) motion of particles is random.

In mixtures of nonreactive gases behave differently, and we introduce concepts such as partial pressure and mole fractions. Dalton's law of partial pressure states that in a mix of gases in a container, the total pressure is the sum of the pressure each of those gases *would* exert on the container if it was alone. Molar fraction is denoted by χ_i , where χ_i is the moles of a certain gas divided by the total moles. Since we know that all gases have the same volume at the same T and P , the partial pressure of any gas is its mole fraction*total pressure.

Partial volume is defined as the volume each gas in a mixture would occupy if it were alone in the container. We can again apply the mole fraction to the volume so partial volume = mole fraction*total volume. This leads us to Gas-Loussac law, also called the combined gas law, which states that at constant T and P , the molar ratio of gases is the same as the ratio in liters, milliliters, hectares or whatever. This makes stoichiometry easier with gases when T and P are fixed

Chapter 6:

Nomenclature follows IUPAC rules in order to systematically name compounds. Binary ionic compounds have a positively charged cation, and a negatively charged anion, and follow these rules:

1. The cation is always named first and the anion second.
2. A monatomic (meaning “one-atom”) cation takes its name from the name of the element. For example, Na^+ is called sodium in the names of compounds containing this ion.

| Cation | Name | Anion | Name |
|-----------|-----------|----------|-----------|
| H^+ | Hydrogen | H^- | Hydride |
| Li^+ | Lithium | F^- | Fluoride |
| Na^+ | Sodium | Cl^- | Chloride |
| K^+ | Potassium | Br^- | Bromide |
| Cs^+ | Cesium | I^- | Iodide |
| Be^{2+} | Beryllium | O^{2-} | Oxide |
| Mg^{2+} | Magnesium | S^{2-} | Sulfide |
| Ca^{2+} | Calcium | N^{3-} | Nitride |
| Ba^{2+} | Barium | P^{3-} | Phosphide |
| Al^{3+} | Aluminum | | |

3. A monatomic anion is named by taking the root of the element name and adding -ide. Thus, the Cl⁻ ion is called chloride.

| Compound | Ions Present | Name | If the ions have more than one possible oxidation state, you have to calculate it, then add the roman numeral like this; |
|-------------------|------------------------------------|------------------|--|
| NaCl | Na ⁺ , Cl ⁻ | Sodium chloride | |
| KI | K ⁺ , I ⁻ | Potassium iodide | |
| CaS | Ca ²⁺ , S ²⁻ | Calcium sulfide | |
| Li ₃ N | Li ⁺ , N ³⁻ | Lithium nitride | |
| CsBr | Cs ⁺ , Br ⁻ | Cesium bromide | |
| MgO | Mg ²⁺ , O ²⁻ | Magnesium oxide | Binary covalent |

compounds are formed between two non-metal compounds, and follow these rules;

1. The first element in the formula is named first, using the full element name.
2. The second element is named as if it were an anion.
3. Prefixes are used to denote the numbers of atoms present.
4. The prefix mono- is never used for naming the first element. For example, CO is called carbon monoxide, not monocarbon monoxide.

| Ion | Systematic Name |
|--------------------------------|----------------------|
| Fe ³⁺ | Iron(III) |
| Fe ²⁺ | Iron(II) |
| Cu ²⁺ | Copper(II) |
| Cu ⁺ | Copper(I) |
| Co ³⁺ | Cobalt(III) |
| Co ²⁺ | Cobalt(II) |
| Sn ⁴⁺ | Tin(IV) |
| Sn ²⁺ | Tin(II) |
| Pb ⁴⁺ | Lead(IV) |
| Pb ²⁺ | Lead(II) |
| Hg ²⁺ | Mercury(II) |
| Hg ₂ ^{2+*} | Mercury(I) |
| Ag ⁺ | Silver [†] |
| Zn ²⁺ | Zinc [†] |
| Cd ²⁺ | Cadmium [†] |

| Compound | Systematic Name |
|-------------------------------|----------------------|
| N ₂ O | Dinitrogen monoxide |
| NO | Nitrogen monoxide |
| NO ₂ | Nitrogen dioxide |
| N ₂ O ₃ | Dinitrogen trioxide |
| N ₂ O ₄ | Dinitrogen tetroxide |
| N ₂ O ₅ | Dinitrogen pentoxide |

| Prefix | Number Indicated |
|--------|------------------|
| mono- | 1 |
| di- | 2 |
| tri- | 3 |
| tetra- | 4 |
| penta- | 5 |
| hexa- | 6 |
| hepta- | 7 |
| octa- | 8 |
| nona- | 9 |
| deca- | 10 |

Lastly, an acid is a molecule in which one or more H⁺ ions are attached to an anion. The rules for naming acids depend on whether the anion contains oxygen. If the name of the anion ends in -ide, the acid is named with the prefix hydro- and the suffix -ic. When the anion contains oxygen, the acidic name is formed from the root name of the anion with a suffix of -ic or -ous, depending on the name of the anion.

| Acid | Name |
|------------------|--------------------|
| HF | Hydrofluoric acid |
| HCl | Hydrochloric acid |
| HBr | Hydrobromic acid |
| HI | Hydroiodic acid |
| HCN | Hydrocyanic acid |
| H ₂ S | Hydrosulfuric acid |

If you memorize these acids you should be pretty set.

| Acid | Name |
|---|-----------------|
| HNO ₃ | Nitric acid |
| HNO ₂ | Nitrous acid |
| H ₂ SO ₄ | Sulfuric acid |
| H ₂ SO ₃ | Sulfurous acid |
| H ₃ PO ₄ | Phosphoric acid |
| HC ₂ H ₃ O ₂ | Acetic acid |

Chapter 7:

In the periodic table, elements in the same column (group) have the same number of valence electrons. Trend properties such as First ionization energy, atomic radius, electron affinity can all be explained by this, and follow simple trends. Atomic radius is lowest in the bottom left corner, and highest in the top right, thus we can say atomic radius increases as we move down and given group and decreases as we move from left to right along a period. This is easily explained by the logic that more electrons means more shells and thus more space, but as the atom increases in mass from protons and neutrons, they pull the shells closer, thus decreasing the size before a new shell must be formed when the radius will increase again. By this logic, we also know that Cations(+) have a smaller atomic radius than their neutral elements, due to having one less electron, and Anions(-) are larger due to one more.

First ionization energy is defined as the energy required to remove the outermost electron and is exactly opposite to the trends of atomic size. This means the highest ionization energies are found in the top right corner, and the lowest in the bottom left. This is rather intuitive because

the less the furthest electron is being pulled to the center, the easier it will be to take it away. Electron affinity is defined as the energy released when an electron is added to the neutral atom or molecule to form an anion(-). Electron affinity follows the same trend as ionization energy, highest in the top right and lowest in the bottom left. It should be noted these are trends not laws so there are many exceptions.

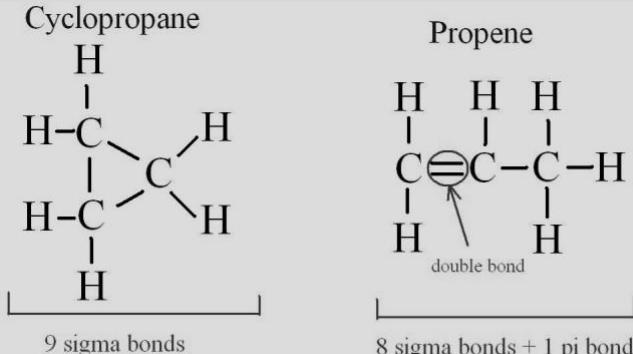
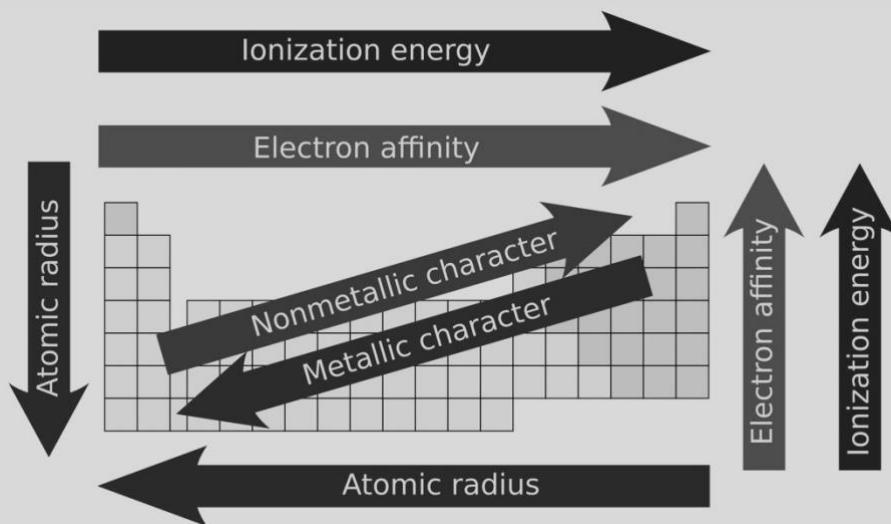
Electronegativity is directly related to electron affinity and is defined as the relative ability of an atom to attract shared electrons. It follows the same trend as electron affinity. Chemical bonds hold atoms together, forming molecules. Bonding offers when an atom can lower its total energy by grouping with an atom who also benefits from this

grouping, bringing all atoms involved to a more stable configuration (octet rule). There exist three types of chemical bonds, Ionic, which involves a transfer of an electron to form a cation and an anion, covalent, in which electrons are equally shared, and polar covalent, where electrons are unequally shared. It's helpful to not think of these as three separate scenarios but rather the intent to share an electron, and then based on electronegativity the even, partial, or one-sided sharing of that electron. In other words, the polarity of a bond depends on the electronegativity difference between the bonded atoms.

Ionic bonds are electrostatic, non-directional bonds between a metal and a non-metal. Ions (+,-) have different sizes from their parent atoms (neutral). Anions are larger (more electrons) and Cations are smaller (less electrons). Ionic compounds form a lattice structure(image page 7). Lattice energy is defined as the change in energy when ions are packed together to form an ionic solid. Ionic bonds happen in 3 steps.

- 1) Ionization of metal ($\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$)
- 2) Ionization of metal ($\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$)
- 3) Ions approach each other

Covalent bonds can be described in the valence bond theory. The theory states that bond length is based on electrostatic attraction (- to +) and repulsion (+ to +), and that bonds can only be formed by oppositely spinning molecules. Covalent bonds can be either single, double or triple. Like ionic bonds, the driving force in covalent bonds is the 'desire' to reach a stable state. Covalent bonds exist as sigma, or pi bonds, where sigma is the first bond, and pi are the following. In sigma bonds, the electron is shared in the center region, while in pi bonds, the electron is shared above and/or below the sigma bond. Pi bonds are weaker than sigma bonds and are less stable. Covalent bonds can be polar or non-polar, based on the involved elements electronegativity. If the molecule is monoatomic, it is nonpolar, if not, it is safe to assume the bond is at least slightly polar if the electronegativities are unknown.



Chapter 8:

Lewis structures show where electrons are, and how elements arrange themselves in a compound. To create a Lewis structure, first sum the total valence electrons of the compound. Then arrange the atoms so the central atom is in the middle and add bonds to the other atoms

and arrange the remaining electrons to satisfy the hydrogen duet rule and the octet for all other elements. Sometimes, while achieving the octet rule there are more than one possible Lewis dot structures. These are called resonance structures, and the resulting molecular structure is the average of these resonance structures.

Formal charge is a concept introduced to make sure a resonance structure is as valid as the others, in the sense that it is just as likely to occur in nature. To calculate formal charge, give the element however many lone pairs are around it, plus .5 electrons for every bond its involved in. Then subtract the result from the number of valence electrons found in the elements neutral state, the result is the formal charge. Formal charge is assigned where it occurs, so that if an element has a formal charge of -2, the – charge will reside on that elements side. After calculating formal charge, and determining all possible resonance structures, the *correct* Lewis structure is the one that has the lowest net formal charge. There can be more than one of these.

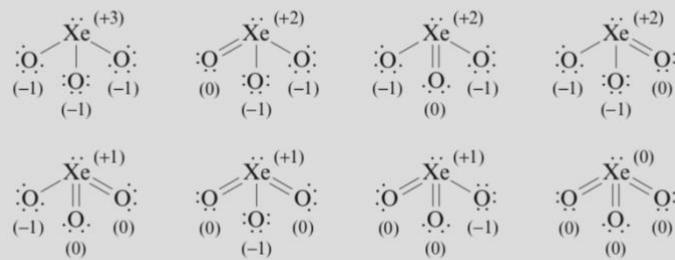
Molecular structures are the three-dimensional arrangement of the atoms in a molecule. The most convenient way to predict this is through the VSEPR model, which is based on the idea of minimizing the electron pair repulsion around an atom, that is to say that the elements

around a central atom will be as far apart as possible. In this model however, we must consider lone pairs as well, and for the purpose of the bond angles, they are treated as an element attached to the central atom but are not drawn in the final model. It should be noted that lone pairs require slightly more room than bonding electrons, resulting in strange but logical distortions of bond angle.

The table above tells us the molecular geometries if no lone pairs are included, but if lone pairs are included, the molecular shapes take a whole different name.

- Find total valence electrons of all atoms involved
- VE – (8*(things bonded to center) + 2*(H bonded to center)) / 2 = lone pairs
- Divide this number by 2 to find available electron pairs
- Add electrons in pairs to outside atoms until they reach their octet(or duet)
- Add remaining electron pairs to central atom
- Calculate formal charge for all elements involved, if == 0 its good
- Choose molecular geometry based on lone pairs on central atom + bonding pairs

For XeO_3 (26 valence electrons) we can draw the following possible Lewis structures (formal charges are indicated in parentheses):



| VSEPR Geometries | | | | | |
|------------------|-----------------------------------|---------------------------------|------------------------------|----------------------|---------------------|
| Steric No. | Basic Geometry 0 lone pair | 1 lone pair | 2 lone pairs | 3 lone pairs | 4 lone pairs |
| 2 | X—E—X Linear | | | | |
| 3 | X—E—X Trigonal Planar | X—E—X Bent or Angular | | | |
| 4 | X—E—X Tetrahedral | X—E—X Trigonal Pyramidal | X—E—X Bent or Angular | | |
| 5 | X—E—X Trigonal Bipyramidal | X—E—X Sawhorse or Seesaw | X—E—X T-shape | X—E—X Linear | |
| 6 | X—E—X Octahedral | X—E—X Square Pyramid | X—E—X Square Planar | X—E—X T-shape | X—E—X Linear |

| n | l | m | orbitale |
|---|---|---------------------------|-------------|
| 1 | 0 | 0 | 1s (è 1) |
| 2 | 0 | 0 | 2s |
| | 1 | -1, 0, +1 | 2p (sono 3) |
| 3 | 0 | 0 | 3s |
| | 1 | -1, 0, +1 | 3p |
| | 2 | -2, -1, 0, +1, +2 | 3d (sono 5) |
| 4 | 0 | 0 | 4s |
| | 1 | -1, 0, +1 | 4p |
| | 2 | -2, -1, 0, +1, +2 | 4d |
| | 3 | -3, -2, -1, 0, +1, +2, +3 | 4f (sono 7) |

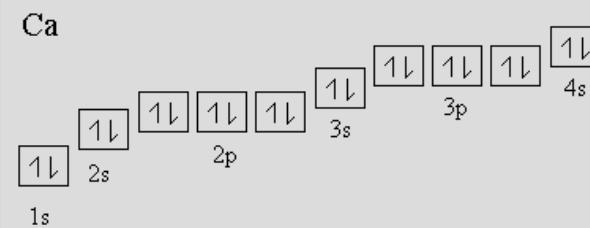
Energy of atomic orbitals depend on the first(n) and second(l) quantum number. Electron spin can be described by these principals. 1) the quantum spin number(ms) can take either -.5 or +.5. 2) Pauli's exclusion principle (also called The Aufbau principle) states that no two electrons in a given atom can have the same set of quantum numbers (n,l,ml,ms) and 3) only two electrons with opposite spins can occupy a given orbital.

The Heisenberg uncertainty principal proves that classical physics cannot be applied to such small scales, because the uncertainty is far too large. Thus, we apply quantum mechanics and can find the probability of an electron occupying a certain space based on 4 quantum numbers.

