SOS

STUDENTS OFFERING SUPPORT

CHEM 112: General Chemistry

Course Package Review

Queen’s SOS: Students Offering Support

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Contents:

1.0 Introduction

Nomenclature:

Valence Shell Electrons:

The most common number of valence shell electrons "involved in bonding" may be found using this guide.

Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII
Valence	+1	+2	+3	+4	-3	-2	-1	0

Oxidation Numbers:

Loss of Electrons: **Oxidation**

- When electrons are lost on a given atom during bond formation, it becomes POSITIVELY charged

Gain of Electrons: **Reduction**

- When an atom gains an electron during bond formation, it becomes NEGATIVELY charged

When you are unsure of an element's oxidation number, look it up on the periodic table

Naming Compounds:

Binary Compounds – Compounds with two atoms bonded together

- For convenience, treat all compounds as ionic compounds, even though many are covalent.
- Compounds have no net charge. Therefore, positive and negative charges on ions have to balance one another.

- Named by metal compound first, followed by non-metal with the suffix "ide"
  - Copper oxide
  - Sodium Bromide
- WHEN CONVERTING NAME TO STRUCTURE ALWAYS MAKE SURE THAT THE CHARGES HAVE BEEN BALANCED
  - I.e. sodium oxide
    - Na_2O

IUPAC Naming System:

- Standardized naming system for chemical compounds
- Used to ensure that two compounds do not have the same name
  - Metals often have different oxidation states which need to be incorporated into the name of a molecule
  - I.e. Copper has 4 oxidation states Cu^+, Cu^{+2}, Cu^{+3}, Cu^{+4}
- We therefore incorporate the oxidation state into the name of a compound by adding it in parentheses using roman numerals
  - I.e. Copper (II) oxide

-OUS and –IC Naming System

- Not commonly used anymore
- For a given an; a lower oxidation state is given the ending –ous and a higher oxidation state is given the ending –ic
- For metals, the Latin name is often used
  - Ie. copper = cuprum
- Examples:
  - Lead – Pb^{2+} = plumb**ous**
  - Pb^{4+}= plumb**ic**

Stoichiometry:

Empirical Vs. Molecular Formula

The **Molecular Formula** is the total number of atoms in a molecule

The **Empirical Formula** is the lowest whole number ratio of atoms

- Can be calculated by looking at the ratio between the number of moles of each atom using the formula: $n = \frac{m}{MM}$

- after the number of moles of each have been calculated, to determine the ration, simply divide each atom involved by the SMALLEST number of moles

- in essence we are assuming that there is only 1 of this atom; however, this can be altered if the resulting ratios are fractional numbers since both empirical and molecular formulae must consist of only **whole** numbers of atoms

i.e. a ratio yielding 1 O, 3 H, 1.5 C would need to be multiplied by two to ensure all numbers are integers:

C_3H_6O

Balancing Equations

- PICK THE METHOD THAT WORKS BEST FOR YOU!!!!
- All that is important here is that you have the same number of each atom present on one side of the equation as you do on the other

2.0 Atomic Structure/ Quantum Mechanics

Electromagnetic Radiation:
Electric and magnetic fields are perpendicular to each other and are in phase with one another

Waves are studied through their:

- Wavelength (λ)
  - The distance in between the consecutive crest
- Frequency (v)
  - The number of oscillations per second
  - Measured in Hertz (s^{-1})
- Speed (c)
  - $c = \lambda \times v$

Interference: the combination of two or more waves

- *Combining same phase increases the amplitude → known as constructive interference*
- *Combined out of phase waves cancel out → destructive interference*

Blackbody Radiation:

- The initial starting point of the wave must be equal to the final point of the wave
- $\lambda = \frac{2L}{n_x}$
- In 3-D boxes we have to worry about 3 dimensions = 3 numbers n_y n_x & n_z

$$\nu = \frac{c\sqrt{\left(n_x^2 + n_y^2 + n_z^2\right)}}{2L}$$

→ More waves at higher frequencies

- Intensity of the wave increases as the frequency increases
- Emitted light/Energy emitted is QUANTIZED meaning only discrete amounts of energy can be emitted from a material
  $E = hv$
  $h = 6.656 \times 10^{-34} Js$

Photoelectric Effect:

- By shining a light on a metal surface the energy of the electron is raised causing one electron to become excited and eject off the surface
- A threshold frequency must be exceeded in order to eject an electron ($v_{EM} > v_0$)
- The energy that is left over is the kinetic energy of the electron
- Increasing the intensity of the electromagnetic waves increases the number of electrons ejected but does not alter the energies of the electrons

Mathematically: $E_{EM} = \Phi + \frac{1}{2}mu^2$

Where ½ mu^2 is the kinetic energy of the ejected electron

Atomic Spectra: atoms that occupy well-defined energy levels

Bohr Model:

- Electrons move in a circular orbit around the nucleus
- The angular momentum (L)
    - $L = \frac{nh}{2\pi}$
    - $L = mr^2\omega$
- Electrons can be excited to a higher orbital by accepting energy, or can be relaxed by emitting energy

In order to measure the energy in the Bohr model the following equation is used

$$E_n = \frac{-R_H}{n^2}$$

R_H: Rydberg energy = 2.179×10^{-18} J

- The energy is more negative for a smaller n, this means that the atom is more stable
- Small n correspond to smaller radii, hence the electrons are closer to the nucleus
- A n=1 state is also known as the ground state
- In order to remove the electron from the atom (excite the electron) the electron needs to be ionized → ionization energy $I = E_\infty - E_1$
    - Ionization energy is hence positive since it is the input energy

Overall the energy is equal to

$$E_n = R_H\left(\frac{1}{n_b^{\ 2}} - \frac{1}{n_t^{\ 2}}\right)$$

Wave:

Finding the wavelength of the particle

$$\lambda = \frac{h}{mu}$$

u: the velocity of the particle

- *From the momentum of the particle we can find the wavelength however there is no way of knowing the position of the electron*

The equation for the momentum is

$$p = mv$$

Quantum Numbers:

n: principle quantum number

- Energy of the orbital
- Represented by positive integer values

l: angular momentum quantum number

- Takes on positive integers from 0 to n-1
- Determines the shape of the orbital

Angular Momentum Quantum Number	Orbitals
l=0	s
l=1	p
1=2	d
1=3	f

m_l: magnetic quantum number

- Can take on integer values from –l to l
- Determines the orientation of the orbitals

m_s: magnetic spin quantum number

- Can be +1/2 or -1/2
- Electrons spinning in clockwise or counter clockwise

All orbitals that have the same principle quantum number are in the same principle shell which contains n^2 *orbitals*

All orbitals with the same principle quantum number and angular momentum quantum number are in the same sub-shell which contains 2l+1 orbitals

Degenerate Orbitals: multiple orbitals that have the same energies

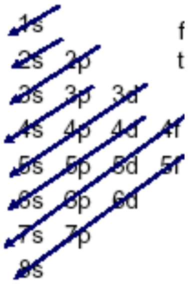
Nodes: used to describe the shape of the orbitals, a node is implemented when there is a change from a positive lobe to a negative lobe

In general orbitals have n-1 nodes

Pauli-Exclusion Principle:

No two electrons can have the same set of quantum numbers

Filling orbitals:



Hunds Rule:

Electrons are placed in unpaired p, d, f suborbitals until each orbital has one electron

Aufbau's Principle:

Electrons are placed in the lowest energy orbitals first until all suborbitals are filled

Noble Gas Abbreviation:

Can use the noble gas in the row above to represent the core electrons followed by the valence electrons

Lewis Diagrams

A **chemical bond** is an interaction that holds two (or more) atoms together in a molecule.

- involve a pair of **valence electrons**, which may originally come both from the same atom or one from each
- the valence electrons are those in the s and p orbitals (so the maximum number is 8)
- elements in the first column of the periodic table (H, Li, etc) have one valence electron; in the second column (Be, Mg, etc) they have two; in the third (B, Al, etc) they have four; and so on (note that this considers the **main group elements** only – those with no unfilled sets of d or f orbitals)
- elements with 1 or 7 valence electrons are particularly reactive (hence the reaction of alkali metals with water, and why halogens exist in pairs as F_2, Cl_2, etc)

In **covalent bonds**, the electrons are shared between two atoms

- the atoms are held together by the attraction of both atoms to the shared electrons
- the electrons will on average be closer to the atom which is more electronegative
- (if the other atom is too electronegative, though, it will take the electrons entirely, producing an ionic bond instead)
- for example, carbon can make four covalent bonds

In **ionic bonds**, the electrons are transferred

- results in two ions, which are then held together by electrostatic interactions
- the ions may be carried apart (especially in solution)
- in the solid phase, will take a crystalline form with alternating positive and negative ions in a large network
- occur especially between alkali metals and halogens, ex NaCl

In **Lewis structures**, atoms are depicted as their atomic symbol, with electrons around them representing the valence electrons

- other electrons are ignored, as they are unreactive
- remember that these electrons will normally act in pairs
- elements in the same column of the periodic table will look the same
- when drawing molecules as Lewis structures, electrons shared between atoms (i.e. covalent bonds) may simply be placed in between the atoms – or may be drawn as a dash, which represents two shared electrons
- Unshared (pairs of) electrons are called **lone pairs** (water has two lone pairs)

Atoms want to get a complete set of valence electrons. They can do this by reaching either 8 or 0.

- (The noble gases already have filled valence shells, which is why they're so stable).
- A notable exception to this rule is hydrogen, which has a filled valence shell when it has two valence electrons.
- Group V elements other than nitrogen may be given up to ten valence electrons if necessary
- Group VI elements other than oxygen may be given up to twelve valence electrons if necessary

The last two points are due to the ability of the d orbitals to take extra electrons. (Nitrogen and oxygen are excluded because they don't have any electrons at energy level 3 or higher).

- the **expanded valence table** can be used to indicate how many bonds and lone pairs each atom tends to form
- do not use the expanded valencies if standard valencies can be used for all atoms

Whenever two atoms can both reach a filled valence shell by the transfer or sharing of electrons (shared electrons being included in the valence shells of both atoms), they will do so by forming a bond

Producing Lewis Structures

- whatever positions fill all your valencies are the ones that you should use
- try to draw and fill the valencies of the central atoms first
- central atoms will generally make the most bonds
- double or triple bonds will also likely be associated with central atoms

- most important: carbons are always central atoms, while hydrogens and halogens are always terminal atoms (halogens may be central in some cases)
- atoms there are only one of might be more likely to be central atoms (other than halogens)
- the order in which they are listed in the chemical formula may give you clues (other than hydrogens, central atoms tend to come before terminal atoms)
- don't miscount the number of atoms, especially for more complex molecules
- ex $COHCO_2H$, $CH_2N(CH_3)_2$, SF_6, CO_2, H_2SO_4

If structures are charged, put brackets around them and then write the charge (ex +, 2+) in the top right.

- to find out which atoms the charges are on, count and see if any of the atoms have greater or fewer bonds than they normally make
- for example, oxygen (normally makes two bonds) is negative if it has only one, and positive if it has three
- also, the total charges of the atoms in a molecule must add to the total charge on the molecule
- other than ionic compounds, no individual atom is ever likely to have a charge greater than +1 or -1
- it is also unlikely for a molecule to have both positive and negative charges (though this is permissible under certain circumstances, if no other options are available)

More precisely, we calculate **formal charge**: count the number of electrons around an atom (counting only one of any pairs of electrons within covalent bonds) and see if this is more or less than the atom's group number.

- for example, oxygen (group VI) is positive if it has five electrons and negative if it has seven
- note that an atom which is not a noble gas may still have a valence shell of eight while still having zero formal charge, because some of those might be shared: formal charge counts only one of the electrons in a covalent bond, while a valence shell counts both
- for example, oxygen with two bonds has a formal charge of zero (six electrons) but a valence of eight – while oxygen on its own with a valency of eight (unlikely to exist) would have all eight electrons entirely to itself and would have a formal charge of –2.