Hybridization is the mixing of native atomic orbitals to form special orbitals used for bonding. Hybrid orbitals can be easily derived after finding the geometry of the molecule. Six electron pairs become d₂s₂p₃ five electron pairs d₃p₃ hybridization four electron pairs s₂p₃ hybridization three electron pairs s₂p₂ hybridization two electron pairs s₁p₁ hybridization. Notice the goal is to achieve as many open shells as is required to bond.

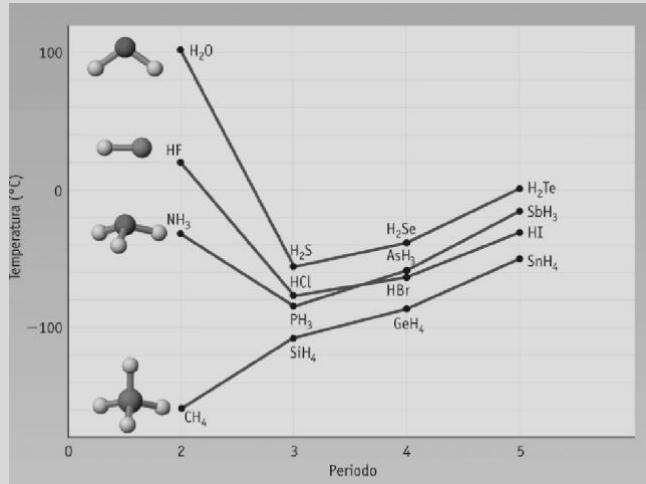
Intramolecular forces are distinguished from intermolecular forces by the idea that intramolecular defines the compound, and changes the arrangement, while intermolecular forces are responsible for states of matter. Water can be boiled into a gas, but the water molecules are still H₂O before and after. This is an example of intermolecular forces. Dipole-Dipole forces are caused by the difference in charge across an atom, hydrogen bonds are an example of dipole-dipole forces and are named separately because they are much stronger than most dipole bonds, where the + charge and - charge of water gives it special properties. Dipole forces are massively weaker than covalent or ionic bonds. London dispersion forces exist among noble gases and nonpolar molecules and are explained by the Heisenberg uncertainty principle. Since electrons are always moving in a cloud around the atom, sometimes they must *happen* to be more on one side than the other, creating an instantaneous dipole. London forces are the weakest, but are the only forces acting on some non-polar molecules and thus are important.

These relatively weak forces together are called Van der Wall forces, and are responsible for melting point, boiling point, vaporization heat and melting heat. As atomic size increases van der wall forces increase.



- a. correct
- b. correct
(since this is the 1 electron in the p sublevel it can be either "spin-up" or "spin-down")
- c. incorrect
(the spin of the 2nd electron depends on the spin of the 1st electron, even though they aren't in the same orbital)
- d. correct
(as long as you draw the first electron in each orbital as "spin-up", you will draw a correct orbital diagram)

To predict boiling point, the most important factor is intermolecular forces. Ionic are strongest, and if any of the compounds has ionic bonding it has a high boiling point. Then are hydrogen bonds, which are formed in when hydrogen bonds with N, O, and F due to their high electronegativity. H₂O forms the strongest hydrogen bonds because it is the most electronegative. 3rd are dipole-dipole interactions, and weakest is London dispersion force. If two compounds have the same kind of bonding, we then check the number of carbons, the higher this number, the higher the boiling point. Lastly, we check the relative branching of a molecule, the more branching, the lower boiling point. These principals are explained by the molecule's polarizability.



Chapter 9:

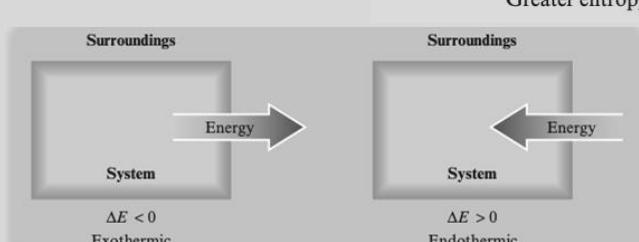
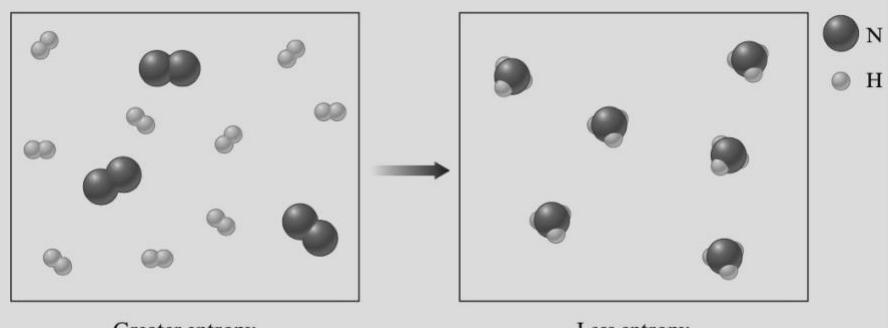
Thermodynamics defines energy as the capacity to do work. Two types of energy are important in chemistry, potential energy, which is energy due to position or composition, and kinetic energy, which is energy due to the motion of an object. Heat involves the transfer of energy between objects to create a temperature change. Work is the amount of work a force does over a distance. A state function, in the same way as a conservative force from physics only depends on initial and final state, not the pathway used to get there.

The three principle laws of thermodynamics are:

1. Energy cannot be created or destroyed, only changed from one form to another
2. The universe tends towards disorder, even if the order of a system is increasing, it will always be necessary to create disorder outside of the system to account for the work done. Entropy law
3. As a system approaches 0 degrees Kelvin, the entropy of the system approaches zero

Reactions are reversible when the products and reactants are never fully consumed, that is they are constantly reacting and being produced. These two reactions occur simultaneously $A+B \rightleftharpoons C+D$ and in both directions. As more A+B is formed, A+B particles interact with each other more and more creating more and more free energy, and eventually enough free energy to break the bonds. This happens of both sides of the reaction. In reversible reactions, we introduce the concept of equilibrium, which is achieved when the free energy of the system is zero. Unlike a reversible reaction, an irreversible reaction can never go back, such as a combustion reaction.

Entropy(S) is a thermodynamic function that describes the number of arrangements (positions and/or energy levels) available to a system existing in a given state.



In thermochemistry we must consider the system, and the surroundings separately. The system is absolutely arbitrarily defined, and the surroundings are everything else. A reaction is exothermic when energy flows out of the system, and endothermic when energy flows into the system. The internal energy of a system is calculated by the PE + KE of all of the particles in the system. This is calculated by the

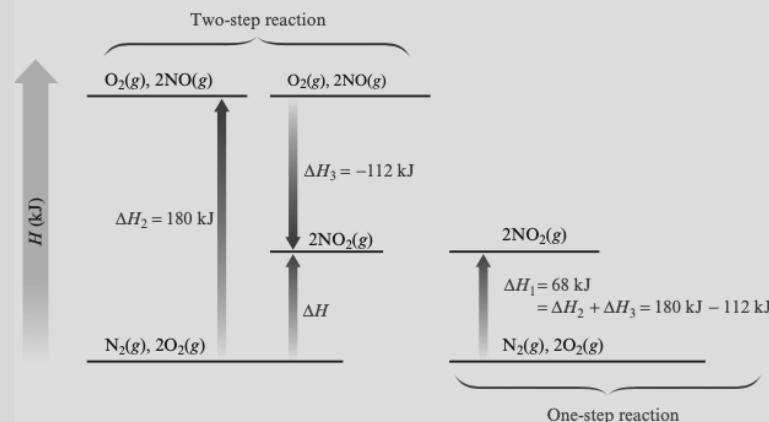
of the system, and endothermic when energy flows into the system. The internal energy of a system is calculated by the PE + KE of all of the particles in the system. This is calculated by the

Gibb's Helmholtz equation, $\Delta G = \Delta H - T\Delta S$, where T is in Kelvin. Thermodynamic quantities are vectors, who's magnitude is a number, and who's direction is the flow of energy, + is flowing into the system(endo) – is flowing out (exo).

When predicting if a reaction is spontaneous, use the Gibbs equation. When ΔG (free energy) is negative, the reaction is spontaneous towards the products. When $\Delta G = 0$, the reaction is at equilibrium. When ΔG is positive, the reaction is nonspontaneous towards the products. Remember to match units when solving.

| Case | Result |
|--|--|
| ΔS positive, ΔH negative | Spontaneous at all temperatures |
| ΔS positive, ΔH positive | Spontaneous at high temperatures (where exothermicity is relatively unimportant) |
| ΔS negative, ΔH negative | Spontaneous at low temperatures (where exothermicity is dominant) |
| ΔS negative, ΔH positive | Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures) |

Enthalpy(ΔH) is $\Delta H = \Delta E + P\Delta V$ and is defined as the change in heat of the system. We can also say $q = \Delta E + P\Delta V$, and therefore $q = \Delta H$ at constant pressure, and is equal to the energy flow as heat. In a chemical equation, $\Delta H = H_{\text{products}} - H_{\text{reactants}}$. Hess's law states that when going



from reactants to products, the enthalpy is the same whether the reaction takes place in one step or in many smaller steps. This implies that if a reaction is reversed, the enthalpy will also be reversed, and that enthalpy is directly proportional to the number of reactants and products, so the ΔH is multiplied by the stoichiometric coefficients in the reactions.

ΔS is the measure of entropy and decreases as a system becomes more ordered. For example, in the reaction $\text{H}_2 + \text{O} = \text{H}_2\text{O}$, the entropy was higher on the reactants side as there are two molecules, and lower in the products side because there is only one, thus the entropy of this reaction is negative.

Standard enthalpy of formation (ΔH_f) is the change in enthalpy associated with the formation of 1 mole of the compound in standard conditions of 25°C and 1 atm and 1 mole of element. Molar entropy comes from the second law of thermodynamics, and is highest in gases > liquids > solids, and increases as atomic mass increases, because elemental complexity increases.



A reaction is spontaneous when the equilibrium favors the production of the product under the conditions in which the reaction is occurring. These reactions decrease in energy towards the products and increase in entropy. Non-spontaneous reactions need activation energy to happen or are not favorable of creating the product.

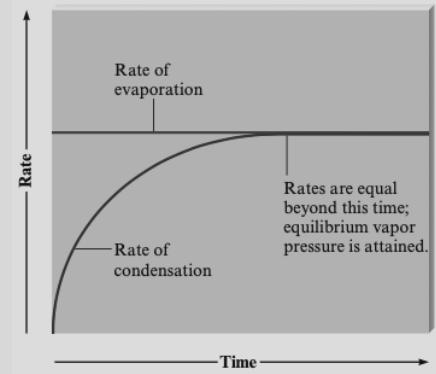
Temperature and pressure affect spontaneity, temperature directly, and pressure as it determines enthalpy values. Heat is the driving force in spontaneous reactions, and ultimately the system wants to reach a state of the lowest possible free energy. This is 0 because a

positive free energy value one means the reaction is spontaneous in the opposite direction. Considering this, heat is mostly important at low temperatures, as an output of heat in a system full of energy doesn't make much of a difference, but for a system of low energy it does.

Chapter 10

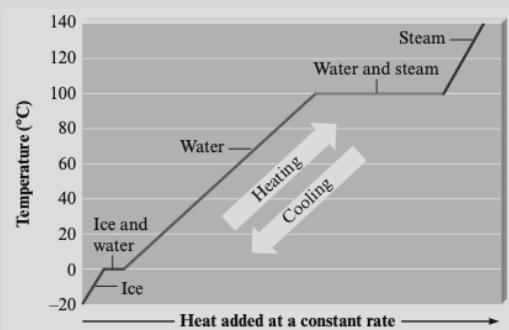
Liquids have their own volume and surface tension. Surface tension is created by intermolecular forces, and shows such phenomenon as the capillary effect, surface tension, and viscosity when the liquid is polar. Crystalline solids are formed by regularly occurring 3d structures. The smallest repeating unit is called the unit cell. Crystalline solids are classified by the type of component, can be atomic solids, ionic solids or molecular solids.

Vaporization or evaporation is the change from liquid to solid state and requires energy(endo) because we have to break bonds. This required energy is called the heat of vaporization at 1ATM. Vaporization is a surface phenomenon, while boiling occurs through. Condensation is the reverse of vaporization, and when temp is constant, the rate of vaporization is constant, but that of condensation is not. When rate of vaporization = rate of condensation the system is at equilibrium. The pressure of the vapor present at this equilibrium point is called the vapor pressure.

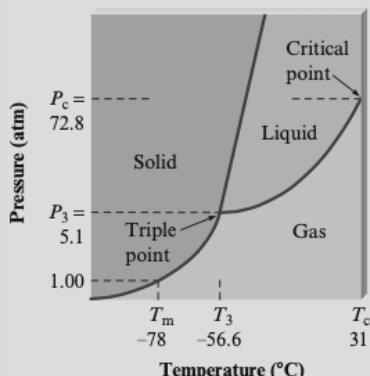


Liquids with high vapor pressure are volatile. Vapor pressure is dependent on intermolecular forces, and temperature. As pressure increases, boiling point decreases, and as elevation increases, pressure increases. This is described by the Clausius Clapeyron equation. On a pressure–temperature (P–T) diagram, the line separating the two phases is known as the coexistence curve. The Clausius–Clapeyron relation gives the slope of the tangents to this curve. Where d is difference, P is pressure, T is temp, L is specific heat of transition, and V is volume. It's good to remember the rule, when intermolecular forces go up, boiling point increases, and vapor pressure decrease(IMF↑, BP↑, VP ↓)

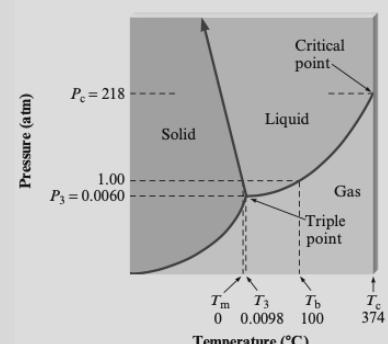
$$\frac{dP}{dT} = \frac{L}{T\Delta v} = \frac{\Delta s}{\Delta v},$$



The heating curve describes the phase transition of a substance when heated or cooled. We said vapor pressure and boiling point are when the rate of condensation is the same as the rate of vaporization. The boiling point is when liquid and gas exist. The melting point is the point when solid and liquid exist. We can see that the heat stops at each of these points. The phase of a system is the position of the system physically and chemically uniform.



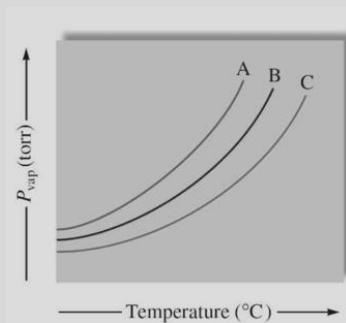
The phase diagram relates temperature and pressure to physical phase and is slightly different for each compound. On the left is the phase diagram of CO₂ and on the right Water. Sublimation is the change from solid directly to gas, no liquids exist. The triple point is the T and P in which we can find solid, liquid and gas. The supercritical phase is above the critical point and shows properties of both gas and liquid. You should be able



to show the points on both these. Another important point to note is that the density of solid water is less than the density of liquid water, which is not the case for CO₂, and is seen by the positive slope between solid and liquid in water and the negative slope in CO₂.

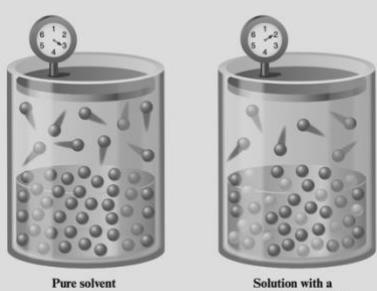
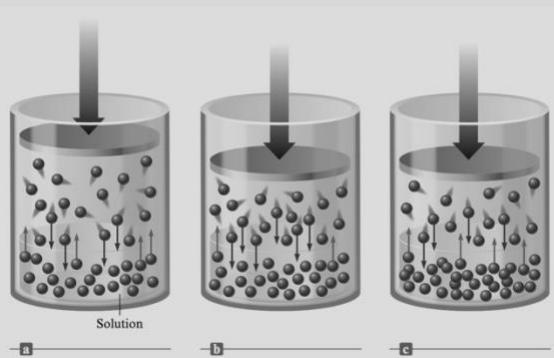
Another graph to be familiar with is the vapor pressure vs temperature graph. To find which has the highest VP, simply draw a vertical line. A>B>C

Dilution occurs when two solutions of different concentrations are mixed. The equation for this is $M_1V_1 + M_2V_2 = M_3V_3$ where M is molarity.



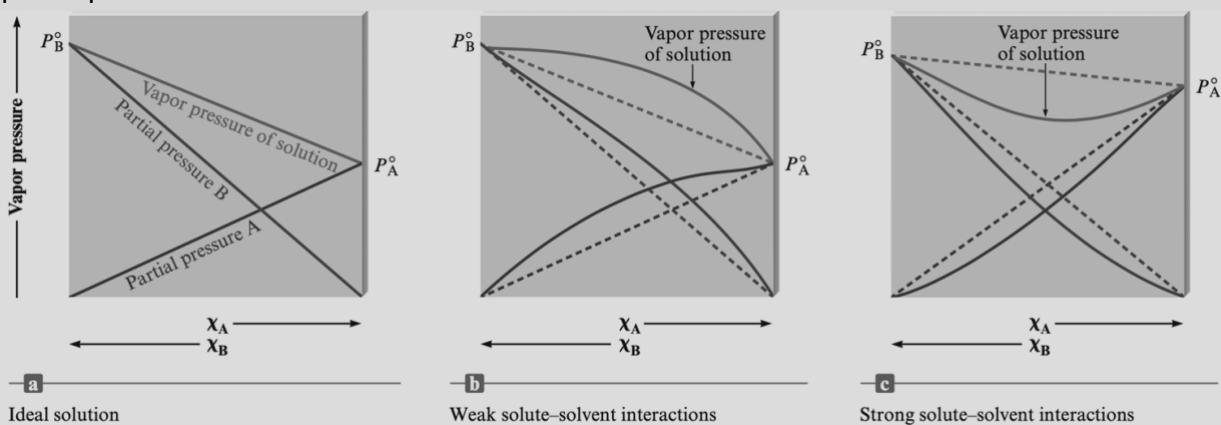
Chapter 11:

Solubility of a substance depends on intermolecular interactions. That is, when AA+BB = 2AB, intermolecular forces between A&A and B&B are broken, which is an endothermic process and costs energy, but when 2AB is formed, energy is released, such is exothermic. When the total enthalpy is positive, (recall $\Delta H = H\text{-products} - H\text{-reactants}$) the formation of the product creates more energy than is required to break the bonds and is endothermic. When the energy required to break the bonds is larger than that produced when the product is formed, enthalpy is negative, and the reaction is exothermic. For a substance to be solvable, the intermolecular interactions must be of the same kind. This means polar solutes are dissolved by polar solvents, and non-polar solutes are dissolved by non-polar solvents. When the process is very endothermic, the solute is only slightly dissolved. When the process is exothermic, the solute is almost fully dissolved.



Henry's law states that the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution. That's to say that as pressure increases, more gaseous molecules enter the liquid. Raoult's Law derives from the fact that when a non-volatile gas is added to a solution, the vapor pressure is lowered. This relationship is defined by $P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}$ where the observed vapor pressure of the solution is equal to the mole fraction of the solvent, times the vapor pressure of the pure solvent. This 'law' is an approximation, and works in ideal solutions, which is the equivalent to ideal gases to solutions, and happens when solute-solvent interactions are very similar.

In the case of non-ideal solutions, the modified formula is $P_{\text{solution}} = P^\circ_A \chi_A + P^\circ_B \chi_B$ which should be self-explanatory. When the solute and solvent release lots of energy, strong interactions exist between solute-solvent, and therefore expect a negative deviation from Raoult's law. When two liquids are endothermic, and need energy, the solute-solvent interactions are weaker, and we expect a positive deviation from Raoult's law. An example of these deviations is a molecule that can form hydrogen bonds, which releases energy and we should expect a negative deviation, or a polar and non-polar solution, in which case we can expect a positive deviation.



Colligative properties of solutions depend on concentration of solute. This concentration can be more quantitatively measured by the Van't Hoff coefficient $i = \frac{\text{Moles of particles}}{\text{Moles of dissolved solute}}$. This formula only depends on the number particles, not their identity. If solutions are electrolytes, meaning they dissolve, you have to calculate i after disassociation. This variable a is called the disassociation degree, and is found by $a = \frac{\text{Disassociated moles}}{\text{Original Moles}}$.

Some general rules for calculating disassociation degree; Strong electrolytes disassociate completely and have $a = 1$. Examples of strong electrolytes are all salts, and strong acids and bases. Weak electrolytes have $0 < a < 1$ and include weak acids and weak bases. Sugars are non-electrolytes and have $a = 0$. We also need to know V , the stoichiometric coefficient of the products, if there are more than one product, $V = a + b + c \dots$ where ABC are coefficients. Now we are ready to calculate i using the equation $i = 1 + a(v - 1)$ where i tells us the factor by which the original moles increase(i^*u). In summary,

| | | |
|--------------------|-------------|-------------|
| Non-Electrolyte | $a = 0$ | $i = 1$ |
| Strong electrolyte | $a = 1$ | $i = v$ |
| Weak electrolyte | $0 < a < 1$ | $1 < i < v$ |

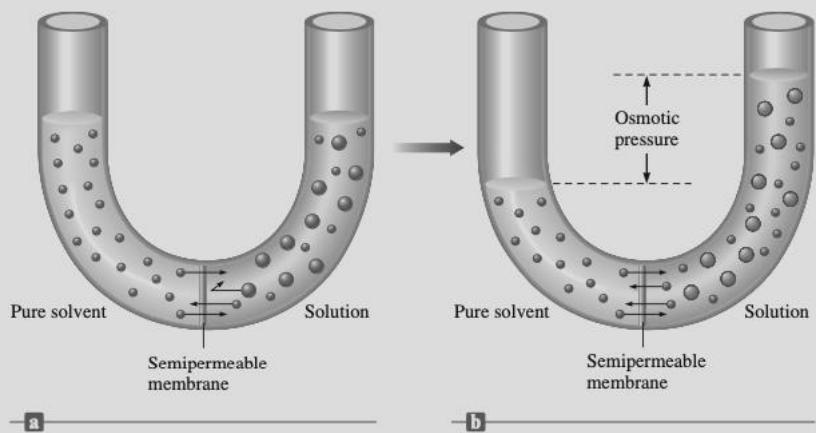
i can be predicted in salts by observing the ions per formula unit.

Boiling point of a liquid increases as non-volatile solute is added. This can be calculated using the formula $\Delta T = (K_b)(m_{\text{solute}})$ where ΔT is change in temperature, K_b is a constant depending on the liquid(0.51 for water), and m is the molality of the solute.

Freezing point in contrast decreases when a non-volatile solute is added. The formula is identical to that of boiling point elevation, except $K_b \rightarrow K_f$ and is the freezing point constant. Lastly, colligative properties produce the phenomenon of osmotic pressure, which can be defined by studying the pressure difference on two sides of a semi-permeable membrane. The osmotic pressure is defined as the pressure needed to increase the two sides of the membrane to the same osmotic level and stop net transition of solvent. The equation for osmotic pressure can be written as

$$\Pi = MRT \text{ where } R \text{ is } 0.821, M \text{ is the Molarity of the solution, and } T \text{ is temp in K.}$$

| Electrolyte | i (expected) |
|-------------------|----------------|
| NaCl | 2.0 |
| MgCl ₂ | 3.0 |
| MgSO ₄ | 2.0 |
| FeCl ₃ | 4.0 |
| HCl | 2.0 |
| Glucose* | 1.0 |

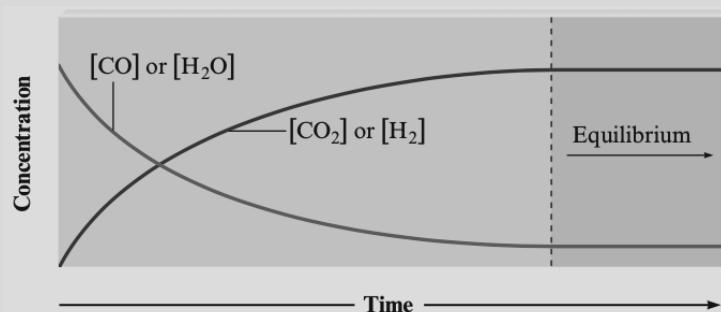


These properties have all been introduced under the presumption that the solutes are non-electrolytes, but they must be tweaked in order to apply to electrolytes. This tweak is the addition of the Van't Hoff coefficient into the formulas. The new formula for boiling and freezing is $\Delta T = iMk$, and $\Pi = iMRT$.

Chapter 12: Chemical equilibrium: Chemical equilibrium: Mass action law. Le Chatelier principle. The concentration, pressure and temperature effects on the equilibrium. Homogeneous and heterogeneous equilibria.

A system reaches chemical equilibrium when the number of products and reactants remains constant with time. Equilibrium will always be reached in an isolated system, it's just a question of time. When the reaction is virtually zero, the reaction is said to lean far to the right. When virtually no product is present, the reaction leans far to the left.

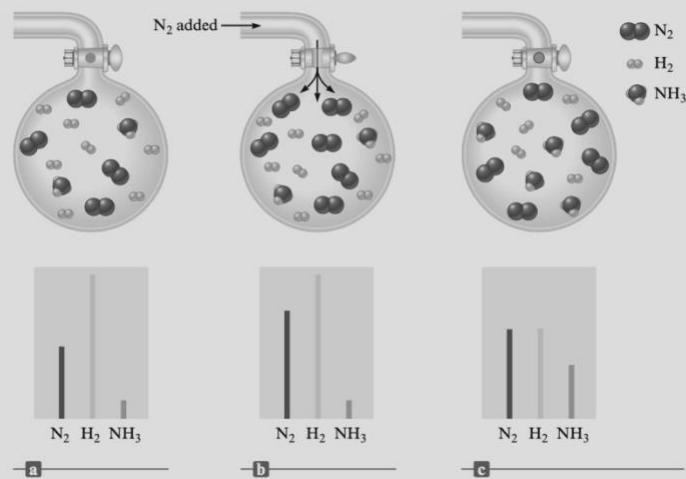
Equilibrium is not a static state, it is a state of constant motion, who's net flow is even, such that products are being made at the same time that reactants are forming. This occurs because as more products are formed, more collisions occur, breaking the products back into the reactants. Systems can appear to be at equilibrium, when in reality their reaction rate is simply too slow to observe any change.



The equilibrium condition is defined by the law of mass action, in which for reaction, $jA + kB \rightleftharpoons lC + mD$, where A,B,C,D are chemical species and j,k,l,m are coefficients, the equilibrium expression is $K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$ gives us the value of the equilibrium constant K. To find the equilibrium constant of the reversed reaction, simply take the inverse of the K value. Also note that when the balanced expression is multiplied by a factor n, the new K value is K^n . Values for A,B,C and D are given at equilibrium, and thus can change based on many factors. Each set of equilibrium data is called an equilibrium position, and there are millions of them for a given reaction. K depends only on pressure and is dimensionless.

Equilibrium constants involving pressure can be calculated using the ideal gas law, where $P=CRT$, and C is molar concentration. Using this, we can calculate the equilibrium partial pressure of the gas K_p . These partial pressure values can then replace A,B,C and D in the equilibrium equation, but we can also derive the equation $K_p = K(RT)^{\Delta n}$ where $\Delta n=(l+m)-(j+k)$

We can qualitatively predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium by using Le Châtelier's principle, which states that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change. The variables that change the equilibrium are pressure, temperature and concentration. This is just to say that if we add more product, the equilibrium will shift towards the left and visa versa. The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.



$$\Delta G^\circ = -RT\ln K_p$$

$$\Delta G^\circ = -RT\ln K_c$$

$$K > 1 \quad \Delta G^\circ < 0$$

products are favourite

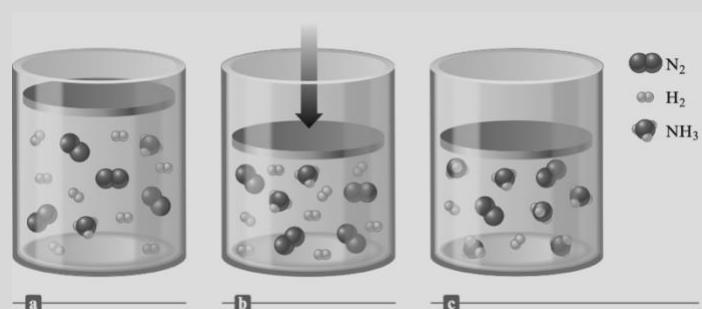
$$K < 1 \quad \Delta G^\circ > 0$$

reactants are favourite

The equilibrium point occurs when the free energy is at a minimum. In a system at equilibrium, if a reactant or product is added, the equilibrium will shift away from the added component. If a component is removed, the system will shift towards the removed component.

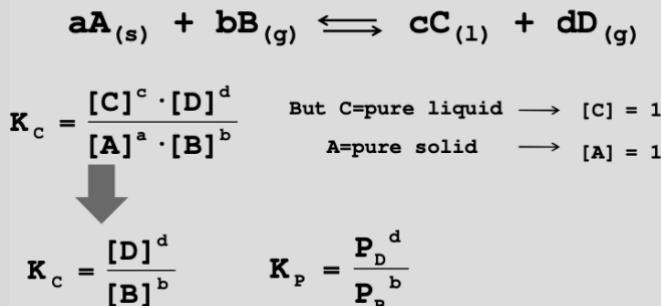
To change the equilibrium, we can also observe pressure. Pressure can be changed in a gaseous system by adding or removing a product or reactant, adding an inert gas, or changing the size of the container. When the size of a container is reduced, the system reduces its volume by decreasing the number of gaseous molecules.

Remember colligative properties here, for example the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, there are four particles on the reactants side, and only two on the products side, so when pressure is increased, the reaction will shift to the right. The opposite is also true when pressure decreases.



Unlike pressure and concentration, which can only change the equilibrium position, but does not alter the equilibrium constant K, temperature does change the value of K. Temperature will shift the direction of the reaction in the same way that adding a product or reactant will, that is in the opposite direction of where the temperature is added.

We can calculate the new K using the Van't Hoff's quotient:



Examples of shifts in equilibrium:

Observe that for temperature:

- $\Delta H^\circ > 0$ endothermic K increases with T
- $\Delta H^\circ < 0$ exothermic K decreases as T increases
- $\Delta H^\circ = 0$ K doesn't change if T change

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Homogeneous equilibria are when all of the reactants and products are in the same phase. Heterogenous equilibria instead is when some are not in the same phase. In heterozygous we don't consider species in the solid or liquid phase.

Table 13.4 | Shifts in the Equilibrium Position for the Reaction
 $58\text{ kJ} + \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

| Change | Shift |
|---------------------------------------|-------|
| Addition of $\text{N}_2\text{O}_4(g)$ | Right |
| Addition of $\text{NO}_2(g)$ | Left |
| Removal of $\text{N}_2\text{O}_4(g)$ | Left |
| Removal of $\text{NO}_2(g)$ | Right |
| Addition of $\text{He}(g)$ | None |
| Decrease container volume | Left |
| Increase container volume | Right |
| Increase temperature | Right |
| Decrease temperature | Left |

Chapter 13: Acid Base Equilibrium

Acid-base equilibrium: Definitions of Bronsted-Lowry and Lewis. Acid halides and oxyacids. Acid strength. Autoionization of water. The pH scale. Calculation of the pH for a solution of: strong acid (base), weak acid (base). Alfa and dissociation degree. Acid-base properties of a salt solution. Buffered solution.
Solubility equilibrium: Precipitation reaction. Common ion effect.

Three models exist for acids and bases, in the Arrhenius model, Acids produce H^+ while Bases produce OH^- . In the Bronsted Lowry model, acids are proton donors, and bases are proton acceptors. In this model, Strong acids completely dissociate into separate H^+ and anions, while weak acids dissociate only slightly. Lastly the Lewis model says that an acid is an electron pair acceptor, while a base is an electron pair donor.