Atoms which have the same numbers of bonds and lone pairs as each other are termed **isoelectronic**.

- ex any carbon atom is isoelectronic with the N in NH_4^+ (both have four bonds, no lone pairs)

Molecules may also exhibit **resonance**

- occurs when there are multiple valid Lewis structures
- the actual molecule is a mix of the individual structures
- if the resonance structures are not equally stable, the most stable one (ex one with fewer charges) will dominate

- only electrons may move; atoms may not

- especially common when a molecule is charged
- also more common around electronegative atoms, like oxygen and nitrogen

3.0 Atomic Structure

Molecular Geometries

- electron pairs assume orientations to minimize electron repulsions

Electron Repulsion Order:
LP-LP > LP-B> B-B

General Rules for Electron Group Geometries:
Electron Group Geometry ≠ Molecular Geometries
i.e. OH_2 and CH_4 both have tetrahedral geometry but do not have the same molecular geometry

Reason: *Lone pairs.*
- Lone pairs decrease the angles between bonded atoms because of their stronger repulsive forces. Therefore OH_2 has a much smaller bond length than CH_4

In General:

- Two electrons = linear
- Three electrons = trigonal planar
- Four electrons = tetrahedral
- Five electrons = trigonal bipyramidal
- Six electrons= octahedral

In order to determine the molecular shape of a molecule

1. **Draw the Lewis structure of the molecule, including all lone pairs and bonds**
2. **Position the molecule so that repulsion between groups is at a MINIMUM**

USE THE FOLLOWING CHART TO DETERMINE VSEPR SHAPES AND ARRANGEMENTS (yes you should memorize this & understand the corresponding theory)

Polar Covalent Bonds

Ionization Energy: Ability of an atom to give up an electron

Electron Affinity: Ability of an atom to accept an electron

Whichever atom has the highest electron affinity will be the atom which will pull the electron slightly towards it.

This will result in this atom having a **partial** NEGATIVE charge (δ-)
and as a result, the other atom in the molecule will have a **partial** POSITIVE charge (δ+).

This can also be explained by electronegativities. *In general,* the most electronegative atom will bear the negative charge.

Based on differences in electronegativities, it is possible to classify the type of bond which being formed.

Large electronegativity differences relate to IONIC BONDS (>1.9).
Medium electronegativity differences relate to POLAR COVALENT bonds (0.5-1.9).
Small electronegativity differences relate to NONPOLAR COVALENT bonds (<0.5).
Note: Numbers are just a rough approximation.

Predicting Dipoles in Molecules:

*In general, symmetry in a molecule results in no Dipole.
- It is always useful to start by drawing the Lewis structure of a molecule, and then assigning the appropriate molecular geometry.
- By comparing the electronegativies of individual atoms, it is then possible to assign polarity to the molecule. (The arrow will point in the direction of increasing electronegativity)

Be careful with molecular geometries like the BENT GEOMETRY.

-> At first glance it may look like the O-H bond dipoles cancel out but since the geometry is not linear, the distance between bonds is less than 180˚ and therefore the molecule is not symmetrical and a dipole exists.

Bond Order vs. Bond Length:

Bond Order – **The number of shared electrons between two atoms**

Bond Length - **The distance between two atomic nuclei**
BOND ORDER INCREASES AS BOND LENGTH DECREASES
i.e. Triple bonds (Bond Order of 3) are shorter than double bonds (Bonder order of 2)

Bond Energies:

- Bond energies can be used to determine reaction energies

- To figure out the changes in enthalpy, we subtract the energies of the products from the energies of the reactants

ΔHrxn= ΣD(reactants) -ΣD(products)

Chemical Bonding:

- The manner in which orbitals interact when atoms come together in a bond
- The overlap of orbitals consists of the sharing of electrons
- Orbitals must have similar energies and correct orientation in order to interact in a favourable fashion
- **Covalent bonds are formed between UNPAIRED ELECTRONS on adjacent atoms**

Hybridization:

- Combining two orbitals
  - i.e. sp^2 combines the s orbital and two p orbitals
    - Results in an orbital lower in energy than a p orbital for the same molecule, but higher than the s orbital
  - The same number of electrons remain in hybridized orbital as in those contributing; however, they are now all equal in energy
  - The total number of electrons contributing to the orbital, the total number of bonds can be formed to the atom
    - i.e. sp^3 hybridized Carbon can form four bonds since it contains 4 electrons in the hybridized orbital (3p orbitals and 1s orbital coming together)

Relating Hybridization to VSEPR:

- Based on the number of bonds surrounding a central atom, it is possible to determine its hybridization
  - Trigonal planar geometry exhibits sp^2 hybridization on the central atom
    - Explained by the fact that three bonds are being formed from the atom. (one CAN be a double bond)
    - e.g Ethene (CH_2=CH_2) OR simply three single bonds BH_3
  - Remember: Lone pairs contribute to a molecules hybridization
  - When a molecule has more than 4 bonds around it, the molecule will contain some 'd' character
  - I.e. PCl_5 ; phosphorous will exhibit sp^3d hybridization
- Single bonds consist of a σ bond

- Double bonds consist of one σ bond and one π bond
- Triple bonds consist of two π bonds and one σ bond
- REMEMBER: Only orbitals which are *in phase* (thereby exhibiting the same sign) can overlap with each other to form a bonding orbital
        - Orbitals which are out of phase will contribute to *antibonding* orbitals

Molecular Orbitals:

- Molecular orbitals allow electrons to be shared in a covalent bond
- The number of molecular orbitals is the same as the number of atomic orbitals combined

  -when two MOs are formed from two AOs, 1 MO is bonding and has a lower energy than the AOs and 1 MO is anti-bonding and has higher energy than the AOs
- Electrons are added to the lowest energy level
    - Only valence shell electrons are shown
- The maximum number of electrons that can contribute to a molecular orbital is 2
- We define the bond order in terms of bonding and anti-bonding orbitals
    - Simply subtract number of antibonding orbitals from number of bonding orbitals

MO Diagrams:

- Bonding orbitals are always lower in energy than their associated anti-bonding orbitals
- σ* is ALWAYS the least stable orbital in a Molecular Orbital Diagram
- The σ_{2S} orbital and the σ_{2P} orbital are always lower in energy than the σ_p and π orbitals
- **Degenerate Orbitals** are those which have the same energy
    - Often result when multiple p orbitals are coming together
    - Degenerate orbitals get one electron each, before the electrons are paired
    - *Paramagnetic* molecules are those with unpaired electrons
- Drawn by indicating the contributing electrons from each atom involved in the bond on each side, and matching those with similar energies to form the Molecular Orbital in the middle.
    - The energies of the MOs are shifted toward those of the atomic orbitals for atoms with the highest electronegativity
        - Consequently, antibonding orbitals are shifted towards the atomic orbitals for the atoms with lower electronegativity

Delocalized Electrons:

- When a pair of π electrons are shared over three electrons
    - 3 p orbitals that are combined
    - Occurs in molecules such as ozone and benzene
        - Each oxygen in ozone and each carbon in benzene is considered to be sp^2 hybridized
    - One combination of p orbitals will result in a bonding orbital, one will result in an anti-bonding orbital, and the third combination will result in a *non-bonding* orbital
        - Non-bonding orbitals result from p-orbitals which are in the wrong orientation to have overlap of any kind (neither positive or negative addition

4.0 Gas Laws

Major Properties of Gases

- little interaction between molecules
- individual molecules are far apart
- individual molecules have relatively high kinetic energy
- compressible (and exert pressure) to a significant degree

Molecules which are gases at room temperature tend to have weak intermolecular forces.

For example, small non-branched alkanes (methane, ethane, etc) are gases at room temperature, but increasing size (and increasing London dispersion forces) raises the boiling point each time. Molecules that hydrogen bond will have higher boiling points than similar molecules that will not.

Gas Pressure → the amount of force a gas exerts on its surroundings/container.

$$\text{Pressure (Pa)} = \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}}$$

Taking this further:

- From physics we know that Force=mass x gravity
- The volume of a fluid in a cylinder is: Volume= cross sectional area x height
    - V= A x h → rearrange for A → A=V/h
- Substituting these into our original pressure equation we get:

$$\text{P} = \frac{\text{mgh}}{V}$$

- We also know that density is mass divided by volume. Therefore we can substitute further ending with:

$$\text{P} = \text{density} \times \text{gravity} \times \text{height}$$

Properties of Ideal Gases

- molecules are point particles (no volume)
- molecules travel in straight lines only – intermolecular forces (and gravity) have negligible effect on motion
- collisions are perfectly elastic (no loss of kinetic energy
- all ideal gases act the same wa*y*
- all ideal gases at the same average kinetic energy have the same temperature, and vice versa (called the **Principle of Equipartition of Energy**)
- all ideal gases obey the Ideal Gas Law

We can also simply say that ideal gases follow the postulates of the **Kinetic Molecular Theory**. (All of the above are postulates or consequences of the KMT).

Most gases are approximately ideal under normal conditions, and the KMT helps explain why they sometimes deviate from this:

- They become less ideal as temperature drops (slower-moving molecules → intermolecular forces act over longer periods of time as molecules pass each other and thus are more significant) or as pressure increases (less space to move in → more collisions, plus molecules are closer to each other, making intermolecular forces stronger).
- A real gas approaches the behaviour of ideal gases at the extremes of approximation (infinite high temperature and molecules infinitely far apart)

The 3 Gas Laws:

1.Avogadro's Law:
  –At a given T and P, different gases in a volume have the same number of moles V= Constant * n
2.Boyle's Law
  –$P_1V_1 = P_2V_2$
3.Charles's Law
  –The volume of a gas is directly proportional to its absolute temperature
  –V=constant * T

The **Ideal Gas Law** states that PV = nRT.

P = pressure (kPa), V = volume (L), n = number of moles,
R = the Universal Gas Constant (8.31 kPa L K^{-1} mol $^{-1}$), T = temperature (K).
(Note the units)

This is your basic equation for understanding gases. In fact, you can get all the other gas laws from it:

- Given constant n, R, T, increasing pressure will decrease volume, and vice versa, or PV=nRT won't be true (**Boyle's Law:** $P_1V_1 = P_2V_2$).
- Given constant n, R, V, increasing pressure will increase temperature, and vice versa, or PV=nRT won't be true (**Amontons' Law:** $P_1/T_1 = P_2/T_2$) *(again, temperature in K)*

- Given constant n, R, P, increasing temperature will increase volume, and vice versa, or PV=nRT won't be true (**Charles's Law:** $V_1/T_1 = V_2/T_2$)

If you don't want to bother with which one(s) to use, apply the **Combined Gas Law** instead:

$P_1V_1/T_1 = P_2V_2/T_2$, which gives you the above three laws all put into one.

If the mass of gas changes, there is an even more general form, $P_1V_1/n_1T_1 = P_2V_2/n_2T_2$

What is the relationship between V and n, with the other quantities constant?
(**Avogadro's Law**)

PV=nRT doesn't say anything about multiple types of molecules, so long as the gas is still ideal; it only talks about number of molecules. Therefore, it applies to both the total number of molecules and the number of molecules for any individual gas (and you get **Dalton's Law** and **Raoult's Law**).

Each gas exerts pressure independently, so $P_T = P_1 + P_2 + ...+ P_n$ and $P_A = x_AP_T$. As a direct consequence of this, $P_A = x_AP_T$.

Since all of these are essentially applications of the Ideal Gas Law, they get less accurate as the ideal gas approximation becomes less accurate.