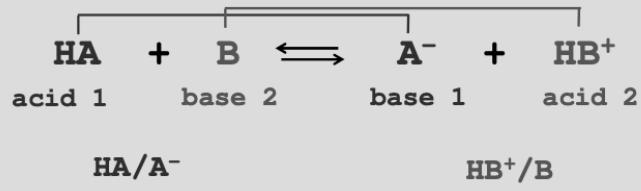
A substance can donate a proton if the X-H or the X-O-H bond is polar. This means that any species containing a H is a possible acid, however, this depends heavily on the strength of the bond, and the polarity of the bond. If a bond is strong and non-polar, the H will not dissociate, and thus the species is not an acid. Similarly, if a bond is polar, but strong, the H will be less likely to disassociate and be a weak acid, as seen in the table. Strong acids have relatively weak bonds that are also polar.

| H-X Bond | Bond Strength (kJ/mol) | Acid Strength in Water |
|----------|------------------------|------------------------|
| H-F | 565 | Weak |
| H-Cl | 427 | Strong |
| H-Br | 363 | Strong |
| H-I | 295 | Strong |

| Δ | Examples |
|----------|---|
| 0 | $\text{HClO} > \text{HBrO} > \text{HIO}$ |
| 1 | $\text{H}_2\text{SO}_3 > \text{H}_2\text{SeO}_3 > \text{H}_2\text{TeO}_3$ |
| 2 | $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4$ |
| 3 | $\text{HClO}_4 > \text{HMnO}_4 > \text{HIO}_4$ |

Most acids are oxoacids, where an acids proton is attached to an oxygen atom. We can relatively calculate the strength of an oxyacid by $\Delta = \#O's - \#H's$ for the generic formula X-O-H. The higher the Δ the higher the electronegativity and thus the stronger the acid. Other acids are formed when the H is attached to something other than O, and we mainly talked about the Hydroxides. Hydroxides are formed when the H is attached to a metal and have a lower electronegativity than oxoacids.

In acid base equilibrium we introduce the definitions of the conjugate acid and the conjugate base. The conjugate acids are formed when the proton is transferred to the base, and the conjugate base is everything remaining of the acid after the proton is lost.



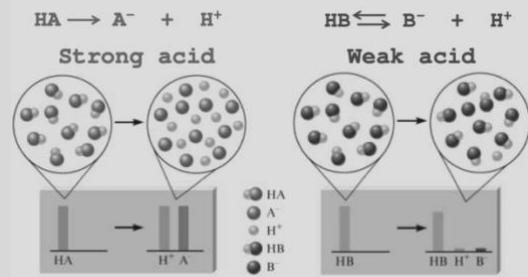
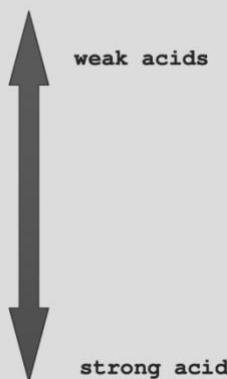
The two bases are competing for the free electron and thus the relative electronegativity of the bases will determine if the reaction lies to the left or the right. This can be calculated by finding the acid disassociation constant K_a . For the reaction:

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-, K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Since the liquid water does change its volume in the reaction, we can rewrite the simple disassociation reaction as $\text{HA} \rightleftharpoons \text{H}^+ \text{A}^-$. Although water is playing the role of the base.

The strength of an acid is predicted by the position of its disassociation constant K_a . When K_a lies far to the right, the acid is strong, and when K_a lies far to the left, the acid is weak.

| acid/base | K_a |
|--|----------------------|
| $\text{HS}^-/\text{S}^{2-}$ | $1.5 \cdot 10^{-13}$ |
| $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ | $1.0 \cdot 10^{-12}$ |
| $\text{HCO}_3^-/\text{CO}_3^{2-}$ | $5.0 \cdot 10^{-11}$ |
| HCN/CN^- | $4.8 \cdot 10^{-10}$ |
| $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ | $6.2 \cdot 10^{-8}$ |
| $\text{H}_2\text{S}/\text{HS}^-$ | $1.0 \cdot 10^{-7}$ |
| $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ | $4.2 \cdot 10^{-7}$ |
| $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ | $1.8 \cdot 10^{-5}$ |
| $\text{HNO}_2/\text{NO}_2^-$ | $5.0 \cdot 10^{-4}$ |
| $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$ | $8.0 \cdot 10^{-3}$ |
| $\text{HSO}_4^-/\text{SO}_4^{2-}$ | $1.3 \cdot 10^{-2}$ |
| $\text{H}_2\text{SO}_3/\text{HSO}_3^-$ | $1.8 \cdot 10^{-2}$ |
| $\text{HNO}_3/\text{NO}_3^-$ | ~ 20 |
| $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ | ~ 100 |



Remember that water is an amphoteric substance because it can be an acid or base, seen in the autoionization of water, where one proton is transferred from one water molecule to the other making $2\text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$. The equilibrium expression for this reaction can be written $K_w = \text{H}_3\text{O}^+ + \text{OH}^- = [\text{H}^+] + [\text{OH}^-]$

where K_w is called the ion-product constant. It is known that $[\text{H}^+] + [\text{OH}^-]$ must equal 1.0×10^{-14} in any aqueous solution. Therefore there are three possibilities.

1. The solution is neutral and $[\text{H}^+] = [\text{OH}^-]$
2. The solution is acidic and $[\text{H}^+] > [\text{OH}^-]$
3. The solution is basic and $[\text{H}^+] < [\text{OH}^-]$

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = (1.0 \cdot 10^{-14})^{0.5} = 1.0 \cdot 10^{-7}\text{ mol/l}$$

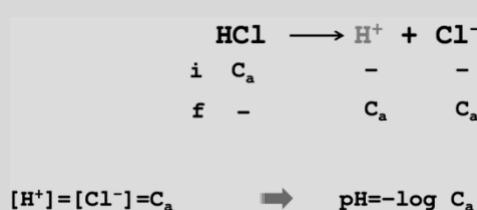
$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}\text{ M} \quad \text{neutral solution}$$

$$[\text{H}_3\text{O}^+] > 10^{-7}\text{ M} \quad \text{acidic solution}$$

$$[\text{H}_3\text{O}^+] < 10^{-7}\text{ M} \quad \text{basic solution}$$

This relationship is nicely summarized by the pH scale.

$\text{pH} = \log[\text{H}^+]$ and $\text{pOH} = \log[\text{OH}^-]$ and $\text{pH} + \text{pOH} = 14$. If $\text{pH} = 7$, the solution is neutral. If $\text{pH} < 7$, the solution is acidic. If $\text{pH} > 7$, the solution is basic.



To calculate pH for strong acids, the pH is equal to the molarity of $-\log[\text{H}^+]$

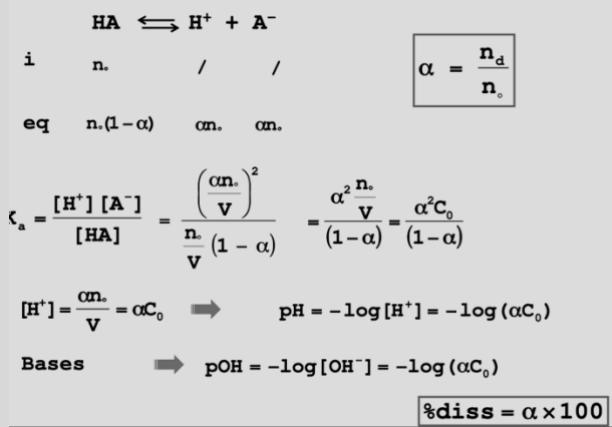
Reciprocal dilution occurs when two acids solutions are mixed, then we have to calculate the M of each acid/base individually and sum the pH's.

The same logic applies to strong bases who disassociate completely, but the measurement pOH is used, and is equal to $14 - \text{pH}$.

Solubility equilibrium: Precipitation reaction. Common ion effect.

Calculating the pH of weak acids/bases is a little more difficult. Here we use the table that shows the concentration of reactants and products, like so. i is for the initial quantity, and can be molarity, or amount. The equation is then given in terms of x, and we must calculate the x, usually given K_a . Since x is equal to the amount of H^+ given, we can easily calculate the Ph from the H^+ using negative log.

There exists a simplified formula which can be used when K_a and C_a are less than 10^{-3} , in which H^+ can be easily calculated by $\sqrt{K_a C_a}$. The same is true for weak base reactions, and us a rule in this class, we will never be expected to know the K_a for a acid/base.



| | | | |
|----|-----------|---|---|
| i | C_a | / | / |
| eq | $C_a - x$ | x | x |

$$K_a = \frac{[H^+] [A^-]}{[HA]} = \frac{[H^+]^2}{C_a - [H^+]} \quad [H^+] = [A^-] = x$$

a and percent disassociation are both used in this section too, and can be calculated with the following equation. Strong acids are always 100% disassociated, and weak are always less.

Polyprotic acids are acids with multiple H such as H_3PO_4 , in which we must calculate K_{a1} , K_{a2} , and K_{a3} for each H that dissociates. These numbers are summed to find the final Ph, but $K_{a1} \gg K_{a2} > K_{a3}$, so in most cases simply calculating the first disassociation is enough.

Salts are formed by a cation and an anion, or a base and an acid. Therefore, salts are strong electrolytes. To solve acid base problems involving salts, always rewrite the disassociation reaction, then find the acid/base that contain those disassociated ions. We then look at how these species react with water, and if the formed solution is neutral, the pH does not change. If however one of more of the anions react with water, then the salt will affect the pH.



A buffer solution is one that resists a change in pH, and are required when a reaction needs constant pH. Buffer solutions contain a weak acid and its salt, or a weak base and its salt. The idea for buffer solutions is that if a base is added, it is consumed in a reaction with the salt, and if an acid is added, it is consumed in a reaction with the base. Plasma is an extremely important physiological buffer. The pH of a buffer solution can be calculated with the Henderson-Hasselbalch equation, which is

$$pH = pK_a + \log(C_s/C_a)$$



| | | | | |
|----------|-----------|-----------|----|-------------|
| i | C_a | C_s | / | |
| Δ | -x | +x | +x | |
| eq | $C_a - x$ | $C_s + x$ | x | $x = [H^+]$ |

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-] [\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(C_s + x)x}{C_a - x} \approx \frac{C_s x}{C_a} \quad \text{if } K_a < 10^{-3}$$

The common ion effect can occur when an ion that is already contained in a solutions, generally decreasing the solubility of the solution. Solubility equilibrium is the dynamic state of equilibrium achieved through dissolving something, similar to a reaction, it does not reach a concentration and stop, but rather is a dynamic state where the production and destruction rates are equal.

Precipitation reactions refer to the formation of an insoluble salt when two solutions containing soluble salts are combined. The insoluble salt that falls out of solution is known as the precipitate, hence the reaction's name. Precipitation reactions can help determine the presence of various ions in solution.

Chapter 14: Chemical Kinetics

Basic concepts of chemical kinetics: . Collision theory. Definition of transition state. Arrhenius equation. Catalysis. Numerical exercises

Reaction rate is the change in concentration over time, and decreases as time increases, because as the concentration decreases, the free energy decreases. For a generic equation $aA + bB = cC$, the rate = $k(A)^m (B)^n$ where m and n are floating point numbers that are found through experimentation, and cannot be determined by the balanced equation, and k is the rate constant.

Rate laws come as differentiable rate laws(simple rate laws) which shows how the reaction rate depends on concentration and integrated rate laws, which shows the concentration of the species in terms of time. Since rate laws are not concerned with species not reacting, or reforming, we don't consider the equilibrium point or its affect on concentration.

Comparing trials 1 and 3, [F] is doubled, while [E] and the rate constant are held constant. This comparison will allow us to determine the order of reactant F:

$$\frac{\text{initial rate } 3}{\text{initial rate } 1} = \left(\frac{[F]_3}{[F]_1} \right)^z$$
$$\frac{2.71 \times 10^{-5} \text{ Ms}^{-1}}{2.73 \times 10^{-5} \text{ Ms}^{-1}} = \left(\frac{0.200 \text{ M}}{0.100 \text{ M}} \right)^z$$

$$0.993 = 2.00^z$$

$$z = 0$$

Therefore, the reaction is zero order with respect to [F].

The rate law can now be written as:

$$\text{Rate} = k[E]^1$$

| Trial | Initial Rate (mole L ⁻¹ s ⁻¹) | [E] (mole L ⁻¹) | [F] (mole L ⁻¹) |
|-------|---|-----------------------------|-----------------------------|
| 1 | 2.73×10^{-5} | 0.100 | 0.100 |
| 2 | 5.47×10^{-5} | 0.200 | 0.100 |
| 3 | 2.71×10^{-5} | 0.100 | 0.200 |

Solution

1. Comparing trials 1 and 2, [E] is doubled, while [F] and the rate constant are held constant. This comparison will allow us to determine the order of reactant E:

$$\frac{\text{initial rate } 2}{\text{initial rate } 1} = \left(\frac{[E]_2}{[E]_1} \right)^y$$
$$\frac{5.47 \times 10^{-5} \text{ Ms}^{-1}}{2.73 \times 10^{-5} \text{ Ms}^{-1}} = \left(\frac{0.200 \text{ M}}{0.100 \text{ M}} \right)^y$$

$$2.00 = 2.00^y$$

$$y = 1$$

Therefore, the reaction is first order with respect to [E].

2. Using the rate law we have just determined, substitute in the initial concentration values and initial rate for any trial and solve for the rate constant:

$$\text{Rate} = k[E]^1$$

Using Trial 1: $2.73 \times 10^{-5} \text{ M s}^{-1} = k(0.100 \text{ M})$

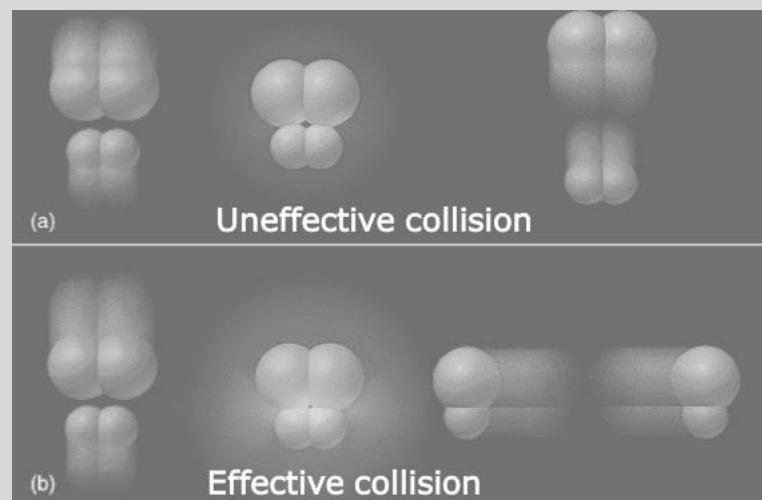
$$k = \frac{2.73 \times 10^{-5} \text{ Ms}^{-1}}{(0.100 \text{ M})}$$
$$k = 2.73 \times 10^{-4} \text{ s}^{-1}$$

Reaction order is the sum of the concentration term exponents (m and n) so for rate = $k[\text{NO}_2]^2$, the reaction order is 2. The rate law can be determined experimentally, so given the data about concentration in different points, during the test these will likely be summarized in a table. To determine the order of reaction of the species, simply find two trials in which the species changed AND all the other species remained constant, and compare the two initial rates.

Then do this same process for all the species given. The sum of these values is the order of the reaction.

First order rate laws are given per second, where second order are given liters per second x moles

Collision theory tells us that reactions occur when reactants collide, and the collision must overcome the energy and steric requirement to be effective. This energy must be equal to the activation energy, E_a . Effective collisions result in a chemical change, which ineffective collisions do not overcome this energy barrier. Whether this is effective or not, is much determined by the orientation of the molecules, also called the steric requirement.



The Arrhenius equation tells us the relationship between collision theory, activation energy, and temperature on rate. For most questions in this test, it will be theory im guessing, so know that if activation increases, rate decreases, as temperature increases, rate increases and as Ae increases, rate increases.

$$k = A e^{-E_a / RT}$$

A catalyst 1) doesn't change during the reaction 2) is not present in the total reaction equation, therefore is canceled on both sides 3) Does not change the reaction thermodynamics. Biological catalysts speed up chemically favorable reactions in the body so they can happen in seconds vs years. Catalysis can happen in many steps, or one.

Formula Sheet

General

$$\text{Density: } \frac{\text{mass}}{\text{volume}}$$

$$\text{Moles: } \frac{\text{given mass (g)}}{\text{gram formula mass}}$$

$$\text{Percent Error: } \frac{\text{measured} - \text{accepted}}{\text{accepted}} \times 100\%$$

$$\text{Percent Composition (by mass): } \frac{\text{mass of part}}{\text{mass of whole}} \times 100\%$$

$$\text{Molarity: } \frac{\text{moles of solute}}{\text{volume of solution}}$$

$$\text{Molality: } \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

Thermochemistry

Heat Transfer: $q = mc\Delta T$

Enthalpy: $\Delta H = H_{products} - H_{reactants}$

Entropy: $\Delta S = S_{products} - S_{reactants}$

Free Energy: $\Delta G = \Delta H - T\Delta S$

| Symbol | Meaning |
|--------|-------------------------|
| q | heat energy |
| m | mass |
| c | specific heat |
| T | temperature (in Kelvin) |
| S | entropy |
| H | enthalpy |
| G | Gibbs free energy |

$$i = 1 + a(v - 1)$$

Solutions, Liquids, Gases

Rauolt's Law:

$$P_{solution} = P_1\chi_1 + P_2\chi_2 + \dots$$

Boiling Point Elevation:

$$\Delta T_{solution} = K_b \cdot m_{solute}$$

Freezing Point Depression:

$$\Delta T_{solution} = K_f \cdot m_{solute}$$

Ideal Gas Law: $PV = nRT$

Combined Gas Law: $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$

Titration: $M_A V_A = M_B V_B$

Dilution: $M_1 V_1 = M_2 V_2$

| Symbol | Meaning |
|--------|-------------------------------|
| P | pressure |
| V | volume |
| n | number of moles |
| T | temperature (in Kelvin) |
| K_f | molal freezing point constant |
| K_b | molal boiling point constant |
| χ | mole fraction |
| m | molality |
| M | molarity |
| c | specific heat capacity |
| M_w | mass of water (Kg) |
| E_h | heat energy released |

Past Tests (some are midterms some are finals)

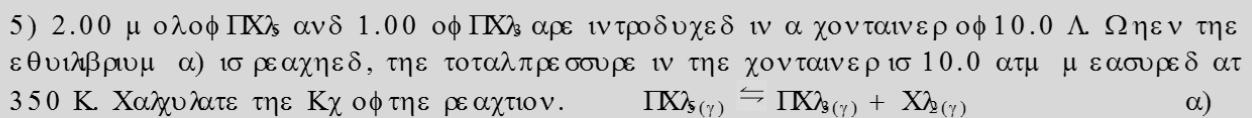
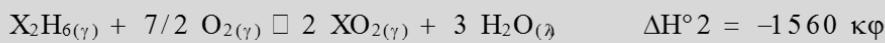
- 1) Which of the following is the electronic configuration of potassium in its ground state and why?
- $1s^2, 2s^2 p^6, 3s^2 p^6 d^1$
 - $1s^2, 2s^2 p^2, 3s^2 p^2 d^0$
 - $1s^2, 2s^2 p^6, 3s^2 p^3 d^4$
 - $1s^2, 2s^2 p^6, 3s^2 p^6, 4s^1$
- 2) a) Define the electron affinity of an element.
 b) Define the first ionization energy of an element.
 c) Consider atoms with the following electron configurations:
 $1s^2, 2s^2 p^6$ and $1s^2, 2s^2 p^6 3s^1$
 Which atom has the largest first ionization energy? Explain your choice.
- 3) A non electrolyte compound X contains C, H, and N in the following percentage by mass: C, 75.95 %, H, 6.33 %, and N, 17.72 %. When 1.18 g of X are dissolved in 23.2 g of water, the resulting solution boils at 100.33°C at atmospheric pressure (kb of water: $0.512^\circ\text{C m}^{-1}$). Calculate both the empirical and the molecular formulas of X.
- 4) Calculate the pH of the following water solutions:
- 0.25 M of HCN ($K_a \text{ HCN} = 7.2 \cdot 10^{-10}$),
 - a solution obtained by mixing 200 mL of a HCN 0.25 M with 250 mL of KOH 0.20 M,
 - a solution obtained by mixing 800 mL of a HCN 0.50 M with 1.0 L of KOH 0.20 M.
- 5) Calculate the molarity and mole fraction of acetone in a 1.00 m solution of acetone (CH_3COCH_3) in ethanol ($\text{C}_2\text{H}_5\text{OH}$). (Density of acetone = 0.788 g/cm³; density of ethanol = 0.789 g/cm³).

1. The correct answer is (d)
2. a) The electron affinity is the energy change associated with the addition of an electron to an atom in the gas phase. b) The first ionization energy is the energy required to remove the highest energy electron from an atom in the gas phase. Indeed, it is a noble gas (Neon) with the largest first ionization energy is the one having the 1s₂, 2s₂ 2p₆ configuration. Indeed, it is a noble gas (Neon) with the second valence shell fulfilled.
3. $\text{C}_5\text{H}_5\text{N} = \text{MW} = 79$ amu and $\text{C}_5\text{H}_5\text{N} = \text{molecular formula}$
4. $\text{A}(\text{pH}) = -\log(1.34 \cdot 10^{-5}) = 4.87$ B) $\text{K} < 10^{-3}$, $\text{C} > 10^{-3}$ C) BUFFERED SOLUTION
5. Molarity = $n/\text{L} = 1/(1.341) = 0.746 \text{ mol/L}$ Mol fraction = $1/22.74 = 4.4 \cdot 10^{-2}$

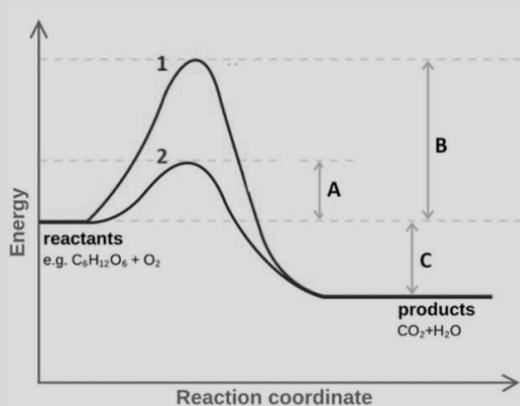
- 1) Να τυραλβρούμε ινες ηασ 2 ισοτοπεσ: $^{79}\text{Br} = 78.92$ αμ ν ανδ $^{81}\text{Br} = 80.92$ αμ ν, ανδ ιτσ ατομικης ητις 79.904 αμ ν. Χαλχυλατε τηε ισοτοπικη χομ ποσιτιον οφ νατυραλβρομ ινε.
- 2) Ινδιχατε, φορεαχη οφ τηε φολλωτινγ παιρσ, τηε χομ πουνδ ηατινγ τηε ηιγηε στ βοιηνγ ποιντ: α) HΦ ορ XH₂; β) XH₄ ορ XH₃XH₃; γ) H₂O ορ XH₃OH. Εξπλαιν ψουρ ανσωερσ ανδ ινδιχατε αλσο τηε πρεδομ ιναντ ιντερμ ολεχυλαρφορχε πρεσεντ ιν εαχη χομ πουνδ.
- 3) Α νον ελεχτρολυτε χομ πουνδ Ξ χονταινσ εξχλυσιαλψ Χ, H, ανδ Σ, ιν τηε φολλωτινγ περγενταγε βψ μ αστ: X, 57.1 %, H, 4.8 % ανδ Σ 38.1 %. Φορηε μ ορε, ωηεν 0.25 g οφ Ξ αρε δισσολαεδ ιν 100.0 μ Λ οφ ωατερ, α σολντιον ηατινγ αν οσμ οτιχ πρεσσυρε οφ 0.728 ατμ ατ 25 °C ισ οβταινεδ. Δετερμ ινε τηε εμ πιριχαλανδ τηε μ ολεχυλαρφορμ υλα οφ Ξ.



γ ιαεν τηε φολλωτινγ τηερμ οχηεμ ιχαλδατα:



6)



α-Ωηατ δοεσ τηε αρρω λαβεζεδ A βεπρεσεντ?

β-Ωηιχη Πλοτ (1 ορ 2) βεπρεσεντσ τηε ενζψμ ε χαταλψεδ βεαχτιον?

χ-Ωηιχη λαβεζεδ αρρω (A, B ορ X) βεπρεσεντσ τηε οτεραλλ χηανγε ιν φρεε ε νεργψ οφ τηε βεαχτιον?

δ-Ισ τηισ αν εξαμ πλε οφ εξοτηερμ ιν δο ιτιμβριαζε βεαχτιον?

d- it is an exothermic reaction

b- plot 2. The reaction has a lower activation energy than plot 1-C-C

a- The activation energy of the reaction 2.

$$6) \quad K_C = 0.047$$

$$5) \quad K_C = 0.47$$

$$4) \quad DH^\circ X = -1411 + 1560 - 285.8 = -136.8 \text{ kJ}$$

3) $\text{CH}_4\text{S} = \text{molecular formula}$

CH₄ and CH₃H₃: dispersion forces (D) c) H₂O > CH₃O and CH₃OH: hydrogen bond

2) a) HF > HCl HF: hydrogen bond HCl: dipole-dipole b) CH₄ < CH₃CH₃

$$1) \quad 50.8 \% = 79\text{Br}$$

$$49.2 \% = 81\text{Br}$$

1)

Natural chlorine has 2 isotopes:

$^{35}\text{Cl} = 34.9689$ amu and $^{37}\text{Cl} = 36.9659$ amu

The atomic weight of natural chlorine is 35.4527 amu. Calculate the isotopic composition of natural chlorine.

2)

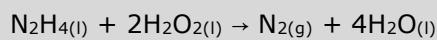
Write: a) the Lewis structure, b) the electronic geometry, c) and the molecular geometry of carbon dioxide. Indicate the hybridization of the central atom. (Apply the Lewis+VSEPR method and explicit each step).

3)

The analysis of an organic compound X, containing exclusively C, H, and N, gave the following results as weight percents: C, 54.54%, and H, 13.64%. Furthermore 52.8 g of X contains $3.6 \cdot 10^{23}$ molecules. Determine the molecular formula of X.

4)

Determine ΔH° for the following reaction:



Given that:



5)

A solution is prepared by mixing 50.0 mL toluene ($\text{C}_6\text{H}_5\text{CH}_3$, d = 0.867 g/cm³) with 125 mL benzene (C_6H_6 , d = 0.874 g/cm³). Calculate the mass percent, mole fraction, molality, and molarity of the toluene.

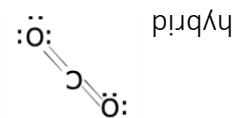
$$\text{Molality} = 4.30 \text{ mol/kg} \quad \text{Molarity} = 2.68 \text{ mol/L}$$

$$\text{Mol fraction} = 0.25$$

$$5) \text{ % by weight} = 28.4 \%$$

$$4) \Delta H^\circ X = -622.2 + 375.6 - 571.6 = -818.2 \text{ kJ}$$

$$3) \text{ C}_2\text{H}_6\text{N} = \text{MW} = 44 \text{ amu}, \text{C}_4\text{H}_{12}\text{N}_2 = \text{molecular formula}$$



2) AX_2 system. Electronic geometry: linear, Molecular geometry: linear, Carbon atom is sp

$$24.2263\% = 37\text{Cl}$$

$$1) 75.7737\% = 35\text{Cl}$$

- 1) Write the electronic configuration of the following elements: $^{79}_{35}Br$ and $^{35}_{17}Cl$. How many neutrons do they have? In what group are they located? Pick the atom with: a. larger size. b. higher ionization energy, c. more favorable (exothermic) electron affinity. Explain your answers.
- 2) Write for PCl_3 : a) the Lewis structure (and the resonance structures, if they are present), b) the electronic geometry, c) the molecular geometry (with the relevant bond angles) d) the hybridization of the central atom. e) Determine if the molecule has a dipole momentum. (*Apply the Lewis+VSEPR method and explicit each step*).
- 3) Balance the following reaction by using the half reaction method:



According to the balanced equation, calculate the volume in liters of NO , measured at 25 °C and 0.300 atm, and the number of molecules of $CuSO_4$ formed when 3.82 g of CuS react with 5.04 g of HNO_3 . Finally write the chemical names of all the reactants and products. (AW in amu: Cu=63.5; S=32.0; H=1.0; N=14.0; O=16.0)

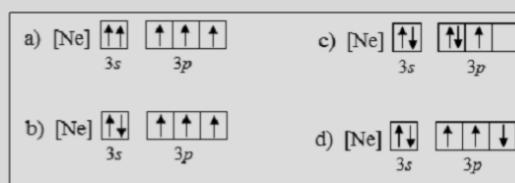
- 4) 8.00 g of a mixture containing $CuSO_4 \cdot 5H_2O$ and KCl are heated with the following complete loss of water molecules. Given that the mass of the sample decreased by 14.4 % after heating, calculate the percentage composition of the mixture and the mass of sulphur atoms. (AW in amu=Cu=63.5; S=32.0; K=39.1; Cl=35.4; H=1.0; O=16)
- 5) For each of the following pairs, indicate the species with the higher boiling point and then explain your answer: a) CH_3OH or CH_3SH ; b) HF or HCl ; c) CH_4 or CH_3CH_3 ; d) $NaCl$ or Cl_2 . Indicate for each compound the most important interparticle forces.

2) Ax_3E tetrahedral Molecular geometry: pyramidal, bond angle less than the predicted 109°. P is sp³d hybrid the molecule has a dipole momentum

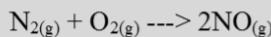
1) ^{35}Br : 1s₂, 2s₂, 2p₆, 3s₂, 3p₆, 3d₁₀, 4s₂, 4p₅ ^{17}Cl : 1s₂, 2s₂, 2p₆, 3s₂, 3p₅ Br=44; Cl=18, 7^o group.
The atomic radius of Br is larger IE of Cl is larger. Then the EA of Cl is larger.
 Br_3 tetrahedral Molecular geometry: pyramidal, bond angle less than the predicted 109°. P is sp³d hybrid the molecule has a dipole momentum

3) $3CuS + 8HNO_3 \rightarrow 3CuSO_4 + 8NO + 4H_2O$, 6.53L
 $CuSO_4 \cdot 5H_2O = 40.0\%$, $KCl = 60.0\%$, g of S = 0.410 g
4) CH_3OH has higher bp CH_3OH Hydrogen bond. CH_3SH . Dipole dipole. HF has higher bp HF Hydrogen bond. HCl Dipole dipole. CH_3CH_3 has higher bp CH_4 Dispersion forces. CH_3CH_3 Dispersion forces. Since CH_3CH_3 has higher MW it is more polarizable and then the dispersion forces are stronger. d) NaCl has higher bp NaCl ionic bond. Cl²⁻ Dispersion forces.

- 1) Which of the following orbital diagrams of phosphorous in its ground state is correct? Explain why the other possibilities are wrong.



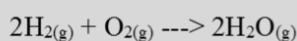
- 2) Given the following thermochemical data:



$$\Delta H_1 = -180.5 \text{ kJ}$$

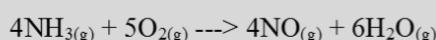


$$\Delta H_2 = -91.8 \text{ kJ}$$



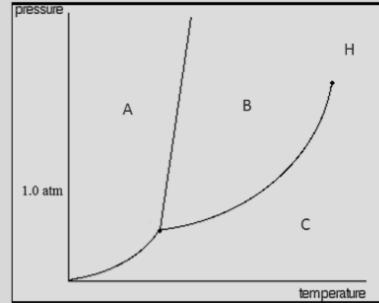
$$\Delta H_3 = -483.6 \text{ kJ}$$

Calculate the enthalpy change for the reaction below:



- 3) Consider the phase diagram of a substance W given beside.