Density: $\rho = m/V$
- m can be calculated from n (and molecular masses)
- the SI units of density are the cubic meter; but we use the cubic decimetre (also called the **litre**, **L**) as a more convenient measurement

Pressure: P = F/A, where F is in Newton's and A is in square meters.
- the SI units of this are in N/m^2, or Pascals (Pa)
- pressure is essentially equivalent at all points of the container
- note that if a gas is exerting a certain pressure, then that same pressure is being exerted by the walls of the container in keeping it inside (by Newton's Third Law)

- Atmospheric pressure is 101.325 kilopascals (kPa), also known as 1.01 bars, 1 atmosphere (atm) and 760 millimetres of mercury in a barometer (mmHg, or Torr)

For any column (including the column of air that extends to the top of the atmosphere to give us atmospheric pressure), the density and pressure equations can be rearranged to give $P = \rho gh$ (h being the height of the column)

The volume of one mole of an ideal gas at 0°C and 101.325 kPa is 22.4 L. If you forget, you can calculate it from PV = nRT.

Conversely, if you forget R but remember 22.4, you can calculate R from this as well. You can also calculate R for other combinations of units.

The **laws of physics** (kinematics, work and energy, momentum, etc) also apply to gases. The lecture notes go into great detail on this point.

- The variables you use are different, though: kinetic energy is e_k, speed is u, impulse is I
- also, N is the number of molecules, and N_A is Avogadro's number
- remember that ideal gas collisions are always perfectly elastic.

- equations you should probably remember in addition to your physics equations are

$$\bar{e}_k = (3/2)RT = (3/2) PV$$

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

- the latter one can also be expressed using Boltzmann's constant, $k_B = R/N_A$

Maxwell-Boltzmann distribution

- a probability distribution, indicating the percentage of gas molecules at any given speed
- the curve starts at 0 m/s, increases to the maximum, then decreases asymptotically to zero as speed approaches infinity
- as temperature increases, the peak becomes lower and the range of speeds becomes wider
- as temperature decreases, the peak becomes higher and the range of speeds becomes narrower
- the area under the curve always remains the same (for the same system)

- different gases have different curves at the same temperature based on their molecular weight (what is the relationship?) u_m, the **modal speed**, is the speed that the peak occurs at (the speed with the greatest number of molecules)
- u_{avg} is slightly to the right of u_m, and u_{rms} is slightly further to the right

- the curve can also be produced mathematically, graphing percentage as a function of speed
- $f(u) = 4\pi(m/2\pi k_BT)^{3/2}u^2e^{(-mu\text{^}2/2kBT)}$

Effusion

- refers to a gas escaping through a small hole in a container (in contrast to diffusion, the spread of molecules through an open space)
- **Graham's Law**: $\sqrt{(MM_1/MM_2)}$ = $rate_2/rate_1$ ("rate" being rate of effusion)
- $rate_2/rate_1$ can be replaced with anything rate is proportional to: average molecular speed, effusion time, amount of gas effused at a given moment in time, distances travelled by molecules

“Real” Gas Law (Van der Waals Equation):

- PV/nRT might not be equal to 1 (if it is greater, molecular volume is important; if it is less, intermolecular forces)
- another way to consider it: z = PV/RT, the **compressibility**, changes based on pressure (whereas for an ideal gas, z = 1, so it is equally easy/difficult to compress a gas regardless of how much it is already compressed)

- $(P + an^2/V^2)(V - nb) = nRT$ instead
- corrects for the assumptions made when dealing with ideal gases
- introduces two constants, (an^2/V^2) and $(-nb)$
- the first corrects for intermolecular forces (which reduce pressure by slowing molecules down before they hit the chamber walls) and the second for molecular size (some of the volume is actually taken up by the particles themselves)
- note that the first constant gets smaller (i.e. making the approximation of an ideal gas more accurate) at high volume

5.0 Phase Transitions and Equilibrium

- A molecule in the liquid phase enters the gaseous phase when its molecular energy is strong enough to pull it out of a rigid association into (essentially) none.
- Atoms are always leaving and entering to some rate; above a liquid, there is always some vapour. (**Vapour** refers to molecules in the gaseous phase above a liquid, in which most molecules are in the liquid phase. The **vapour pressure** is the pressure exerted by these molecules once equilibrium between the two phases has been attained).
- All phase changes require energy.
- Considering the closed system - there is also an atmospheric pressure that will try to “push down” on the liquid.
- If the “outwards” pressure the liquid can exert (its vapour pressure) is greater than that of the other gases in the atmosphere pushing down, then it will “defeat” the other gases and be able to take up as much space as it likes – there will be a mass exodus of molecules out of the liquid into the gaseous phase.
- Since the vapour pressure above the liquid increases with temperature, this process is linked to temperature. The temperature at which this occurs is called the **boiling point** (and the **normal boiling point** refers to the temperature associated with P = 1 atm).
- This is analogous for freezing (though in this case, intermolecular forces are generally not broken; it is rather the entropy/randomness of the molecules that is increasing as heat is applied).
- Also note that boiling and freezing can occur due to both increases in temperature and decreases in atmospheric pressure. (Also, if the pressure is low enough, the transition would be solid to gas instead).

Trouten's Rule: the entropy of vaporization for most liquids is very similar.
(Exception: liquids that form hydrogen bonds. Why might this be?)

Vapour pressures are related to temperatures by the **Clausius-Clapeyron equation**:

$$\ln\frac{P_2^*}{P_1^*} = -\frac{\Delta H_V^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(Given the enthalpy of vaporization and the vapour pressure at one temperature, the vapour pressure at any temperature can be obtained).

- In general, liquids cannot exist at temperatures above their boiling point (whatever the boiling point might be given the pressure). Any increase in the energy of the molecules will just put more of them into the gaseous phase, taking the extra energy with them.
- Superheating can occur when there are no nucleation points in the solution where bubbles can form. (A liquid can supercool for the same reason).

Note that phase transitions are also associated with entropy (liquids have more entropy than solids, and gases have more entropy than liquids).

Relative Humidity: the pressure of water in the air divided by the vapour pressure of water at the current temperature: RH = $P(H_2O)/P^*(H_2O)$

- as temperature drops, $P^*(H_2O)$ also drops while $P(H_2O)$ remains the same, so RH increases
- the **dew point** is the temperature at which $P^*(H_2O) = P(H_2O)$ and RH = 100% (and the air is saturated with water vapour)
- if the temperature is below the dew point, fog or dew will form
- as temperature rises, $P^*(H_2O)$ also rises while $P(H_2O)$ remains the same, so RH increases

Phase Diagrams

- a graph with temperature on the horizontal axis and pressure on the vertical axis
- shows what phase a substance is in, given any temperature and pressure
- approximately, solid tends to be in the top left, gas in the top right, liquid in the bottom right
- we can also move around on the graph to see what increasing/decreasing pressure/temperature would do

If you choose a temperature and pressure that puts you on the border between two phases (a **coexistence line**), the liquid is in equilibrium between those phases. If there is an equilibrium between three phases, you are at a **triple point**.

The slope of the solid-liquid coexistence line for water is negative, but for most substances it is positive. (Why is this?)

If you increase both temperature and pressure high enough along the liquid-gas line, the substance will reach the **critical point** (at the **critical temperature** and **critical pressure**) and become a **supercritical fluid**. The boundary between liquid and gas will disappear.

- compressibility of a critical fluid tends to be 0.25 to 0.35
- the ratio of normal boiling point to critical temperature tends to be 0.58 to 0.65

Intermolecular forces indicate how strongly molecules resist being pulled apart; they are dependent on the arrangement of atoms in each molecule. From weakest to strongest,

London dispersion forces

- electrons gather by chance at one end of a molecule, creating a temporary dipole
- this induces a temporary dipole in the next molecule over, resulting in an attraction for the short length of time the dipoles exist
- found in all molecules
- increase in strength with the size of the molecule (=greater probability of an asymmetric distribution)

Dipole-dipole interactions

- between polar molecules (which have permanent dipoles, as opposed to the temporary dipoles of London dispersion forces)
- increase with the polarity of the molecule

Hydrogen bonds

- only occurs in liquids
- an H bonded to N, O, or F is very electron-deficient since it's beside such an electronegative atom
- a lone pair on a neighbouring molecule will be attracted to the H
- increases with the number of hydrogens bonded to N/O/F, and with the number of lone pairs on the molecule

(Beyond these, we have molecules that associate ionically, and then molecules that associate covalently.)

6.0 Solutions

- One substance is mixed with another, at the molecular level, until the overall (molecular) composition is uniform. A solution can be solid, liquid, or gaseous.
- (If the substances are reacting with each other, you're not really forming a solution).

- Physical properties generally change. For example, freezing point depression, boiling point elevation; similarly, a solution of NaCl in water will conduct electricity but neither component can do so on its own.

- The major component of a solution is the **solvent**, and all other components are **solutes**. The more solute there is, the more **concentrated** and less **dilute** the solution becomes.
- Eventually, there will be too much solute for the solution to hold, and it will precipitate out (or bubble out, in the case of a gas). This is because the solution is formed by multiple solvent molecules surrounding and interacting with each solute molecule, and eventually there will be too much solute – all the solvent will already be taken up.

- Solutions are usually described in terms of **molarity** (mol/L, or M), the number of moles of solute per litre of solution, or **molality** (mol/kg, or m), the number of moles of solute per kilogram of solvent.
- Molarity is affected by temperature, since volume changes with temperature, while molality is not.

- Solutions are also described in terms of **mass fraction** (mass of solute over total mass) and **mole fraction** (moles of solute over total mass). Either of these can also be expressed as a percentage.

- Gas phase solutions form easily; solid phase solutions are more difficult (and usually require melting). Liquids may or may not form solutions, based on their molecular properties. If they can form a solution, the liquids are called **miscible** (if not, **immiscible**).
- Miscible liquids can be separated by **distillation**, in which the temperature is raised above the boiling point of one liquid but not above the boiling point of the other. The lower-boiling liquid will enter gaseous phase (and is drawn off) while the higher-boiling liquid stays where it is.

- (In practice, though, it's not perfect, since some molecules from the higher-boiling liquid will have enough energy to enter the gaseous phase as well).

- In general, a liquid solution of A and B will not form if the intermolecular forces between the molecules of A are stronger than those that would be formed between A and B. The molecules of A will not readily enter the weaker interactions with the other molecules.
- Thus, in general, the interactions of A with A, B with B, and A with B need to all be approximately the same strength (or A with B greater).
- Note that all of this also applies to solids and gases dissolved in liquids as well. Most gases are not very soluble in water, though, since they have weak intermolecular forces or they wouldn't be gases in the first place.

- If A with B is just a little bit weaker, you still will get a solution forming. In this case, the extra entropy from the different types of molecules being mixed together will make up the difference.

- For example, water (forms H-bonds with itself) will not dissolve hexane (forms London dispersion forces with itself), since the interactions between water and hexane would also be London dispersion forces, which are much weaker than H-bonds. The same is true for any non-polar substance in water; by contrast, water will dissolve most polar molecules, as well as ions.

This can also be viewed in terms of enthalpy.

- stronger IMFs take more energy to break than weaker IMFs, and release more energy when formed
- anything that promotes the formation of stronger IMFs will be favoured and thus spontaneous
- anything that does not promote the formation of stronger IMFs will not be favoured, and will not be spontaneous
- in the second case, an input of energy (like shaking the container) would be required*?]* (you will never make it a solution though, since there's no way you can make it truly homogenous at the molecular level by doing that)

When the A-A, B-B, and A-B intermolecular forces are exactly equal (for example, benzene and toluene), then the solution is an **ideal solution**.

Also, considering the case when gases are in solution, we get another gas law (**Henry's Law**): the amount of gas dissolved in the solvent is directly proportional to the pressure above the solvent that the gas exerts.

The constant of proportionality is **K_H**, the **Henry's Law Parameter**, which is a constant for every different solvent. $C_A = K_H P_A$

Fraction graphs*)* are graphs in which the x-axis represents mole fraction for two substances. (Take the example of water and acetone).

- the graph goes from 0 to 1 for water, and 1 to 0 for acetone
- 0 represents pure acetone, and 0.2 represents 80% acetone and 20% water (by number of molecules), 0.5 represents equal moles of each, 1 represents pure water, etc

The y-axis of a fraction graph can be anything. (When the y-axis is temperature or pressure, you have a **two-component phase diagram**, although out of those two, you are only responsible for the case of temperature).

Consider the water-acetone fraction graph with vapour pressure as the y-axis.

- if the solution were ideal, the vapour pressure of water would rise linearly moving from 0 to 1, and the vapour pressure of acetone would fall linearly moving from 0 to 1
- the total pressure (which is the sum of the other two, by Dalton's law) would move linearly as well

- this is based on Raoult's Law (the vapour pressure of each liquid is directly proportional to the amount of liquid present)

However, most solutions (like this one) are non-ideal; in such cases, there can be a positive or negative deviation from Raoult's Law.

- in general, if the two liquids are soluble in each other (like water and acetone), the deviation is negative; if they aren't, then the deviation is positive
- (use intermolecular forces to determine whether they are soluble or not – discussed above)
- the pressure exerted by each liquid will be slightly lower (negative deviation) or higher (positive deviation) than expected from Raoult's Law, which predicts a straight line
- the deviation is greatest when the proportions are close to 50%, and none when you have a pure substance (i.e. at the end of the fraction curve)

Note that Dalton's Law still holds; the total pressure will be the sum of the individual partial pressures. However, the total pressure will still deviate, since the individual partial pressures that you are adding have deviated.

Now consider graphing the melting temperature as the y-axis on the fraction graph

- the two substances do not melt at the same time, and the temperatures depend on the mole fractions – so there will be two curved lines, one above the other
- this lines actually represent a phase diagram (and the y-axis is more commonly graphed as simply temperature, which is how it was presented to you)
- note that the lines on the phase diagram are not necessarily horizontal, so this means that by moving along the graph horizontally (i.e. changing the mole fraction) can result in phase changes

A horizontal line drawn on the graph, from one curve to the other, is a **tie line**. The tie line associated with any given temperature tells you the mole fractions of the mixture in the liquid phase and solid phase at that temperature.

(Tie lines can also be drawn for the vapour pressure diagrams).

In the case where the solid phases are immiscible but the liquid phases are, the phase diagram will resemble a horizontal line with two parabolic arcs over top (presented in your lecture notes with the example of NaCl and NaBr).

- in the part below the horizontal line, both substances are solid; between the horizontal line and each parabolic arc, both are found in the liquid phase but only one in the solid phase
- tie lines on this phase diagram are applied in the same way, except that there are different places you can put it (so a tie line between a parabolic arc and the side of the graph is associated with the equilibrium between the solid phase on that side and the mixture)

The point between the two arcs, where they meet the horizontal line, is the **eutectic point**.

- as temperature changes, the mixture will always cross the horizontal line at this point
- if we try to freeze the mixture (at any mole fraction), one of the substances will start to change phase first; this moves the mole fraction of what remains closer to the fraction of the eutectic point
- in fact, the path will be along the parabolic arc, until it reaches the eutectic point (and then freezing completes, and the original mole fractions are restored (though now everything is solid)
- similarly, melting the mixture will result in the first liquid that forms to have the mole fraction associated with the eutectic point
- the path will then follow the parabolic arc until the entire mixture is liquid and the original mole fractions are restored
- if your starting mole fraction is that of the eutectic point, the substances will freeze/melt together

This also applies to solutions of solids in water. The main ideas are the same; it's just that the melting points of the pure substances will be very far apart.

You can also find the maximum possible solute concentration (i.e. the concentration of the saturated solution) at any given temperature by seeing how far to the right you can go before you reach the region where solid solute starts to occur. (Increasing the temperature will let you dissolve more).

An **azeotrope** is a mixture for which the boiling point is either at a minimum or maximum.

- changing the composition in either direction will decrease it (for a maximum-boiling azeotrope) or increase it (for a minimum-boiling azeotrope)
- if the mixture is boiled, it gives a gas with the same composition as the liquid
- this also means that distillation cannot be used to purify a minimum-boiling azeotrope (as distillation makes the composition move towards a mixture with a lower boiling point)
- maximum-boiling azeotropes can be purified by distillation since the lowest boiling point is actually the pure substance

Colligative properties are properties which are dependent on the number of molecules of solute present in a solvent, but not on the type of molecules.

- assumes that solutions are ideal and that the solute is non-volatile
- colligative properties transpire because of the changes in **entropy** of the solution when we add a solvent to a solute. By doing so, the entropy increases and requires energy to reorder
- (note that to make sure that enthalpy as close to zero as possible, we only generally consider solutions that are very dilute; accuracy decreases as concentration increases)

- colligative properties include **boiling point elevation**, **freezing point depression**, **vapour pressure lowering**, and **osmotic pressure**
- don't forget that ionic substances dissociate in solution; the number of particles includes all ions (so 0.1M NaCl dissociates to give 0.2M of particles)

Vapour pressure lowering is the same idea as with the Raoult's Law deviations above, except that only one of the substances is volatile.

- the other substance is there, but is not contributing to the overall vapour pressure; and since it decreased the mole fraction of the substance that is volatile, the overall pressure lowers thus vapour pressure of the solution can be determined using the following relationship:

$$P_{solution} = P_{solvent} = \chi_{solvent} \times P^{*}_{solvent}$$

- the amount of lowering obeys Raoult's Law, since we assume ideal solutions for colligative properties

Boiling point elevation

- a direct consequence of vapour pressure lowering
- a substance boils when its vapour pressure has risen high enough to equal atmospheric pressure
- since the vapour pressure for any given temperature is lower, you will need a higher temperature to reach the same vapour pressure
- on a phase diagram, the line between liquid and gas moves right
- $\Delta T_b = ik_bm$ (**boiling point elevation constant** times **molality** times the electrolyte factor)
- "i" is the number of ions an electrolyte dissociates into
- in practice, "i" is normally slightly less than that, since there is some small fraction which remains undissociated

Freezing point depression

- again, a direct consequence of vapour pressure lowering
- a substance freezes when the vapour pressure of the liquid has dropped to be equal to the vapour pressure of the pure solid
- since the vapour pressure for any given temperature is lower, you will reach that vapour pressure at a higher temperature
- on a phase diagram, the line between solid and liquid moves left

  $\Delta T_f = ik_fm$ (**freezing point elevation constant** times **molality** times the electrolyte factor)

Osmotic pressure

- refers to movement through a semi-permeable membrane (which solvent can pass through but solute cannot)
- flow of the solvent will be to the side with the higher concentration of solute
- the more solute particles present, the stronger the flow (and the flow is called the **osmotic pressure**)

  $\Pi = inRT/V$ (and since $n/V = M_{solute}$, we could also write that as $\Pi = MRT$)

7.0 Thermodynamics

Is used to study the transfer of energy that will determine if a given process is possible. There are three key definitions in thermodynamics:

- *System: the material we are examining*
- *Surroundings: the area outside the system*
- *Universe: is the system and the surrounding studied as a whole*

Systems:
Since we are studying the transfer of energy it is essential to understand which type of system we are studying. In an *open system* the energy and matter can be transferred, in a *closed system* only the energy can be transferred (no exchange of material), and in an *isolated system* there is no escape of energy or material. In a isolated system there is no work done on the system since there no work done to the surrounding and there is no work done on the system. However in an open system and a closed system work can be done.

State Function:
Is a time/path-independent value. Hence a state function is dependent on an initial and final state but it is independent of the path taken.

Zeroth Law of Thermodynamics:

- If state A and C are in thermal equilibrium with B then A is in a thermal equilibrium with C.
- If two objects are in thermal contact with one another then the temperature of the two objects will change till they reach the same temperature
- This concerns itself with temperature and thermal equilibrium among bodies.

First Law of Thermodynamics:

- Energy is conserved it can be changed from one form to another, however it can not be created nor destroyed.
- $\Delta U = q + w$
- ΔU = change in internal energy (J)
- q = heat released/absorbed
- w = work done on/by the system

Heat (q): is not a state function and refers to the thermal transfer

- *If exothermic process heat is departing the system therefore internal energy is decreased (-ΔU)*
- *If endothermic process heat is deposited into the system therefore the internal energy is*

increased (+ ΔU *)*

Work (w): is the transfer of energy into or out of the system

- *Work done ON a system transfers energy into the system (+* ΔU *)*
- *Work done BY the system uses energy to do work on the surroundings (-* ΔU *)*

$W = P\Delta V$

Second Law of Thermodynamics:
If a reaction is spontaneous entropy of the universe increases

Calorimetry:
Is the measure of heat change. The heat absorbed or released is given by the following equation.

$q = mc\Delta T$
m: mass
c: specific heat
ΔT : change in temperature

Special cases:

- Adiabatic: no heat enters of leaves the system (q=0)
- Isothermal: constant temperature is maintained (ΔT =0)

Heat: measured in Joules or calories

- *Endothermic reactions absorb heat energy (+q)*
- *Exothermic reactions release heat (-q)*

The second law can be integrated into the zero$^{\text{th}}$

$$\text{Heat Lost} = -(\text{Heat Gained})$$

$$m_1c_1\left(T_f - T_{1_o}\right) = m_2c_2\left(T_f - T_{2_o}\right)$$

Enthalpy:
Preformed under constant pressure (1atm). Enthalpy is used to express the heat changes at constant pressure. The change in the enthalpy is equal to the heat absorbed/released. This a state function that depends on the initial and final states but not the path used to get there. Hence

$\Delta H_{Rxn} = H_{products} - H_{reac\tan ts}$
$\Delta H_{Rxn} = \Delta H^\circ{}_f\text{(products)} - \Delta H^\circ{}_f\text{(reactants)}$

- Endothermic: ΔH_{Rxn} is positive

- Exothermic: ΔH_{Rxn} is negative
- In the standard state the heat of formation is zero (ex: O_2)
- Additive (Hess' Law)
- If the pressure is not constant then we measure the internal energy in a similar manner

Spontaneity:

A spontaneous reaction is a process that happens with no external intervention.

- The spontaneity of a reaction depends **not** ONLY on the enthalpy of reaction but also a new property **ENTROPY→ the amount of randomness in a system**
  - For any spontaneous process, the entropy of the universe must increase. ($\Delta S_{\text{universe}} > 0$)
  - Work is organized energy transfer, while heat increases the disorder on a system, thus entropy must some how depend on *q* (heat) by calculation and substitution we can derive this formula relating entropy to heat:

$$\Delta S = \frac{q_{rev}}{T}$$

    - Note, there is no entropy change for reversible processes

By integration we can further expand on the idea that heat is related to entropy. Further calculation gives us this equation relating the change in entropy to different temperature states of a substance:

$$\Delta S(T_1 \to T_2) = \int_{T_1}^{T_2} \frac{CdT}{T} = C\ln\left(\frac{T_2}{T_1}\right)$$

Phase Transitions

- Phase transitions occur at a single temperature so we can use the simplified equation:

$$\Delta S = \frac{q_{rev}}{T}$$

- Knowing that D*H* = q_p and restricting ourselves to constant pressure conditions, we can determine the entropy change for any phase transition

Ex.

$$\Delta S_v = \frac{\Delta H_{vaporization}}{T_{vaporization}}$$

- Similarly, for pressure changes, we have

-
$$\Delta S(P_1 \to P_2) = -nR\ln\left(\frac{P_2}{P_1}\right)$$

Third Law of Thermodynamics

- The entropy of a pure crystalline substance at absolute zero temperature (0 K) is zero.
- We can determine and tabulate absolute entropy values, such as tables of *entropy of formation* ΔS^{O}_{f}

Gibbs Free Energy

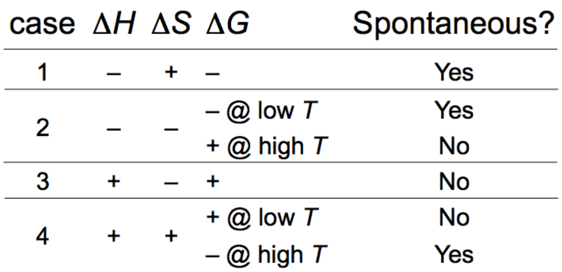
- Gibbs free energy takes into account the entropy, enthalpy and the temperature of a system to show the spontaneity of the reaction.
- Spontaneous reactions **ALWAYS HAVE NEGATIVE GIBBS FREE ENERGY (-ΔG)**
  - Δ*G* Negative → system is spontaneous as written
  - Δ*G* zero → system is at equilibrium
  - Δ*G* Positive → system is non-spontaneous as written (it may be spontaneous in the reverse direction)
- Gibbs free energy can be calculated through the following two equations:

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

$$\Delta G^o = \sum \Delta G^o{}_f(\text{products}) - \sum \Delta G^o{}_f(\text{reactants})$$

  - NOTE: this latter equation is only good for D*G at T*=25ºC since that is the temp at which values of DG_f° are tabulated.