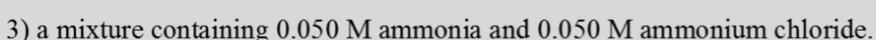
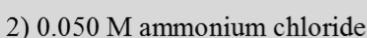
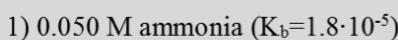
- a) What phases are present at points A, B, C, and H? Graphically indicate: b) the triple point, c) the critical point, and d) the boiling point of the substance W at 1.0 atm.



- 4) In a 3 L container the number of moles of PCl_5 , PCl_3 , and Cl_2 is 0.225, 0.18, and 0.18, respectively. a) Calculate the K_c of the equilibrium. b) If PCl_3 is added, the number of moles of PCl_5 will decrease or increase at the new equilibrium? c) Calculate how many moles of PCl_5 will be present at the new equilibrium, after the addition of 1.88 moles of PCl_3 .



- 5) Calculate the pH of each of the following solutions.



5) $\text{pH} = 10.98$ B) $\text{pH} = 5.28$ C) $\text{pH} = 9.26$

increase at the new equilibrium, $C(\text{PCl}_5) = 0.375$

4) $K_c = 0.048$ B) On the ground of the Le Chatelier's principle the moles of PCl_5 will

3) A = solid, B = liquid, C = vapor, H = supercritical fluid.

2) $\Delta H^\circ X = -361 + 183.6 - 1450.8 = -1628.2 \text{ kJ}$

1) b) is the correct configuration.

1) Write: a) the Lewis structure, b) the electronic geometry, c) and the molecular geometry of bromine trifluoride (BrF_3). Indicate the hybridization of the central atom. (Apply the Lewis+VSEPR method and explicit each step).

2) Write the following substances in order of decreasing boiling point and explain the answer:

- a) H_2O , b) H_2S , c) H_2Se , d) H_2Te

3) Balance the following reaction by using the half reactions method:

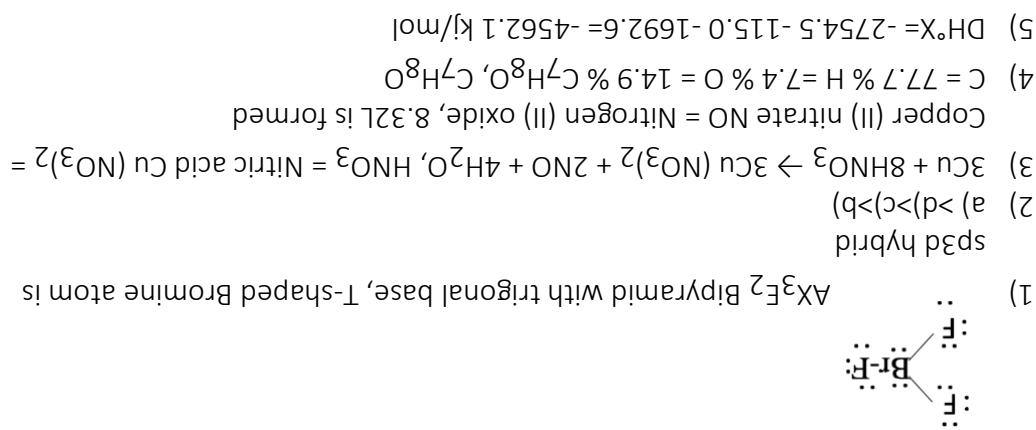


a) Write the chemical names of HNO_3 , $\text{Cu}(\text{NO}_3)_2$, and $\text{NO}_{(g)}$.

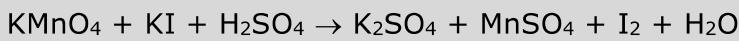
b) A sample of 44.20 g of Cu is added to 136 mL of HNO_3 6.0 M. Calculate the NO volume, measured at 25°C and 0.60 atm, formed in this reaction.

4) The complete combustion of 0.4039 g of a compound X containing C, H, and O produces 1.1518 g of CO_2 and 0.2694 g of H_2O . Its molecular weight is 108.1 amu. Determine: a) its percentage composition by mass; b) its empirical formula, and c) its molecular formula.

5) The standard enthalpies of formation (ΔH°_f) of carbon dioxide and cycloheptane ($\text{C}_7\text{H}_{14(l)}$) are -393.5, 115.0, respectively, meanwhile the standard enthalpy of combustion of hydrogen is -241.8 kJ mol^{-1} . Use the previous thermochemical data to calculate the enthalpy of combustion of cycloheptane.



- 1) Write for each of the following isotopes the number of neutrons, protons, and electrons:
 $^{24}_{12}Mg^{2+}$, $^{47}_{24}Cr$, $^{60}_{27}Co^{3+}$, $^{35}_{17}Cl^-$, $^{124}_{50}Sn^{2+}$, $^{90}_{38}Sr$
- 2) Write for XeF_2 : a) the Lewis structure (and the resonance structures, if they are present), b) the electronic geometry, c) the molecular geometry (with the relevant bond angles) d) the hybridization of the central atom. e) Determine if the molecule has a dipole momentum. (*Apply the Lewis+VSEPR method and explicit each step*).
- 3) Balance the following reaction by using the half reaction method:



According to the balanced equation, calculate the grams and the number of molecules of I_2 formed when 9.13 g of KI react with 3.95 g of $KMnO_4$ (H_2SO_4 is in excess).

- 4) Determine the standard enthalpy of formation of pentane ($C_5H_{12(l)}$) given the following thermochemical data:
- ΔH° of combustion of $C_5H_{12(l)}$ = -3505.8 kJ/mol
- ΔH° of formation of $CO_{2(g)}$ = -393.5 kJ/mol
- ΔH° of formation of $H_{2O(g)}$ = -241.7 kJ/mol
- 5) For each of the following pairs, indicate the species with the higher boiling point and then explain your answer: a) CH_3OH or CH_3SH ; b) CH_3OCH_3 or CH_3CH_2OH ; c) CH_4 or CH_3CH_3 ; d) Br_2 or I_2 .

1) $^{24}_{12}Mg^{2+}$: 12 neutrons, 12 protons, 10 electrons. $^{47}_{24}Cr$: 23 neutrons, 24 protons, 24 electrons. $^{60}_{30}Co^{3+}$: 33 neutrons, 27 protons, 24 electrons. $^{35}_{17}Cl^-$: 18 neutrons, 17 protons, 18 electrons. $^{124}_{50}Sn^{2+}$: 74 neutrons, 50 protons, 48 electrons. $^{90}_{36}Sr$: 52 neutrons, 38 protons, 38 electrons.

2) AX₂E₃ bipyramidal with trigonal base, linear, bond angle 180°, Xe is sp³d hybrid, the molecule has not a dipole momentum

3) $2KMnO_4 + 10KI + 8H_2SO_4 \rightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$, 6.98 g, Molecules = 1.65 · 10²²

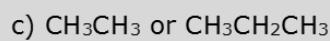
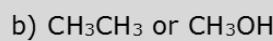
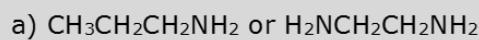
4) $\Delta H^\circ_X = +3505.8 - 1967.5 - 1450.2 = 88.1 \text{ kJ/mol}$

5) CH_3OH has higher bp H_3OH hydrogen bond. CH_3SH , Dipole dipole. b) CH_3CH_2OH has higher bp CH_3OCH_3 Dipole dipole. CH_3CH_2OH hydrogen bond c) CH_3CH_3 has higher MW it is more polarizable and then the dispersion forces are stronger.

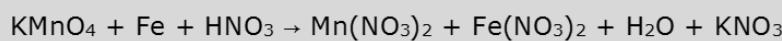
6) I_2 has higher bp Br_2 Dispersion forces. I_2 Dispersion forces. Since I_2 has higher MW it is more polarizable and then the dispersion forces are stronger.

1) Write: a) the Lewis structure, b) the electronic geometry, c) and the molecular geometry of sulphur dioxide. Indicate the hybridization of the central atom. (*Apply the Lewis+VSEPR method and explicit each step*).

2) Predict which substance in each of the following pairs would have the stronger intermolecular forces, and explain :



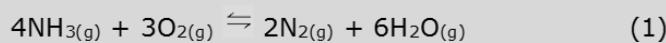
3) Balance the following reaction by using the half reactions method:



a) Write the chemical names of all the reactants and products.

b) Calculate the number of grams of $\text{Fe}(\text{NO}_3)_2$ that is formed when 500 mL of HNO_3 0.5 M are mixed with 100 mL of KMnO_4 0.25 M, in excess of solid Fe.

4) What will happen to a reaction mixture at equilibrium (1) if



in each of the following cases (explain your answers)? In which cases the equilibrium constant will change?

a) $\text{H}_2\text{O(g)}$ is removed.

b) The temperature is decreased (the reaction is exothermic).

c) $\text{N}_2\text{(g)}$ is added.

d) The volume of the container is compressed.

e) A catalyst is added

5) Calculate the pH and the percent dissociation in a 0.35 M solution of each of the following acids, and write the relevant dissociation reactions.

a) Hydrochloric acid (HCl)(Strong acid)

b) Acetic acid ($\text{CH}_3\text{CO}_2\text{H}$)($K_a = 1.8 \cdot 10^{-5}$)

c) Hypochlorous acid (HOCl)($K_a = 2.9 \cdot 10^{-8}$)

5) A) 0.456, and 100%, B) 2.60 and .71%, C) 4.00 and 0.28%

change.

the left. The equilibrium constant does not change. The reaction rate increases. The equilibrium constant does not shift to the left. D) The equilibrium constant does not change. E) $\Delta n > 0$. The equilibrium constant shifts to the right. The equilibrium constant increases. F) The equilibrium constant increases.

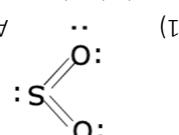
= 11.24

3) $2\text{KMnO}_4 + 5\text{Fe} + 16\text{HNO}_3 \rightarrow 2\text{Mn}(\text{NO}_3)_2 + 5\text{Fe}(\text{NO}_3)_2 + 8\text{H}_2\text{O} + 2\text{KNO}_3$, formed $\text{Fe}(\text{NO}_3)_2 = n \cdot \text{MW} = 0.0625 \cdot 179.9$ bonds

hydrogen bonding interactions are effective because of the electronegativity difference. In HBr there are not hydrogen dispersion forces are significant, and then the polarizability of the molecules is the predominant parameter. Since the polarizability depends on the MW of the compound, the dispersion forces decrease with the MW. d) HBr: the dispersion forces are significant, and then the polarizability of the molecules is the predominant parameter. Since CH₃OH: the hydroxyl group can form hydrogen bonds, not accessible to CH₃CH₃ c) CH₃CH₂CH₃: in hydrocarbons the

2) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$: the presence of one $-\text{NH}_2$ group more allows the formation of additional hydrogen bonds b)

1) AX_2E system B) Electronic geometry: trigonal planar c) Molecular geometry: bent, Sulphur atom is sp² hybrid



- 1) In a 3 L container the number of moles of PCl_5 , PCl_3 , and Cl_2 is 0.225, 0.18, and 0.18, respectively. a) Calculate the K_c of the equilibrium. b) If PCl_3 is added, the number of moles of PCl_5 will decrease or increase at the new equilibrium? c) Calculate how many moles of PCl_5 will be present at the new equilibrium, after the addition of 1.88 moles of PCl_3 .



- 2) Calculate the pH of each of the following solutions.

1) 0.050 M ammonia ($K_b = 1.8 \cdot 10^{-5}$)

2) 0.050 M ammonium chloride

3) a mixture containing 0.050 M ammonia and 0.050 M ammonium chloride.

- 3) A water solution of sodium chloride freezes at -0.0275°C at atmospheric pressure. Calculate the molality of this solution ($k_f \text{ H}_2\text{O} = 1.86^\circ\text{C} \cdot \text{kg/mol}$).

- 4) In a liquid solution containing benzene and toluene, the mole percentage of benzene is 32.8%. Calculate the mole fraction of benzene in the vapor phase in equilibrium with the solution at 25°C . (25°C : vapor pressure of pure benzene = 95.1 torr; vapor pressure of pure toluene = 28.4 torr).

- 1) 0.048, On the ground of the Le Chatelier's principle the moles of PCl_5 will increase at the new equilibrium, $\text{PCl}_5 = 0.225 + 0.15 = 0.375$
- 2) $\text{pH} = 10.98$, B) $\text{pH} = 5.28$ C) $\text{pH} = 9.26$
- 3) $m = 7.39 \cdot 10$
- 4) $p = 95.1 \cdot 0.328 + (28.4 \cdot 0.672) = 50.3 \text{ torr}$ B) $x_{\text{ben}} = 95.1 \cdot 0.328 / 50.3 = 0.620$

- 1) Write the following elements in order of increasing atomic radius and explain the answer:
- a) C, b) N, c) F, d) O
- 2) Which of the following substances has the lower vapor pressure (explain the answer)?
- a) H₂O, b) H₂S
- 3) 1.000 mol of PCl₅ and 1.000 mol of Cl₂ are introduced in a container of 1.000 L. Given that K_c = 0.0220, calculate the concentration of all the species when the following equilibrium is reached.
- $$\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$$
- 4) Balance the following reaction by using the half reactions method:
- $$\text{H}_3\text{PO}_4 + \text{Zn} + \text{HCl} \rightarrow \text{PH}_3 + \text{ZnCl}_2 + \text{H}_2\text{O}$$
- a) Write the chemical names of H₃PO₄, HCl, and ZnCl₂
- b) Knowing that PH₃ is a gas, on the ground of the balanced equation, calculate the volume of PH₃ measured at 1.0 atm and 300.0 K, that is formed when 3.25 grams of Zn are added to 1.625 L of a HCl solution 0.040 M (H₃PO₄ is in excess).
- 5) The K_{sp} for AgCl is 1.8·10⁻¹⁰. Calculate the solubility of AgCl in each of the following cases:
- 1) water
 - 2) 0.10 M AgNO₃

1) F < O < N < C

2) H₂O has the lower vapor pressure

3) K_c = 0.0220, x₁ = 0.021, x₂ = -1.043

4) H₃PO₄ + 4Zn + 8HCl → 4ZnCl₂ + PH₃ + 4H₂O

a. H₃PO₄ = Phosphoric acid ZnCl₂ = Zinc(II) chloride HCl = Hydrochloric acid

b. V = 0.2 L

a. s = 1.8·10⁻⁹ mol/l

b. S = 1.3·10 mol/l

5) a. s = 1.8·10⁻⁹ mol/l

Maleic acid is an organic compound composed of 41.39% C, 3.47% H, and the rest oxygen. If 0.129 mole of maleic acid has a mass of 15.0 g, what are the empirical and molecular formulas of maleic acid?

How many moles of NO can be formed when 3.00 mol of NH₃ react with 4.00 mol of O₂?
$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$

Balance the following equation: NH₄Cl(s) + Ca(OH)₂(s) → NH₃(g) + CaCl₂(s) + H₂O(l)

How many grams of NH₃ can be formed when 33.00 g of NH₄Cl react with 33.00 g of Ca(OH)₂? How many grams of the exceeding reactant will remain? (AW (amu)=Ca=40.1; Cl=35.4; H=1.0; O=16; N=14.0)

CaCO₃ loses CO₂ after heating, then forming CaO. Calculate the mass of CaO resulting from the heating of 10.4 g of CaCO₃. (AW (amu)=Ca=40.1; C=12.0; O=16)

The MW of a compound having the X₂Y₃ molecular formula is 76.01 amu. Since the MW of another compound having the X₂Y₅ formula is 108.01 amu, calculate the AW of X and Y (X and Y are the atoms of two unknown elements).

1The heating of a hydroxide having the M(OH)₂ formula forms the relevant MO oxide, after losing H₂O that corresponds to the 18.13 % of the mass. Determine the AW of M.

13.71 g of a mixture containing CaCl₂·6H₂O and NaCl are heated with the following complete loss of water molecules. Given that the mass of the sample decreased by 32.6 % after heating, calculate the percentage composition of the mixture. (AW (amu)=Ca=40.1; Cl=35.4; H=1.0; O=16)

Example Solutions:

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 kJ/mol. Calculate the vapor pressure of water at 50°C.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{ev}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{P_2}{23.8} = \frac{43900}{8.31} \left(\frac{1}{(25+273)} - \frac{1}{(50+273)} \right) = 1.37$$

$$P_2 = 93.7 \text{ torr}$$

Ex. 7.10: Calculate the molarity of a solution obtained by mixing:

400 ml of 2.00 M HCl (36.5 amu)

+ 400 ml of 36.2% HCl by mass ($d=1.18 \text{ g/ml}$)

$$n_1 + n_2 = n_3 \quad (M \cdot V)_1 + (M \cdot V)_2 = (M \cdot V)_3 = M_3 (V_1 + V_2)$$

In 1 liter of the second solution

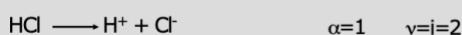
$$g_{\text{HCl}} = \frac{d \cdot V \cdot \%}{100}$$

$$n = \frac{g}{\text{MW}} = \frac{d \cdot V \cdot \%}{100 \cdot \text{MW}} = \frac{1.18 \cdot 1000 \cdot 36.2}{100 \cdot 36.5} = 11.7 \rightarrow 11.7 \text{ M}$$

$$M_3 = \frac{(M \cdot V)_1 + (M \cdot V)_2}{(V_1 + V_2)} = \frac{(2.00 \cdot 0.400) + (11.7 \cdot 0.400)}{(0.400 + 0.400)} = 6.85 \text{ mol/l}$$

Ex. 8.7:

Calculate the osmotic pressure at 25 °C of a solution arising from the mixing of the following: 1.0 L of 0.12 M HCl and 200 mL of 0.18 M HCl (HCl is a strong electrolyte).



$$(M \cdot V)_1 + (M \cdot V)_2 = (M \cdot V)_3$$

$$M_3 = \frac{(M \cdot V)_1 + (M \cdot V)_2}{V_3} = \frac{(M \cdot V)_1 + (M \cdot V)_2}{V_3} = \frac{(0.12 \cdot 1.0) + (0.2 \cdot 0.18)}{1.2} = 0.13 \text{ mol L}^{-1}$$

$$\pi = MRT_i = 0.13 \text{ mol L}^{-1} \cdot 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1} \cdot 298 \text{ K} \cdot 2 = 6.36 \text{ atm}$$

Ex 7.2: Calculate how many ml of solution 0.167 M of HCl (36.5 amu) contain 100 mg of solute.

100 mg of HCl:

$$n = g / \text{MW} = 0.100 / 36.5 = 2.74 \cdot 10^{-3} \text{ moles}$$

$$M = n / V$$

$$V = n / M = 2.74 \cdot 10^{-3} / 0.167 = 1.64 \cdot 10^{-2} \text{ L} = 16.4 \text{ ml}$$

Ex. 7.11: Calculate at 50 °C the composition of the vapor above the solution formed by

- 1) Benzene C_6H_6 (3 moles; $P^\circ = 270 \text{ mmHg}$ at 50°C)
2) CCl_4 (3 moles; $P^\circ = 310 \text{ mmHg}$ at 50°C)

Dalton's law

$$P_i = \chi_i P_{\text{soln}}$$

Raoult's law

$$P_{C_6H_6} = P^\circ_{C_6H_6} X_{C_6H_6}$$

$$P_{CCl_4} = P^\circ_{CCl_4} X_{CCl_4}$$

$$X_{C_6H_6} = X_{CCl_4} = 0.5$$

$$P_{\text{soln}} = P_{C_6H_6} + P_{CCl_4} = (270 \cdot 0.5) + (310 \cdot 0.5) = 290 \text{ mmHg}$$

$$P_i = \chi_i P_{\text{soln}}$$

$$\chi_{C_6H_6} = 135 / 290 = 0.466 \quad \chi_{CCl_4} = 155 / 290 = 0.534$$

A food contains 0.10 % by weight of C_6H_5COONa (B). How many mg of Na does a person eating 74.5 g of that food intake?

a) $g_B = 74.5 \cdot 0.10 / 100 = 0.0745 \text{ g}$

b) $MW = (12 \cdot 7) + (1 \cdot 5) + (2 \cdot 16) + (1 \cdot 23) = 144 \text{ amu}$

c) $n_B = 0.0745 / 144 = 5.17 \cdot 10^{-4} = n_{Na}$

d) $mg_{Na} = 5.17 \cdot 10^{-4} \cdot 23 \cdot 1000 = 11.89 \text{ mg}$

A mineral has the formula $LiAlSi_2O_6$. Since the abundance of 6Li is 7.40 %, how many 6Li atoms are present in a 518 g sample of that mineral?

a) $MW = (1 \cdot 6.941) + (1 \cdot 26.981) + (2 \cdot 28.0855) + (6 \cdot 15.999) = 186.09 \text{ amu}$

b) $n_{\text{mineral}} = 518 / 186.09 = 2.78 \text{ mol}$

c) $n_{Li} = 2.78 \text{ mol}$

d) $n_{^6Li} = 2.78 \cdot 0.0740 = 0.206 \text{ mol}$

e) $N_{^6Li} = 0.206 \cdot N_A = 1.24 \cdot 10^{23} \text{ atoms}$

Two compounds of Cl and X (XCl_n and XCl_m) have MW and percentages by mass of Cl as follows: 137 amu, 77.5 % Cl; 208 amu; 85.1 % Cl. Determine the formulas of both the compounds.
(AW: Cl = 35.5 amu)

a) Mass of Cl in 1 mol of XCl_n :

$$MW \% Cl / 100 = 137 - 77.5 / 100 = 106.2 \text{ g of Cl}$$

c) Moles of Cl in 1 mol of XCl_n :

$$g / AW = 106.2 / 35.5 = 2.99 \approx 3 = n$$

b) Mass of Cl in 1 mol of XCl_m :

$$MW \% Cl / 100 = 208 - 85.1 / 100 = 177.0 \text{ g of Cl}$$

d) Moles of Cl in 1 mol of XCl_m :

$$g / AW = 177.0 / 35.5 = 4.98 \approx 5 = m$$

e) Mass of X in 1 mol of XCl_n :

$$MW - Cl = 137 - 106.2 = 30.8 \text{ amu}$$

f) Mass of X in 1 mol of XCl_m :

$$MW - Cl = 208 - 177.0 = 31 \text{ amu}$$

PCl₃ and PCl₅

A mineral has the formula $LiAlSi_2O_6$. Since the abundance of 6Li in the natural Li is 7.40 %, how many 6Li atoms are present in a 518 g sample of that mineral?

a) $MW = (1 \cdot 6.941) + (1 \cdot 26.981) + (2 \cdot 28.0855) + (6 \cdot 15.999) = 186.09 \text{ amu}$

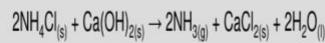
b) $n_{\text{mineral}} = 518 / 186.09 = 2.78 \text{ mol}$

c) $n_{Li} = 2.78 \text{ mol}$

d) $n_{^6Li} = 2.78 \cdot 0.0740 = 0.206 \text{ mol}$

e) $N_{^6Li} = 0.206 \cdot N_A = 1.24 \cdot 10^{23} \text{ atoms}$

How many grams of NH_3 can be formed when 33.00 g of NH_4Cl react with 33.00 g of $\text{Ca}(\text{OH})_2$? How many grams of the exceeding reactant will remain?



f) Determine the number of the reacted moles of $\text{Ca}(\text{OH})_2$
 $n_{\text{reacted}} \text{ Ca}(\text{OH})_2: 0.308 \text{ mol}$

g) Determine the number of the exceeding moles of $\text{Ca}(\text{OH})_2$
 $n_{\text{starting}} - n_{\text{reacted}} = 0.446 - 0.308 = 0.138 \text{ mol}$

h) $\text{g Ca}(\text{OH})_2 = n \cdot \text{MW} = 0.138 \cdot 74 = 10.2 \text{ g}$

CaCO_3 loses CO_2 after heating, then forming CaO . Calculate the mass of CaO resulting from the heating of 10.4 g of CaCO_3 . (AW (amu)=Ca=40.1;C=12.0;O=16)

a) Calculate the MW of CaCO_3 : $40.1 + 12.0 + (16.0 \cdot 3) = 100.1 \text{ amu}$

b) Calculate the number of moles of CaCO_3 : $\text{g/MW} = 10.4 / 100.1 = 0.104 \text{ mol}$

c) Moles of $\text{CaO} = \text{moles of CaCO}_3$
 $\text{MW CaO: } 40.1 + 16.0 = 56.1 \text{ amu}$
 $\text{g CaO: } n \cdot \text{MW} = 0.104 \cdot 56.1 = 5.83 \text{ g}$

13.71 g of a mixture containing $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and NaCl are heated with the following complete loss of water molecules. Given that the mass of the sample decreased by 32.6 % after heating, calculate the percentage composition of the mixture. (AW (amu)=Ca=40.1;Cl=35.4;H=1.0;O=16)

$$\frac{g_{\text{tot}} \cdot \%}{100 \cdot 6 \cdot \text{MW}(\text{H}_2\text{O})} = n \text{ of moles of CaCl}_2 \cdot 6\text{H}_2\text{O}$$

$$\frac{13.71 \cdot 32.6}{100 \cdot 6 \cdot 18} = 0.0414 \text{ mol}$$

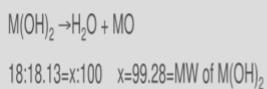
MW of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$: $40.1 + (35.4 \cdot 2) + (1.0 \cdot 12) + (16.0 \cdot 6) = 218.9 \text{ amu}$

g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$: $n \cdot \text{MW} = 0.0414 \cdot 218.9 = 9.06 \text{ g}$

% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} = 9.06 / 13.71 \cdot 100 = 66.1 \%$

% $\text{NaCl} = 100 - 66.1 = 33.9 \%$

The heating of a hydroxide having the M(OH)_2 formula forms the relevant MO oxide, after losing H_2O that corresponds to the 18.13 % of the mass. Determine the AW of M.



$$\text{AW(M)} = \text{MW}(\text{M(OH)}_2) - 2\text{AW(O)} - 2\text{AW(H)} = 99.28 - 32.0 - 2.0 = 65.3 \text{ amu}$$



1- Number of valence electrons in the central atom: 4

2- Total number of valence electrons: $4+(2 \times 6)+1+1 = 18$

3- Divide by 2 the total number of valence electrons, to have the total number of electron pairs ($18/2=9$) that are used first as bonding pairs, then as lone pairs of the ligands, until the octet is reached

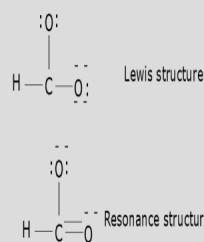
4- If electron pairs remain, they must be put on the central atom

5- Calculate the formal charge of all atoms

$$C=4-(0+6/2)=+1$$

$$O=6-(6+2/2)=-1$$

The central atom belongs to the II period, then add double bonds until it reaches the octet



Hybridization: C sp²



1- Number of valence electrons in the central atom: 4

2- Total number of valence electrons: $4+(2 \times 6)+1+1 = 24$

3- Divide by 2 the total number of valence electrons, to have the total number of electron pairs ($24/2=12$) that are used first as bonding pairs, then as lone pairs of the ligands, until the octet is reached

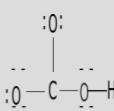
4- If electron pairs remain, they must be put on the central atom

5- Calculate the formal charge of all atoms

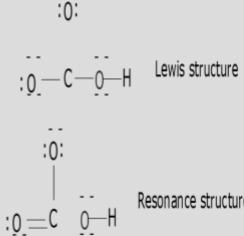
$$C=4-(0+6/2)=+1$$

$$O=6-(6+2/2)=-1$$

$$O=6-(4+4/2)=0$$



The central atom belongs to the II period, then add double bonds until it reaches the octet

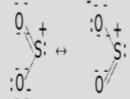


Hybridization: C sp²

Lewis structure



Resonance structures



Electronic geometry AX₂E Trigonal

Molecular geometry AX₂E Bent; bond angle less than 120° due to the lone pair repulsion

Hybridization S: sp²

Dipole momentum YES



1- Number of valence electrons in the central atom: 6

2- Total number of valence electrons: $(1 \times 6)+(2 \times 6)=18$

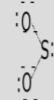
3- Divide by 2 the total number of valence electrons, to have the total number of electron pairs ($18/2=9$) that are used first as bonding pairs, then as lone pairs of the ligands, until the octet is reached

4- If electron pairs remain, they must be put on the central atom

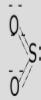
5- Calculate the formal charge of all atoms

$$S=6-(2+4/2)=+2$$

$$O=6-(6+2/2)=-1$$



The central atom belongs to III period, then add double bonds until the formal charge becomes zero



A particular sample of carbon contains 3.28 % by mass of S. When this sample is burned, sulphur is converted to gaseous SO_2 . What volume of $\text{SO}_{2(g)}$, measured at 23°C and 738 mmHg, is formed when $1.2 \cdot 10^{-5}$ kg of this carbon sample is burned?

$$\text{molSO}_2 = \frac{\text{g}_{\text{tot}} \cdot \%}{100} \cdot \frac{1}{\text{MW}_S} = \frac{1.2 \cdot 10^9 \cdot 3.28}{100} \cdot \frac{1}{32.1} = 1.23 \cdot 10^6$$

$$V = \frac{nRT}{P} = \frac{1.23 \cdot 10^6 \cdot 0.0821 \cdot 296 \cdot 760}{738} = 3.1 \cdot 10^7 \text{ L}$$

A 53.7 L tank contains $\text{N}_{2(g)}$ at a pressure of 28.2 atm and 26 °C. What mass of $\text{Ne}_{(g)}$ is necessary to be added to increase the total pressure to 75.0 atm?

$$\text{molN}_2 = \frac{PV}{RT} = \frac{28.2 \cdot 53.7}{0.0821 \cdot 299} = 61.7 \quad \text{moltot} = \frac{\text{molN}_2 \cdot P_2}{P_1} = \frac{61.7 \cdot 75.0}{28.2} = 164$$

$$\text{moltot} = \text{molN}_2 + \text{molNe} = 164 \\ g_{\text{Ne}} = (\text{moltot} - \text{molN}_2) \cdot \text{MW}_{\text{Ne}} = (164 - 61.7) \cdot 20.2 = 2.07 \cdot 10^3 \text{ g}$$

Calculate the volume of $\text{H}_{2(g)}$ at 26 °C and 751 Torr needed to react with 28.5 L of $\text{CO}_{(g)}$ measured at 0 °C and 760 Torr, in the following reaction: $3 \text{CO}_{(g)} + 7 \text{H}_{2(g)} \rightarrow \text{C}_3\text{H}_{8(g)} + 3 \text{H}_2\text{O}_{(l)}$

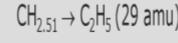
$$\text{molCO} = \frac{PV}{RT} = \frac{28.5 \cdot 760}{0.0821 \cdot 273 \cdot 760} = 1.27 \quad \text{molH}_2 = \text{molCO} \cdot \frac{7}{3} = \frac{1.27 \cdot 7}{3} = 2.96$$

$$V_{\text{H}_2} = \frac{nRT}{P} = \frac{2.96 \cdot 0.0821 \cdot 299 \cdot 760}{751} = 73.5 \text{ L}$$

A gaseous hydrocarbon containing 82.7 % by mass of C has a density of 2.33 g/L at 23 °C and 746 mmHg. Write the molecular formula of this hydrocarbon.

$$\text{MW} = \frac{dRT}{P} = \frac{2.33 \cdot 0.0821 \cdot 296 \cdot 760}{746} = 57.7 \text{ amu}$$

$$\text{molC} = \frac{\%}{\text{AW}} = \frac{82.7}{12} = 6.89 \quad \text{molH} = \frac{\%}{\text{AW}} = \frac{100 - 82.7}{1} = 17.3$$



3.57 g of a sample of KCl-KClO₃ is decomposed by heating, then yielding 119 mL of $\text{O}_{2(g)}$, measured at 22.4 °C and 738 mmHg. Calculate the mass percent of KClO₃ in the mixture.
 $2\text{KClO}_{3(s)} \rightarrow 2\text{KCl}_{(s)} + 3\text{O}_{2(g)}$

$$\text{molO}_2 = \frac{PV}{RT} = \frac{119 \cdot 738}{1000 \cdot 295.4 \cdot 760 \cdot 0.0821} = 0.00476$$

$$\text{molKClO}_3 = \text{molO}_2 \cdot \frac{2}{3} = 0.00317$$

$$\% \text{KClO}_3 = \frac{(\text{mol-MW})\text{KClO}_3}{\text{g}_{\text{tot}}} \cdot 100 = \frac{(0.00317 \cdot 122.5)}{3.57} \cdot 100 = 10.9\%$$

A gas occupies a volume of 10 L at n.c., and weighs 15.2 g. Calculate: a) its MW; b) the number of molecules contained in 10 L at n.c.; c) the mass of one molecule; d) the new volume if the temperature is kept constant and the pressure is reduced to 1/100 of the initial one; e) the new volume if the pressure is kept constant and the temperature is 100 K.