- Since Δ*G* has to be negative for a spontaneous reaction to occur this is a good summary table showing effect of temperature, enthalpy and entropy on Gibbs free energy:



case	Δ*H*	Δ*S*	Δ*G*	Spontaneous?
1	–	+	–	Yes
2	–	–	– @ low *T*	Yes
			+ @ high *T*	No
3	+	–	+	No
4	+	+	+ @ low *T*	No
			– @ high *T*	Yes

- Since Δ*G* is zero at a phase change we can also apply Gibbs free energy to phase changes and rearrange to give us the temperature of a phase change

$$T_{\text{phase change}} = \frac{\Delta H^\circ_{\text{phase change}}}{\Delta S^\circ_{\text{phase change}}}$$

The applications for Gibbs free energy are very wide, and can be applied to many different systems and reactions. The following equations are the product of many derivations and calculations relating Gibbs free energy to other variables and conditions:

- Under non-standard conditions (because enthalpy is constant under changing pressure while entropy is not)

$$(G - G^\circ) = RT\ln\left(\frac{P}{P^\circ}\right) \qquad \text{Reaction Quotient} = \frac{[\text{products}]}{[\text{reactants}]} = Q$$

can rearrange to get

$$\Delta G = RT\ln(Q/K)$$

$$\Delta G^\circ = -RT\ln(K)$$

REARRANGE TO GET

$$K = e^{\left(\frac{-\Delta G^\circ}{RT}\right)}$$

*Don't freak out because of all these equations. They are merely rearrangements of each other relating different variables. They have NOT been tested on in the past but do appear on your formula sheet if needed.

8.0 Practice Questions

Gas Laws Questions

12.0g of liquid nitrogen is placed in an evacuated container and is allowed to boil. The pressure is later measured to be 50 kPa. How large was the container?

(What if there was also 0.2 mol of oxygen in there?)

Decreasing the ambient pressure can have negative effects on living organisms. The ultimate cause of these effects is that:

a) the molecular speed of gas molecules increases
b) by Boyle's Law, the decrease in pressure also causes a decrease in the volume of oxygen in our tissues
c) by Henry's Law, less gas is able to dissolve in our blood
d) the gases in our system are not ideal gases
e) by the Ideal Gas Law, P has decreased while nRT has remained constant, so the volume of CO_2 in our tissues increases

In a parallel universe, the Universal Gas Constant is 16.62 kPa L K^{-1} mol $^{-1}$. (All other parameters are the same). We would expect

a) the average temperature of the universe to be higher
b) Boyle's Law to be invalid
c) the Ideal Gas Law to be invalid
d) intelligent pink rabbits
e) none of the above

Solutions Questions

Which of these melts at the lowest temperature?

Diethyl ether, chlorohexane, acetone, ammonium sulfate

What about the highest?

Dimethylformamide (DMF) has the structural formula $(CH_3)_2NCOH$. Which of the following can form hydrogen bonds with DMF?

H_2O, CH_2O, CH_3CH_2OH, $CCl_3CH_2CH_3$, $CaCl_2$

(There is more than one answer).

Acetate ion forms dimers in water. If an aqueous solution of 0.1M sodium acetate is formed, what is the value of the electrolyte factor for the purposes of colligative property calculations?

Which of these statements is false?

a) ethylene diol ($HOCH_2CH_2OH$) is soluble in water
b) a solution of chloroform ($CHCl_3$) and acetone $(CH_3)_2CO$ does not involve hydrogen bonds
c) a solution of nitrogen dioxide (a reddish-brown gas) in carbon dioxide (a colourless gas) will have a homogenous brown appearance
d) a solution of 0.3M sucrose in ethanol has a lower vapour pressure than a solution of 0.2M sucrose and 0.2M fructose in ethanol
e) if you come across a container of fluorine gas in the lab, dropping a burning match into it is a bad idea

Phase Transitions Questions

Dr. Mombourquette has synthesized two compounds, both liquids; together, they form Mixture X, which is both a minimum-boiling and a maximum-boiling azeotrope (it has both a maximum and a minimum on a melting point fraction curve). If distillation is the only technique available to us,

a) we can always purify this mixture
b) we can purify it for some initial temperatures but not others
c) we can purify it at some initial compositions but not others
d) we can purify it if the liquids are both polar
e) we can never purify this mixture

Carbon in the solid phase exists as large networks of covalently linked carbon atoms, which can take on two distinct forms, graphite and diamond. (Applying very high pressure to graphite will produce diamond). We would expect the phase diagram for carbon to show

a) that decreasing the pressure for liquid carbon will produce graphite
b) that graphite melts between 50 and 100 °C
c) no gaseous phase

d) two triple points
e) none of the above

Lewis Structures Questions

What is wrong with the structural formula $CH_3COHCOH_2$?

$SOCl_2$, thionyl chloride, is used in the production of organic chlorine-containing compounds. How many major resonance structures does it have?

PRACTICE MULTIPLE CHOICE QUESTIONS

1. What is the change in internal energy of a system in which 25 kJ of work is done on the system by the surroundings and 15 kJ of heat is given up by the system to the surroundings?

a) +35 kJ
b) -10 kJ
c) -35 kJ
d) +10 kJ
e) +25 kJ

2 The molar mass of a gas wihich has a density of 1.429 g/L at 101.3 kPa and 273 K is:

a) 16 g/ mol
b) 32 g/mol
c) 14 g/mol
d) 28 g/mol
e) 8 g/mol

3. Calculate the value of ΔH^o for the reaction

$CuCl_2(s) + Cu(s) \rightarrow 2\ CuCl(s)$

given the information

$Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$ $\Delta H_f = -206$ kJ/mol

$2\ Cu(s) + Cl_2(g) \rightarrow 2\ CuCl(s)$ $\Delta H_f = -36$ kJ/mol

a) -242 kJ/mol
b) +170 kJ/mol
c) -170 kJ/mol
d) -188 kJ/mol

e) +242 kJ/mol

4. What are the hybrid orbitals used in explaining the bonding of boron in BF_3?

a) sp^3d
b) sp^2
c) sp^3d^2
d) sp
e) sp^3

5. What is the energy of an X-ray photon with a wavelength of 0.154 nm?

a) 1.02×10^{-43} J
b) 1.95×10^{18} J
c) 1.02×10^{-33} J
d) 1.29×10^{-15} J
e) 1.54×10^{-9} J

6. What is the partial pressure of benzene in the vapour phase in equilibrium with a 29%, by mass, solution of benzene (C_6H_6) in octane (C_8H_{18}) at 20°C? The vapour pressure of benzene at 20°C is 10kPa.

a) 2.9 kPa
b) 10 kPa
c) 25 kPa
d) 5.2 kPa
e) 3.7 kPa

7. 2.227 g of copper oxide when heated strongly in hydrogen gave 1.978 g of pure copper. What is the empirical formula of the copper oxide?

a) Cu_2O
b) Cu_2O_3
c) CuO
d) CuO_2
e) Cu_3O_2

8. Which of the following molecules is non polar?

a) SeO_2
b) NH_3
c) H_2O
d) ClF_5
e) XeF_4

9. The chemical formula for aluminum sulfite is:

a) Al_2SO_3
b) $Al(SO_3)_3$
c) $Al_2(SO_3)_3$
d) $Al_3(SO_3)_2$
e) none of these

10. The normal boiling point of chloroform ($CHCl_3$) is 61.2°C. At a pressureof 1.1 atm, the boiling point is expected to be:

a) <61.2°C
b) >61.2°C
c) 61.2°C
d) 61.1°C
e) none of these

11. Which of the following compounds would be expected to have the highest normal boiling point (the strongest intermolecular bonds)?

a) I_2
b) ICl
c) HI
d) KI
e) NH_3

12. What is the mole fraction of the solute in a 4.45 molal aqueous (water solvent) solution?

a) 0.074
b) 0.080
c) 0.223
d) 0.437
e) 0.666

13 The ground state electronic configuration for S^{2-} is:

a) $1s^22s^22p^6$
b) $1s^22s^22p^62d^8$
c) $1s^22s^22p^63s^23p^2$
d) $1s^22s^22p^63s^23p^4$
e) $1s^22s^22p^63s^23p^6$

14 Which of the following statements is true for a solution consisting of two volatile components in which the attractive forces between solute and solvent molecules are stronger than solute-solute or solvent-solvent attractive forces?

a) Raoult's Law is obeyed
b) A positive deviation from Raoult's Law is observed.
c) A negative deviation from Raoult's Law is observed.

15. In which of the following substances should hydrogen bonding contribute significantly to the attractive interactions among the molecules?

a) H_2O (l)
b) HF (l)
c) NH_3 (l)
d) All of these
e) None of these

16. In a given atom, the maximum number of electrons which can have the quantum numbers n=4, l=2, m_l=0 is:

a) 0
b) 2
c) 6
d) 10
e) 32

17. The molecular shape (arrangement of the atoms) for the molecule PF_3 can best be described as:

a) trigonal pyramidal
b) trigonal planar
c) trigonal bipyramidal
d) tetrahedral
e) T-shaped

18. A possible Lewis structure for hydrogen cyanide is [H:C:::N:] where (::: represents a triple bond). The formal charges on the H, C and N atoms respectively are:

a)-1, 0, 0
b) 0, -1, 0
c)0, 0, -1
d) 0, 0, 0
e)-1, +1, -1

19. Which set of quantum numbers could describe an electron in a 3d orbital?

a) $n=3, l=0, m_l=0, m_s=1/2$
b) $n=2, l=2, m_l=1, m_s=1/2$
c) $n=3, l=2, m_l=-1, m_s=1/2$
d) $n=3, l=1, m_l=0, m_s=1/2$
e) $n=3, l=2, m_l=3, m_s=1/2$

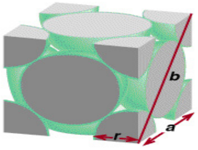
20. Which of the following is a possible set of n, l, m_l, and m_s quantum numbers for the last electron added to form an As^{3-} ion?

a) $n=3, l=1, m_l=-1, m_s=1/2$
b) $n=2, l=0, m_l=0, m_s=-1/2$
c) $n=4, l=2, m_l=0, m_s=-1/2$
d) $n=4, l=1, m_l=-1, m_s=1/2$
e) $n=5, l=0, m_l=0, m_s=1/2$

21. The bond between the carbon atoms in ethyne, HCCH, consists of:

a) a sigma (σ) bond only
b) three pi (π) bonds
c) two sigma (σ) bonds and one pi(π) bond
d) one sigma (σ) bond and two pi (π) bonds
e) one sigma (σ) and one pi (π) bond