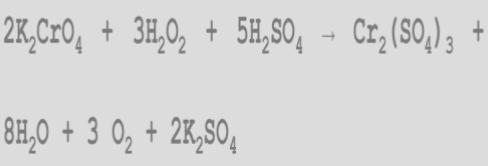
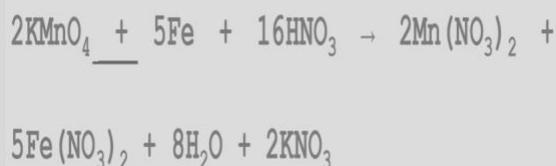
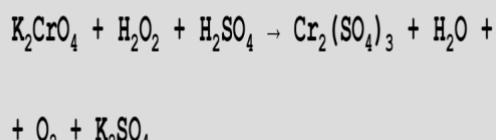
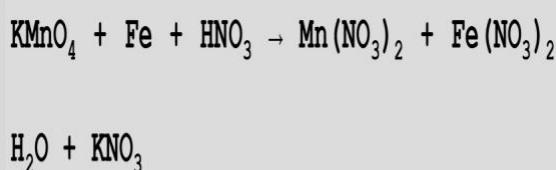
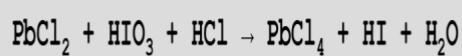
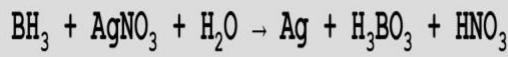
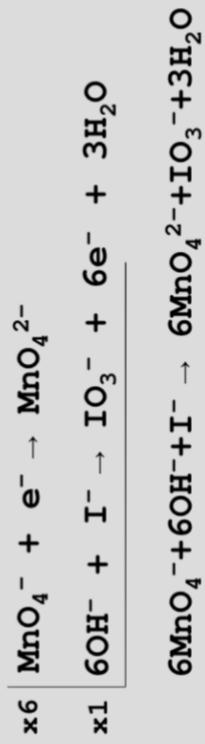
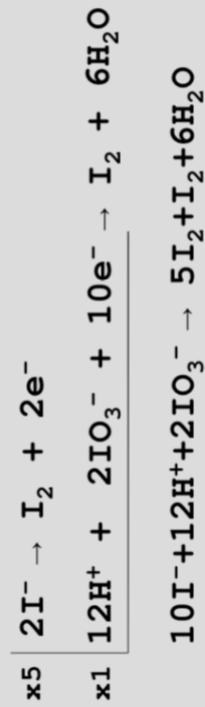
$$\text{a) } PV = \frac{g}{\text{MW}} RT \quad \text{MW} = \frac{gRT}{PV} = \frac{15.2 \cdot 0.0821 \cdot 273.15}{1 \cdot 10} = 34 \text{ amu}$$

$$\text{b) } N = \frac{N_A \cdot PV}{RT} = \frac{6.02 \cdot 10^{23} \cdot 1 \cdot 10}{0.0821 \cdot 273.15} = 2.7 \cdot 10^{23}$$

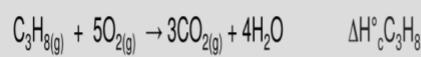
$$\text{c) } m_{\text{molecule}} = \frac{\text{MW}}{N_A} = \frac{34}{6.02 \cdot 10^{23}} = 5.6 \cdot 10^{-23} \text{ g}$$

$$\text{d) } V = \frac{g}{\text{MW} \cdot P_{\text{init}}} RT = \frac{15.2 \cdot 0.0821 \cdot 273.15 \cdot 100}{34 \cdot 1} = 1002 \text{ L}$$

$$\text{e) } V = \frac{g}{\text{MW} \cdot P} RT = \frac{15.2 \cdot 0.0821 \cdot 100}{34 \cdot 1} = 3.67 \text{ L}$$



The complete combustion of 5.00 L of a gaseous mixture of propane (C_3H_8) and butane (C_4H_{10}), measured in STP conditions, release a heat of -580 kJ. Given that the enthalpies of combustion of propane and butane are -2219.2 and -2877.5 kJ/mol, respectively, calculate the percentage composition by moles of the mixture.

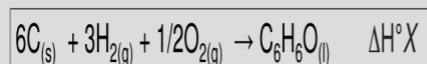
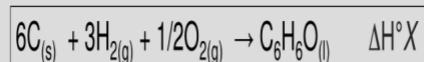
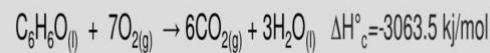
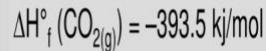
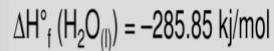
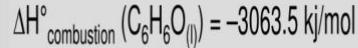


$$n_{\text{tot}} = \frac{PV}{RT} = \frac{1.5}{0.0821 \cdot 273} = 0.223 \quad x = \text{moles of } C_3H_8 \quad y = \text{moles of } C_4H_{10}$$

$$\begin{cases} x+y=0.223 \\ 2219.2x + 2877.5y = 580 \end{cases}$$

$$x=0.094 \rightarrow 42.2\% \quad y=0.129 \rightarrow 57.8\%$$

Calculate the standard enthalpy of formation of liquid phenol ($C_6H_6O_{(l)}$) at 25°C, using the following thermochemical data:



$$\Delta H^\circ X = 6\Delta H^\circ_f + 3\Delta H^\circ_f - \Delta H^\circ_c = -2361 - 857.55 + 3063.5 = -155.0 \text{ kJ/mol}$$

A 1.37 M solution of citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$) in water has a density of 1.10 g/cm³. Calculate the mass percent, molality, mole fraction.

1 L of solution

$$g_{\text{tot}} = dV = 1.10 \text{ g/mL} \cdot 1000 \text{ mL} = 1100 \text{ g}$$

$$g_{\text{ca}} = n \cdot \text{MW} = 1.37 \text{ mol} \cdot 192 \text{ g/mol} = 263.04 \text{ g}$$

$$\%_{\text{ca}} = \frac{263.04 \text{ g}}{1100 \text{ g}} \cdot 100 = 23.9 \%$$

$$g_{\text{water}} = g_{\text{tot}} - g_{\text{ca}} = 1100 - 263.04 = 836.96 \text{ g}$$

$$m_{\text{ca}} = \frac{n}{Kg_{\text{Water}}} = \frac{1.37 \text{ mol}}{0.83696 \text{ Kg}} = 1.64 \text{ mol/Kg}$$

$$n_{\text{water}} = \frac{g}{\text{MW}} = \frac{836.96 \text{ g}}{18 \text{ g/mol}} = 46.5 \text{ mol}$$

$$X_{\text{ca}} = \frac{n_{\text{ca}}}{n_{\text{tot}}} = \frac{1.37 \text{ mol}}{1.37 \text{ mol} + 46.5 \text{ mol}} = 0.029$$

How would you prepare 1.00 L of a 0.50 M solution of each of the following?

- a. H_2SO_4 from "concentrated" (18 M) sulfuric acid
- b. HCl from "concentrated" (12 M) reagent
- c. NiCl_2 from the salt $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$
- d. HNO_3 from "concentrated" (16 M) reagent
- e. Sodium carbonate from the pure solid

a) $V_1 = \frac{(MV)_2}{M_1} = \frac{0.50 \text{ mol/L} \cdot 1.00 \text{ L}}{18 \text{ mol/L}} = 0.0278 \text{ L}$ Then add water: $V_2 - V_1 = 0.972 \text{ L}$

b) $V_1 = \frac{(MV)_2}{M_1} = \frac{0.50 \text{ mol/L} \cdot 1.00 \text{ L}}{12 \text{ mol/L}} = 0.0417 \text{ L}$ Then add water: $V_2 - V_1 = 0.958 \text{ L}$

c) $\text{MW} = 58.7 + (35.4 \cdot 2) + (18 \cdot 6) = 237.5 \text{ amu}$

$\text{g NaCl}_2 \cdot 6 \text{ H}_2\text{O}$: $n \cdot \text{MW} = 0.50 \text{ mol} \cdot 237.5 \text{ g/mol} = 118.7 \text{ g}$ in 1.00 L of water

d) $V_1 = \frac{(MV)_2}{M_1} = \frac{0.50 \text{ mol/L} \cdot 1.00 \text{ L}}{16 \text{ mol/L}} = 0.0312 \text{ L}$ Then add water: $V_2 - V_1 = 0.969 \text{ L}$

e) $\text{MW} = (23 \cdot 2) + 12 + (16 \cdot 3) = 106 \text{ amu}$

$\text{g Na}_2\text{CO}_3$: $n \cdot \text{MW} = 0.50 \text{ mol} \cdot 106 \text{ g/mol} = 53 \text{ g}$ in 1.00 L of water

A solution was prepared by mixing 50.00 mL of 0.100 M HNO_3 and 100.00 mL of 0.200 M HNO_3 . Calculate the molarity of the final solution of nitric acid.

$$(MV)_1 + (MV)_2 = (MV)_3$$

$$M_3 = \frac{(MV)_1 + (MV)_2}{V_3} = \frac{(0.100 \text{ mol/L} \cdot 0.050 \text{ L}) + (0.200 \text{ mol/L} \cdot 0.100 \text{ L})}{0.150} = 0.167 \text{ mol/L}$$

Which solvent, water or hexane (C_6H_{14}), would you choose to dissolve each of the following?

- a. $\text{Cu}(\text{NO}_3)_2$ Water
- b. $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OH}$ Hexane
- c. CS_2 Hexane
- e. HCl Water
- c. CH_3OH Water
- f. C_6H_6 Hexane

Calculate the molarity and mole fraction of acetone in a 1.00 m solution of acetone (CH_3COCH_3) in ethanol ($\text{C}_2\text{H}_5\text{OH}$). (Density of acetone = 0.788 g/cm³; density of ethanol = 0.789 g/cm³).

Consider 1 Kg of ethanol that occupy the V_{et} $V_{\text{et}} = \frac{g}{d} = \frac{1000 \text{ g}}{0.789 \text{ g/mL}} = 1267.4 \text{ mL}$

1 mol of acetone occupy the V_{ac}

$$V_{\text{ac}} = \frac{g}{d} = \frac{n \cdot \text{MW}}{d} = \frac{1 \cdot [(12 \cdot 3) + (6 + 16)] \text{ g}}{0.788 \text{ g/mL}} = 73.6 \text{ mL}$$

$$V_{\text{tot}} = V_{\text{et}} + V_{\text{ac}} = 1267.4 \text{ mL} + 73.6 \text{ mL} = 1341 \text{ mL} = 1.341 \text{ L}$$

$$M = n/V = 1.00 \text{ mol}/1.341 \text{ L} = 0.746 \text{ mol/L}$$

$$X = \frac{n_{\text{ac}}}{n_{\text{ac}} + (g/\text{MW})_{\text{et}}} = \frac{1.00 \text{ mol}}{1.00 \text{ mol} + (1000 \text{ g}/46 \text{ g/mol})} = 0.044$$

Calculate the enthalpy of evaporation and the vapor pressure of benzaldehyde (C_6H_5CHO) at 100 °C, given that its boiling point at 1 atm is 179.0 °C and its triple point is 422 °C at 45.9 atm.

Using the Clausius Clapeyron equation

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{ev}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

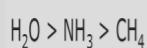
$$\ln\left(\frac{45.9}{1}\right) = \frac{\Delta H_{\text{ev}}}{8.31} \left(\frac{1}{452} - \frac{1}{695} \right)$$

$$\Delta H_{\text{ev}} = 41101 \text{ J/mol}$$

$$\ln\left(\frac{P}{1}\right) = \frac{41101}{8.31} \left(\frac{1}{452} - \frac{1}{373} \right)$$

$$P = 0.098 \text{ atm}$$

Put in descending order of critical temperature the following substances and explain your answer: a) CH₄, b) NH₃, c) H₂O



The critical temperature depends on the strength of the intermolecular interactions. Stronger are the intermolecular interactions, higher is the critical temperature.

H₂O forms hydrogen bonds stronger than NH₃ since O is more electronegative than N. CH₄ interacts through dispersion forces.

Which of the following substances can exist in liquid state at 298 K?

| Substance | T _c (K) |
|------------------|--------------------|
| H ₂ | 33.3 |
| N ₂ | 126.2 |
| O ₂ | 154.8 |
| CH ₄ | 191.1 |
| CO ₂ | 304.2 |
| HCl | 324.6 |
| NH ₃ | 405.7 |
| SO ₂ | 431.0 |
| H ₂ O | 647.3 |

Calculate the van't Hoff coefficient and the α value for the following electrolyte solutions: a) 0.050 m HCHO_2 (monoprotic acid) that freezes at -0.0986 °C (k_f water = 1.86 °C Kg mol⁻¹); b) 0.100 M HNO_2 that has a concentration of NO_2^- ions equal to $6.9 \cdot 10^{-3}$ M.

$$i=[1+\alpha(\gamma-1)]$$

a) 0.050 m HCHO_2 freezing point: -0.0986 °C. k_f water = 1.86 °C Kg mol⁻¹

$$\Delta T_f = k_f \cdot m \cdot i \quad i = \frac{\Delta T_f}{k_f \cdot m} = \frac{0.0986^\circ\text{C}}{1.86^\circ\text{C} \cdot \text{Kg} \cdot \text{mol}^{-1} \cdot 0.050 \text{ mol} \cdot \text{Kg}^{-1}} = 1.06$$

$$\alpha = 0.06$$

b) 0.100 M HNO_2 $[\text{NO}_2^-] = 6.9 \cdot 10^{-3}$ M.

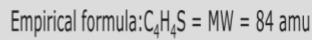
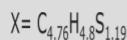
$$\alpha = \frac{6.9 \cdot 10^{-3} \text{ mol/L}}{0.100 \text{ mol/L}} = 6.9 \cdot 10^{-2}$$

$$i=[1+\alpha(\gamma-1)]=(1+\alpha)=(1+0.069)=1.069$$

A non electrolyte compound X contains C, H, and S in the following percentage by mass: C, 57.1 %, H, 4.8 %, and S, 38.1 %. When 0.867 g of X are dissolved in 44.56 g of benzene, the freezing point depression is 1.183 °C (k_f of benzene: 5.12 °C Kg mol⁻¹). Calculate the empirical and the molecular formulas of X.

100 g of X contains:

| | | |
|-------------|-------------|--|
| 57.1 g of C | 57.1 g of C | $n_C = 57.1 \text{ g} / 12 \text{ g/mol} = 4.76 \text{ mol}$ |
| 4.8 g of H | 4.8 g of H | $n_H = 4.8 \text{ g} / 1 \text{ g/mol} = 4.8 \text{ mol}$ |
| 38.1 g of S | 38.1 g of S | $n_S = 38.1 \text{ g} / 32 \text{ g/mol} = 1.19 \text{ mol}$ |



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

$$\Delta T_f = \frac{g_X \cdot k_f \cdot i}{\text{MW}_X \cdot \text{Kg} \cdot \text{mol}^{-1}}$$

$$\text{MW}_X = \frac{g_X \cdot k_f \cdot i}{\Delta T_f \cdot \text{Kg} \cdot \text{benzene}^{-1}} = \frac{0.867 \text{ g} \cdot 5.12^\circ\text{C} \cdot \text{Kg} \cdot \text{mol}^{-1} \cdot 1}{1.183^\circ\text{C} \cdot 0.04456 \text{ Kg}} = 84.2 \text{ g/mol}$$