22. The unit cell indicated below



a) represents a simple cubic structure
b) contains 4 octahedral holes and 4 tetrahedral holes
c) represents a body centre cubic structure
d) contains 2 atoms per unit cell
e) contains 8 tetrahedral and 4 octahedral holes

23. Atom A has 3 electrons in its valence shell and atom B has 6 electrons in its valence shell. The formula expected for a compound of A and B is:

a) A_3B_2
b) A_3B_6
c) B_2A
d) A_2B
e) A_2B_3

. Photons of minimum energy 486 kJ/mol are needed to ionize sodium atoms. If light of 600 kJ/mol is used, what is the velocity of the emitted electrons?

a) 3.75 x 10^{-3} m/s
b) 6.45 x 10^{-5} m/s
c) 2.53 x 10^{2} m/s
d) 6.45 x 10^{5} m/s
e) 3.75 x 10^{4} m/s

25. A ground state neutral atom, whose atomic number is 13, contains:

a) 7 electrons is “s” orbitals
b) some electrons in “d” orbitals
c) 7 electrons in “p” orbitals
d) 2 electrons in the outermost orbital
e) 5 electrons in its valence shell

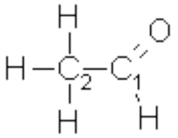
26. An ideal solution is composed of two substances, X and Y. The mole fraction of Y in the liquid phase is 0.40. Pure liquid substance X has a vapour pressure of 0.80 atm and pure Y is involatile. What is the vapour pressure of X over the solution?

a) 0.24 atm
b) 0.32 atm
c) 0.48 atm
d) 0.80 atm
e) 1.20 atm

27. The density of diamond (which is made up entirely of carbon atoms) is 3.51 g/cm^3. Given that the diamond lattice has a unit cell that is cubic in nature and contains 8 atoms, determine the lattice parameter (one side) of the diamond cell.

a) 2.80 x 10^{-8} cm
b) 3.57 x 10^{-8} cm
c) 4.46 x 10^{-9} cm
d) 4.54 x 10^{-23} cm
e) 3.80 x 10^{-23} cm

28. How do we describe the hybridization around the carbon atoms (labelled 1 and 2) in the following molecule?

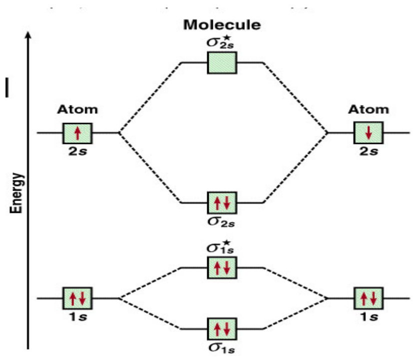


a) sp^3 around both C_1 and C_2
b) sp^2 around both C_1 and C_2
c) sp around C_1 and sp^3 around C_2
d) sp^2 around C_1 and sp around C_2
e) sp^2 around C_1 and sp^3 around C_2

29. A grey, lustrous metal was examined using X-ray diffraction. The results of the analysis indicated that this metal is an element and crystallizes in the body centred cubic (bcc) structure, with a lattice parameter of 0.288 nm (1 nm = 10^{-9}m). The density of the metal was found to be 7.23 g/cm^3. What metal is this?

a) Cr
b) Fe
c) Rh
d) Na
e) Al

30. For the following correlation diagram, it can be concluded that.



a) Bond order is 3, and the substance is paramagnetic
b) Bond order is 1 and the substance is paramagnetic
c) Bond order is 3, and the substance is diamagnetic
d) The molecule is Li_2
e) The molecule is B_2

31. The coordination number is the number of:

a) tetrahedral holes in a unit cell
b) atoms or ions in a unit cell
c) molecules in a crystal lattice
d) octahedral holes in a unit cell
e) neighbours in contact with an atom or ion in a crystal lattice

32 Gallium and sulfur react directly to form gallium sulfide, Ga_2S_3. If we heat 2 mol of gallium and 2 mol of sulfur, what is the maximum number of moles of Ga_2S_3 that can be formed?

a) 1/3
b) 2/3
c) ½
d) 1
e) 2

33. An ore contains 1.34% Ag_2S, by mass. How many grams of this ore would have to be processed to obtain 1.00 g of pure silver, Ag?

a) 74.6 g
b) 85.7 g
c) 107.9 g
d) 134.0 g
e) 171.4 g

34. What is the core charge on a Cl^- ion?

a) -1
b) 0
c) +7
d) +8
e) +17

35. The "nb" term in the van der Waals equation (see information sheet) allows for the fact that:

a) real gases liquefy
b) molecules in real gases have a finite mass
c) molecules in real gases have a finite volume
d) molecules in real gases attract each other
e) molecules in real gases have dipole moments

9.0 Chemical Equilibria

Equilibrium: Defined as a dynamic balance of forward and reverse processes

A chemical equilibrium must satisfy these: i) the system is **closed** ii) Shows no visible evidence of change iii) Reached through a spontaneous process.

Properties of a system at equilibrium: there is a continuous exchange between reactants and products at the molecular level with out a change in concentration **Caveat:** Absence of observable change *does not prove* the existence of equilibrium because the reaction may just be really slow or a steady state may exist (where the products or reactants are being removed/added)

The Equilibrium Constant:

Note: Equilibrium constant will be obtained regardless of direction from which it was approached (when temperature is constant)

We will focus on this general reaction formula where the capitals are molecules and the lowercase letters represent the molar coefficients: (*note the arrow represents a **double headed equilibrium arrow**)

- The equilibrium constant is based on the fact that regardless of the original concentrations of A B C or D, the ratio of **Products/Reactants** is constant and this is known as the **Law of mass action**.
- The equilibrium constant expression (K_{eq}) is represented here: ***AT EQUILIBRIUM!**

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

- **Anything with a concentration of 1 is not included in the equilibrium expression (ex. $NaCl_{(s)}$ or $H_2O_{(l)}$)**
- If K is large (ex 1000 or higher) [products]>>>[reactants] indicating a reaction that goes close to completion similarly if K is small 0.001 [products]<<<[reactants] indicating that reaction doesn't go that well in *that direction*
- If K=1 the concentrations of both products and reactants are close to equal

K_{eq} can also be described in terms of partial pressure if the reaction contains gaseous species. Instead of using concentrations as before we will replace them with the partial pressures of the gasses. K_P (*K using partial* ***p****ressures***) is related to K_C** *(K using* ***c****oncentrations)* **by this equation:** *(R is the ideal gas constant and T is temperature in Kelvin)*

$$K_P = K_C(RT)^{(c+d)-(a+b)}$$

- In addition to K_P K_C there is a **thermodynamic equilibrium constant** represented by **K**

- **K** is a unit less constant found by using ratios of effective partial pressures to a reference pressure of 1.0atm (or using concentrations with a reference concentration of 1.0mol/L. These ratios are called **activities**
- Recall that at any temperature $\Delta G^o = \Delta H^o - T\Delta S^o$ can be calculated for substances *in their standard states*
- For a reaction (ex. A+B→C)where the molecules involved are NOT in their standard states $\Delta G = \Delta G^o + RT\ln\left(\frac{[C]^c}{[A]^a[B]^b}\right)$ and at equilibrium $\Delta G = 0$ and $\frac{[C]^c}{[A]^a[B]^b} = K$

  Therefore: $\Delta G^o = -RT\ln K$ rearranged to $K = e^{-(\Delta G^o/RT)}$

- We use the thermodynamic equilibrium constant because it can be calculated from ΔG° (Which is from ΔH° and ΔS°) which means the extent of equilibrium can be found using thermodynamic data (no experiments required)

Relative Activity

The activity of a substance refers to the effectiveness of a substance in a reaction to influence equilibrium.

- The relative activity is the activity relative to activity in standard state.
- Standard sate activities for solutions is 1.0mol/L and for gasses is 1.0atm (*note: **in this course we will assume that all systems are ideal so** since both of these values are 1 when you calculate activities when finding K it doesn't change the concentration or pressure values (dividing by one) but rather cancels out the units)
  - In non-ideal solutions different parts of the solution may interact with each other and not be available to affect equilibrium this is the **effective concentration** which are called activities.
    - In sufficiently dilute solutions stoichiometric concentrations and effective concentrations are the same
    - Pure liquids and pure solids ($H_2O_{(l)}$ and $NaCl_{(s)}$) are assigned relative activities equal to 1

Ex. To find the activity of hydrogen if it's partial pressure is 2.9atm

$$a[O_2] = \frac{2.9atm}{1.0atm} = 2.9$$

Types of Equilibria

Homogeneous equilibrium→ when all reactants and products are all of the same phase

Heterogeneous equilibrium→ when **not** all reactants and products are all of the same phase

- In a heterogeneous system involving a gas the final equilibrium is independent of the amount of pure solid or liquid there is because they have relative activities (and concentrations) of 1

Reaction Quotient

- <u>Calculated in the same way as K</u> **except** it can be calculated at any point during the reaction (not just at equilibrium like K) which allows us to determine whether the reaction is at equilibrium and if it is not we can determine which way the reaction will shift to establish equilibrium:
  - **If Q=K the system is at equilibrium**

- **If Q>K** there is greater product than reactant and reaction will shift towards the reactants (Left)
- **If Q<K** there is greater reactant than product and the reaction will shift towards the products (right)

Example Q calculation: $Q = \frac{[\text{products}]}{[\text{reactants}]}$

Factors Effecting Equilibrium

Le Chatelier's Principle→ the reaction will shift in response to a change to re-establish equilibrium

- Pressure will never change the value of **K** but changing pressure (by removing or adding a substance in the system) the reaction will shift to restore equilibrium
- Temperature will **always** change the value of **K** because adding heat to a system will change the rate of forward reaction differently than the reverse rate (example: adding heat to a highly exothermic reaction generally will slow the forward reaction and decrease value of K because there will be more reactants than products relatively at equilibrium)
- When the equation is reversed **K** becomes **1/K**
- When a reaction equation is multiplied by a constant (*n)* the equilibrium constant becomes $\mathbf{K^n}$
- When you add two equilibrium equations together the new **K** value is equal to :
  $\mathbf{K_{total}=K_1}$⍰$\mathbf{K_2}$

To solve equilibrium problems we use ICE tables where "I" refers to ***i****nitial concentrations "C" refers to the* ***c****hanges that take place and "E" refers to the equilibrium concentrations composed of the initial concentrations and the changes that have occurred to establish equilibrium*

Occasionally we run into some problems and we must assume a reaction goes to completion and then do another ICE table with the reverse reaction to find equilibrium concentrations

10.0 Thermodynamics and Equilibrium

Thermodynamics refers to a chemical reaction as a flow of atoms from reactants to products carried out at constant pressure and temperature

Recall: $\Delta G<0$ means the reaction is spontaneous in the forward direction and at equilibrium $\Delta G=0$

- ΔG refers to the free energy available to do work (TΔS is the unavailable energy lost from the reaction in the form of heat

Isothermal Processes (for reactions in the gas phase)

Remember that if a pressure of an ideal gas is changed from P_1 to P_2 at constant T:

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

And the reaction is *isothermal* so $\Delta H=0$ and therefore

2) $\Delta G = -T\Delta S$

And for an isothermal reaction entropy can be calculated solely from the partial pressures

3) $\Delta S = -nR\ln\frac{P_2}{P_1}$

And substituting equation three into equation two we get the complete equation:

4) $\Delta G = nRT\ln\frac{P_2}{P_1}$ ***note from before the pressure ratio is equal to **K** the equilibrium constant

And remember from before this equation:

$$\Delta G = \Delta G^o + RT\ln\left(\frac{[C]^c}{[A]^a[B]^b}\right)$$

Example: For a chemical reaction involving gases is could be shown that for the following reaction:

$$aA(g) + bB(g) \Leftrightarrow cC(g) + dD(g)$$

$$\begin{aligned}\Delta G \quad &= \Delta G^o + RT\ln[(P_C/P_{ref})^c(P_D/P_{ref})^d]/[(P_A/P_{ref})^a(P_B/P_{ref})^b] \\ &= \Delta G^o + RT\ln[a(C))^c(a(D))^d]/[(a(A))^a(a(B))^b]\end{aligned}$$

These equations would be used to determine the free energy for a chemical reaction where the reactants and products are not in their standard states (note the use of activities by dividing by a reference pressure)

- The standard state refers to a gas with a pressure of exactly 1 bar or a solution with a concentration of exactly 1M and when all components are in their standard states $\Delta G = \Delta G^o$

At equilibrium

Involving solutions ΔG=0 and therefore ΔG° is calculated the same fashion as shown in the equilibrium section; in total:

$$\Delta G = -RT\ln K$$

Where the **K** refers to **K_C**

Similarly if this were a reaction involving gasses $K=K_P$

Relationship between ΔG° and the Extent of Reaction

Because $K = e^{-\left(\Delta G^o/RT\right)}$ these relationships can be made:

- If ΔG° is large and negative K will also be large meaning at equilibrium there will be more products than reactants
- If ΔG° is large and positive K will be very small, meaning at equilibrium there will be much more reactants than products
- If ΔG° is close to zero then K is close to 1 which means that you have similar amounts of product and reactant at equilibrium

In a reaction the K value changes with temperature. Using the *van't Hoff equation* we can determine the K at any temperature:

$$\ln\frac{K_2}{K_1} = \frac{-\Delta H^o}{R\left[1/T_2 - 1/T_1\right]}$$

Alternatively we can calculate K by determining the enthalpy and entropy values to find free energy and use this equation:

$$K = e^{-\left(\Delta G^o/RT\right)}$$

11.0 Acid and Base Chemistry

Arrhenius Definition

Acid: substance that releases hydrogen ions when dissolved in water.

ex. $HCl \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Base: substance that releases hydroxide ions when dissolved in water.

ex. $NaOH(s) \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

Arrhenius Neutralization

Suggests that neutralization reactions between an acid and base produce a salt and water.

ex. $HCl_{(aq)} + NaOH(aq) \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

The net ionic equation for this reaction demonstrates the neutralization of the acid and base ions.

ex. $H^+ + OH^- \rightarrow H_2O_{(l)}$

Bronsted-Lowry Definition

Acid: substance that donates a proton (hydrogen ion).

Base: substance that accepts a proton

Every acid - base reaction occurs in a conjugate pairing

$RCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons RCOO^-_{(aq)} + H_3O^+_{(aq)}$

Acid Base Conj. Base Conj. Acid

The Conjugate base is what is left behind after the acid donates a proton

The Conjugate acid is what is created after the base accepts a proton.

Identifying an acidic Hydrogen

The proton to be donated will usually appear sequestered on one side of the chemical formula.

ex. CH_3COOH or H_3O^+

These are the hydrogen ions that are most susceptible to donation

Often due to proximity to highly electronegative substance (oxygen in carboxylic acid)

The most recent and accurate definition of an acid that we have today was proposed by LEWIS. Hence, they are aptly named “Lewis acids”. A new definition was needed because although the Bronsted-Lowry definition showed the importance of hydrogen transfer in acids and bases, it could not explain the basic effects exhibited by NH3 in solution or the acidic effects observed by BH3 in a reaction. The Lewis definition explains that:

- A Lewis acid is an electron pair acceptor
- A Lewis base is an electron pair donor

For example, OH^- and NH_3 are Lewis bases, because they can donate a lone pair of electrons.
Some compounds, such as H_2O, are both Lewis acids and Lewis bases, because they can both accept a pair of electrons and donate a pair of electrons, depending upon the reaction. That being said, all Bronsted-Lowry acids and bases are Lewis acids/bases BUT NOT THE OTHER WAY AROUND.
Ex. A simple example would be BCl3 which the boron is electron DEFICIENT (due to the high negative charge on the Cl atoms). Therefore it wants to accept an electron pair which by definition makes it an acid (in lewis terms). However, because it does not create hydronium or hydroxide ions OR donate a proton it is technically NOT an acid by Arrhenius or Bronsted-Lowry definition.

Water as both an acid and a base

Amphiprotic: substance that can both donate and receive protons.

Water is amphiprotic, so it can act as **both an acid and a base**.

Self-Ionization of Water

$$2\ H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + OH^-_{(aq)}$$

Water acts as both an acid and a base towards itself to create a hydroxide and hydronium (H_3O^+) ion

The equilibrium constant K_w for this process is the product of the two ion concentrations, which is a known constant at 25 °C.

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

Strong Acids and Bases

A strong acid or base completely ionizes in an aqueous solution.

A strong acid is fully deprotonated
A strong base is fully protonated

Favoured direction of acid-base reactions is from the stronger acid or base to the weaker conjugate partner.

List of Strong Acids and Bases

Acids

- HCl
- HBr
- HI
- H_2SO_4
- HNO_3
- $HClO_3$
- $HClO_4$

Bases

- NaOH
- KOH
- RbOH
- CsOH
- $Ca(OH)_2$
- $Sr(OH)_2$
- $Ba(OH)_2$

pH Scales

pH or “Potential of Hydrogen ion in solution” scale

Logarithmic scale for determining the concentration of hydrogen ions (or hydronium ions) within a given solution.

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

which can be rearranged to solve for the hydronium ion concentration if pH is given to form

$$[H_3O^+] = 10^{-pH}$$

The general pH scale is centered at 7

- $pH = 7$ is neutral
- $pH < 7$ is acidic
- $pH > 7$ is basic

pOH or “Potential of Hydroxide ion in solution” scale

$$pOH = -\log[OH]$$

pOH is related to pH via the negative log of the equilibrium constant for the self-ionization of water as long as the solution is at 25° C.

$$pK_w = pH + pOH = 14.00$$

Weak acids and bases

A weak acid or base does not completely ionize, but instead establishes an equilibrium.

Acid Dissociation Constant (K_a)

A general formula for dealing with acids is,

$$HA_{(aq)} + H_2O \rightleftharpoons A^-_{(aq)} + H_3O^+$$

where HA is the initial acid   water is acting as the base
A^- is the conjugate base   Hydronium ion is conjugate acid

$$K_a = [A^-][H_3O^+] / [HA]$$

This is the equilibrium constant for acids. Note that water is omitted because it has an activity of 1.

This value can be used to determine the strength of an acid. A larger acid dissociation constant means more protons in solution, so greater acidity.

A standard value used is the pKa, which is the negative log of the acid dissociation constant. The lower the pKa, the stronger the acid.

Base Dissociation Constant (K_b)

Another general formula for bases is,

$B_{(aq)} + H_2O \rightleftharpoons HB^+_{(aq)} + OH^-$

where B is the initial base		water is acting as the acid

HB^+ is the conjugate acid		Hydroxide ion is conjugate base

$K_b = [HB^+][OH^-] / [B]$

As with acids, the higher the K_b the stronger the base and the opposite for the pK_b value.

The acid and base dissociation constants for a reaction are related to each other via the negative log of the self-ionization constant of water.

$$pK_a + pK_b = pK_w$$

Note that the stronger the original acid or base the weaker its conjugate partner will be.

Polyprotic acids

Save for sulphuric acid, all acids containing multiple, ionisable hydrogens are considered weak.

For example H_3PO_4 undergoes three different deprotonations, each one slightly weaker than the last.

Each deprotonation is weaker because a departing hydrogen leaves behind a negative charge on the phosphate group, which holds more closely to its remaining hydrogens.

So we can assume that

A) most of the protons released into solution were released during the first deprotonation.
B) Little $H_2PO_4^-$ is used up for second deprotonation so the concentration of this species is equal to the concentration of hydronium ions.
C) $[HPO_4^{2-}]$ which is the product of the second deprotanation is roughly equal to the acid dissociation constant of this second reaction (Ka_2).

12.0 Hydrolysis of Salts

Acidic and basic solutions may also be produced by the hydrolysis of salts. Meaning that occasionally when a salt dissolves it can react with water to produce acidic or basic solutions.

- A salt is an ionic compound made up of an atom(s) of a non-metal bonded a metallic atom. They arise from the neutralization reaction of an acid and a base. Salts usually contain an anion and cation bonded forming a neutral compound.
- In solutions these soluble salts break into their anions and cations

General Rules:

i. Salts containing the anions of **weak acids** will form **basic** solutions
ii. Salts containing the cations of **weak bases** will form **acidic** conditions
iii. Anions of **strong acids** and the cations of **strong bases** react little with water creating **neutral** solutions (ex. Cl^- from HCl, Na^+ from NaOH)

For calculations involving salts use Ka values and ICE tables to determine pH.

- If a salt contains an anion and cation which experience hydrolysis you must look at both hydrolysis reactions to determine pH.
- *Usually* the reaction with the larger K value will determine whether the pH of the solution is greater or less than 7:
  - Ka>Kb, the pH will be <7 (solution is slightly acidic)
  - Kb>Ka, the pH will be >7 (solution is slightly basic)

13.0 Common Ion Effect & Titration

Occurs when two different compounds release a common ion between them when put into an aqueous environment.

> ex. CH_3COOH is a weak acid that, when put into water, donates a hydrogen to create an acidic solution. This reaction creates a hydronium ion and an acetate ion (CH_3COO^-).
>
> $NaCH_3COO$ is a salt that when dissolved in water also releases an acetate ion.

The presence of a common ion impacts the acid/base reaction.

> According to Le Chatelier's Principle, an equilibrium will shift to compensate if there is an excess at one side of the equation.
>
> So, with the increase in acetate anion, the acid/base equilibrium will shift to favour the reverse process.
>
> This will alter the pH.
>
> > ex. The weak acid CH_3COOH when in the same solution as $NaCH_3COO$ will experience an increase in pH, as the reverse reaction is favoured and the amount of H_3O^+ being produced is lowered.

Buffer Solutions

- Is a solution that resists changes in pH with the addition of acid or base
- Usually are effective because of the common ion effect

→ *To make a buffer solution either:*

i. Add a weak acid to a salt containing its conjugate base
ii. Add a weak base to a salt containing its conjugate acid

- Effective buffer solutions have concentrations of the weak acid (or base) and its corresponding conjugate base (or acid) as equal as possible.
- Ensuring this will contain an acid with a pKa close to the desired pH

**note: if $Ka=[H_3O^+][A^-]/[HA]$ and $[A^-]=[HA]$

then Ka= $[H_3O^+]$=pH

The Henderson-Hasselbalch equation can be used to approximate pH when the original concentrations are known (or can be used to prepare buffer solutions with a certain pH value). **This equation is:** (note the subscript “o” stands for “original”)

$$pH = pKa + \log \frac{[A^-]_o}{[HA]_o}$$

Acid-Base Titrations:

→ A titration is performed when you want to determine the concentration of an unkown acid or base by using a precise volume of another acid or base which you know the concentration of

- An indicator is added to signal the point at which the reaction is complete. Usually observed as a change in colour
- Different indicators change colour at different pH
- When choosing an indicator it is **very** important to pick a pH indicator that changes colour at a pH somewhere along the vertical portion of the pH curve

End point→ occurs when the acid base indicator changes colour indicating that the **stoichiometric amount** of the first reactant has been added to the second.

Equivalent point→ is the point in titration where the solution has been neutralized (for every mole of hydroxide a mole of hydronium has been added)

- When the equivalent point has been reached the pH is not always 7(because of the salt formed!)

Determining the pH of a point on the titration curve:

- Determine the number of moles of each reactants present (n=CV)
- Determine which reagent is in excess and find how much of the reactant and product is left when the reaction has stopped
- Determine the concentrations of all remaining substances in solution (C=n/V)
- Finally, identify solution type→ strong acid solution, buffer solution, salt solution etc. and determine pH

14.0 Electrochemistry

What’s important:

- Redox reactions
  - Identify reduction and oxidation
  - Balancing redox reactions
- Galvanic and Electrolytic cells
  - Recharging, electroplating, etc.
- Cell condition calculations
  - Standard and nonstandard conditions

Redox Reactions:

- A reaction involving changes in oxidation state of molecules involved

  - Example: $CH_3CH_2OH + MnO_4^- \rightarrow CH_3CH_2COOH + MnO_2$
  - Carbon 3 has increased in oxidation state (oxidation)
  - Manganese has decreased in oxidation state (reduction)

- Two easy ways to remember redox definitions:

  - LEO (Loss of Electrons is Oxidation) the lion says GER (Gain of Electrons is Reduction)
  - OIL (Oxidation Is Loss) RIG (Reduction Is Gain)
  - "Agent" means the opposite!
  - "Reducing Agent" is oxidized
  - "Oxidizing Agent" is reduced

- Treat the compound as ionic – the more electronegative element gets the electrons
- Example: SO_4^{2-}, the sulfate anion
  - Oxygen is more electronegative then sulfur, therefore oxygen will satisfy its octet first, placing each oxygen at the -2 state
  - The sum of sulfur and oxygen oxidation states must add up to total charge, so (-2)*4+x=-2, x=?
  - Sulfur's oxidation state in sulfate is +6
- $H_2\ O_2$ - hydrogen peroxide
  - Oxygen is at -1 (usually -2)
- $HOCl$ – hypochloric acid
  - Chlorine is at +1 (usually -1)
- Always check electronegativity on the given periodic table
- Sum of oxidation states must add up to total charge

Balancing redox reactions:

- $I^- + IO_3^- \rightarrow I_2$
- Step 1: Identify oxidation states of reagent
  - I- is at -1
  - I in iodate is at +5
- Step 2: Identify oxidation states of product
  - I2 is at 0
  - Oxidation of iodide ion
  - Reduction of iodine in iodate ion
- Step 3: Write half-reactions
  - $2I^- \rightarrow I_2 + 2e^-$
  - $2IO_3^- + 10e^- \rightarrow I_2$
- Step 4: Determine conditions
  - Acidic: use H+ and H2O to balance
  - Basic: use OH- and H2O to balance
  - If unstated: assume acidic
- Step 5: Balance
  - $2I^- \rightarrow I_2 + 2e^-$
    - X5 to balance electrons
    - Result: $10I^- \rightarrow 5I_2 + 10e^-$
  - $2IO_3^- + 10e^- \rightarrow I_2$

        - Add 12 H+ to balance charge on left
        - Add 6 H2O to balance elements on right
        - Result: $12H^+ + 2IO_3^- + 10e^- \rightarrow I_2 + 6H_2O$
- Step 6: Add Half-Reactions
    - $10I^- \rightarrow 5I_2 + 10e^-$ (oxidation)
    - $12H^+ + 2IO_3^- + 10e^- \rightarrow I_2 + 6H_2O$ (reduction)
        - Cancel out across the reaction arrow
        - Your electrons should ALWAYS cancel
    - Result: $12H^+ + 2IO_3^- + 10I^- \rightarrow 6I_2 + 6H_2O$
        - Simplify by dividing by 2
    - $6H^+ + IO_3^- + 5I^- \rightarrow 3I_2 + 3H_2O$

An example in base

- $Fe(OH)_2 + H_2O_2 \rightarrow Fe(OH)_3 + H_2O$
    - Iron increases in oxidation from +2 to +3
    - Oxygen decreases in oxidation from -1 to -2
    - Write half-reactions:
        - $Fe(OH)_2 \rightarrow Fe(OH)_3 + e^-$ (oxidation)
        - $H_2O_2 + 2e^- \rightarrow 2OH^-$ (reduction)
    - Balance charge and elements
        - $2Fe(OH)_2 + OH^- \rightarrow 2Fe(OH)_3 + 2e^-$
        - $H_2O_2 + 2e^- \rightarrow 2OH^-$
    - Result:

$2Fe(OH)_2 + H_2O_2 \rightarrow 2Fe(OH)_3$

Galvanic and Electrolytic cells:

- Essentially, batteries
    - Galvanic cells:
        - Spontaneous (energetically favoured)
        - Release energy
    - Electrolytic cells:
        - Nonspontaneous (energetically disfavoured)
        - Consume energy
- Cell notation:
    - Anode|Electrolyte||Electrolyte|Cathode
    - Zn(s)|ZnSO4(aq)||CuSO4(aq)|Cu
- Anode-Oxidation, Cathode-Reduction
    - An (Anode) Ox (Oxidation) and a Red(Reduction) Cat (Cathode)
- $Q = It$
    - Q represents charge flow in Coulombs
    - I represents current in Amps
    - t represents time in seconds
- Each mole of electrons possess 96485 C
- This can be used to calculate changes in mass of electrodes

Example:

A Cu-Zn cell has 1.0 A of current passed through it for 10 hours at standard conditions. How much copper is gained?

- Step 1: Balance the redox reaction

  - Step 2: Solve Q=It – Q=3600
  - Step 3: Convert charge to electrons – 3600/96485 = 0.037 mol of electrons
  - Step 4: Determine mass – 2 mols of electrons are required for each mol of Cu, therefore 0.0185 mol Cu is gained
- All electrodes are measured against a hydrogen electrode to determine their potential under standard conditions
  - Positive potential means greater reductive power (more powerful cathode)
- Standard potential:
  - 1 M concentration
  - 100 kPa (1 atm) pressure
  - Inert metal electrode used for nonmetals
- For a standard cell:
  - Find half-reactions, reverse lowest reaction
    - Note: do not reverse the E°value
  - Balance electrons by multiplying half-reactions by integers
    - Again, do not change the E° value
  - Add E° values, a positive E° indicates the reaction is spontaneous
- $w_{elec} = -Q\Delta E = -It\Delta E = -nF\Delta E = \Delta G$
  - A negative number for work means the system is doing work (galvanic)
  - A positive number for work means the surroundings are doing work (electrolytic)
- With this we can determine free energy of any pair of half-cells
- $\Delta E_{cell} = \Delta E°_{cell} - \frac{RT}{nF}\ln Q$
- Use this for nonstandard cell conditions
  - n represents # of electrons transferred in the redox reaction
  - Q represents the reaction quotient, not charge!
    - For $aA + bB \rightarrow cC + dD$,
    - $Q = \frac{[A]^a[B]^b}{[C]^c[D]^d}$
- Can also use $\Delta E°_{cell} - \frac{0.0592}{n} log\, Q$Identical compounds, different electrolyte concentrations

  - Reaction driven by entropy
- Can be used to determine Ksp!
  - Note: $\Delta E°_{cell} = 0$

Example:

  - Ag|AgNO3(1.0M)||AgI(1.0M)|Ag
  - $\Delta \mathrm{E}_{\mathrm{cell}} = 0.476\mathrm{V}$
  - Ag|AgI(1.0M)||AgNO3(1.0M)|Ag, 0.476V
- Step 1: Set up the equation
  - $\Delta E_{cell} = \ \Delta E°_{cell} - \frac{0.0592}{n} log\, Q$
  - $0.476 = 0 - \frac{0.0592}{1}\log\left(\frac{[Ag]}{1}\right)$
- Step 2: Solve for unknown concentration
  - $[Ag] = 10^{-\frac{0.476}{0.0592}}$ =9.108*10^-9
- Step 3: Solve for Ksp

  - $K_{sp} = [Ag][I]$
  - B/c AgI is a diatomic ion,
  - $K_{sp} = [Ag]^2 = (9.108 * 10^{-9})^2$
  - $K_{sp} = 8.297 * 10^{-17}$

Corrosion:

- Metal acts as both anode and cathode
  - Note: not a concentration cell
- Protect structural metals by:
  - Protective coatings
  - Passivation (self-sacrifice)
  - Galvanizing (Zn coating)
  - Sacrifical anode (use a more easily corroded metal)

15.0 Organic Chemistry

What's important?

- Identifying and naming
  - IUPAC system
  - Archaic names
- Isomerism
  - Types of isomers
  - Chirality
- Reactivity
  - Reactions
  - Retrosynthesis

Chain length:

- Number side chains by the carbon they are attached to on the main chain
- Count carbons such that the chain is as long as possible
  - 2,2-dimethyl butane, NOT 1,1,1-trimethyl propane

Classes of Organic Compounds:

- Alkane
  - Saturated C chain, not much else
  - Name ends in –ane, e.g. hexane
- Alkene
  - C chain containing a C=C bond
  - Name ends in –ene, e.g. 1-hexene
- Alkyne
  - C chain containing a C-C triple bond
  - Name ends in –yne, e.g. 1-hexyne
- Alcohol
  - Contains a hydroxyl (-OH) group
  - Name ends in –ol, e.g. hexanol

- Alkyl Halide
    - Contains a halogen (F, Cl, Br, I)
    - Start with halo-, e.g. 1-bromohexane
- Ether
    - Contains an ether (C-O-C) group
    - Named by chain-oxy-chain, e.g. 1-methoxyhexane
- Amine
    - Contains an amino group
    - Name starts with amino-, e.g. 1-aminohexane
    - Comes in three types:
        - Primary: 2 hydrogens bound to nitrogen
        - Secondary: 1 hydrogen bound to nitrogen
        - Tertiary: no hydrogens bound to nitrogen
- Carbonyl
    - Contains a carbonyl (C=O) group
    - Aldehyde:
        - Comes at the end of a chain
            - H bound to carbonyl C
        - Name ends in –al, e.g. hexanal
    - Ketone:
        - In between two other carbon atoms
            - 2 C bound to carbonyl C
        - Name ends in –none, e.g. 2-hexanone
- Carboxylic Acid
    - Contains a carboxyl (-COOH) group
    - Name ends in –oic acid, e.g. hexanoic acid
- Ester
    - Contains an ester (-COO) group
    - Named by:
        - Name the group connected to the oxygen with –yl
        - Name the group connected to the carbon with –oate
        - E.g. methyl hexanoate
- Amide
    - Contains an amide (CONH2) group
    - Name ends in –amide, e.g. hexanamide
- Difference between benzyl and phenyl:
    - Benzyl – C6H5-CH2-
    - Phenyl – C6H5-

Organic Reaction questions:

- Given ethene, please give a synthetic pathway for ethylamine
    - Addition of HX
    - Substitution of –NH2
- Given ethene, please give a synthetic pathway for ethyl ethanoate
    - Addition of H2O
    - Oxidation to ethanoic acid
    - Substitution with ethanol

Isomerism:

- Isomers made simple:
    - Same formula, different structure
- Several types of isomer:
    - Structural isomers
        - 1-chloropentane vs 2-chloropentane
    - Stereoisomers
        - Same bond structures, but with different geometry
            - Geometric isomers – restricted rotation
            - Enantiomers – handedness
        - Named based on priorities
- Heaviest atom = highest priority
    - If there's a tie, go to the next atoms in line
    - Double/Triple bonds multiply (C=O is counted as C bonded to two O)
    - Example:
- Used for:
    - Determining R-S isomerism
    - Determining cis-trans isomerism
- Most commonly seen about a double bond
    - Cis-trans notation
        - Cis refers to compounds where the highest priority groups on either side of the double bond point towards the same side
        - Trans refers to compounds where the highest priority groups on either side of the double bond point in opposite directions
    - E-Z notation
        - Same as cis-trans, E=trans, Z=cis
        - German origin – E (Entgegen, apart), Z (Zusammen, together)
- Left vs right hand – mirror images
- Caused by chiral centres
    - A C bonded to 4 different groups
    - E.g. bromochlorofluoromethane, CHFClBr
- R-S nomenclature
    - Assign priority
    - Rotate molecular structure so that priority 4 (lowest) is facing into the page
        - Clockwise priority rotation – R
        - Counter-clockwise priority rotation - S