SOS

STUDENTS OFFERING SUPPORT

CHEM 112: General Chemistry

December Final Course Package Review

Raising Marks, Raising Money, Raising Roofs

www.queensSOS.com

Authors: Kevin Cho and Stephanie Hammond

6 December 2012

Students Offering Support Sponsors:

Blue Sky

Manulife Financial

KPMG

Preface:

This package is intended for Queen's University students looking for additional study materials for CHEM 112 to prepare for the December final exam in 2012. It is intended to aid, not replace studying with the required course materials. These study materials have been compiled without affiliation with CHEM 112 professors.

Contents

1. The Basics

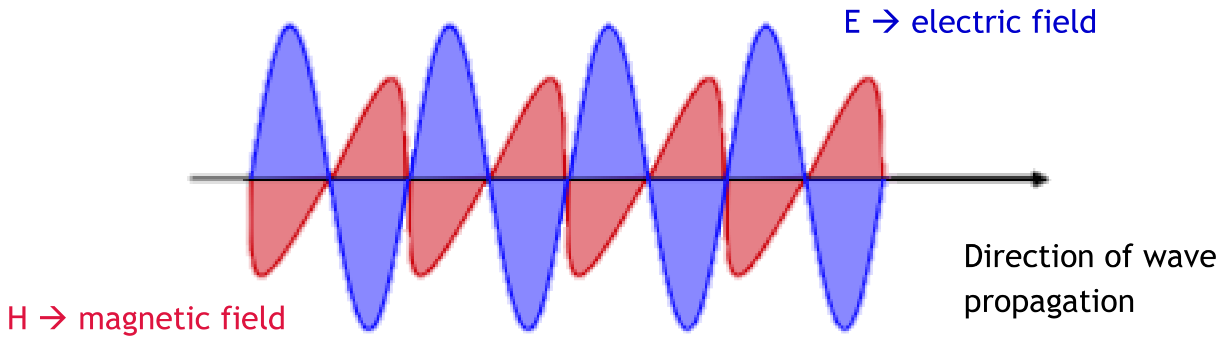
Empirical vs. Molecular Formula

- The **Empirical Formula** is the lowest whole number ratio of atoms, ex. CH_2O
- The **Molecular Formula** indicates the total number of atoms in a molecule, ex. $C_2H_4O_2$ or $C_6H_{12}O_6$
- Calculate empirical formula by looking at the ratio between the number of moles of each atom using the formula: $n = \frac{m}{M}$
  - After n has been calculated for each atom, divide n for each atom involved by the **smallest** number of moles.
  - If this results in fractions multiply to obtain the lowest whole number.

2. Quantum Mechanics

Electromagnetic Radiation

Electric and magnetic fields are perpendicular to each other and are in phase with one another, radiating toward one direction.



Max Plank postulated:

- Discrete quantities of light (a type of electromagnetic radiation) are emitted
- Discrete quantities of radiation are emitted

Properties of waves:

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

Blackbody Radiation

- A blackbody emits radiation when heated, imagine it as a box
- The initial starting point of the wave must be equal to the final point of the wave
- $\lambda = \frac{2L}{n_x}$ where L is the length of the box and n_x is the quantum number
- In 3-D boxes there are 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
- $E = h\nu$ $h = 6.656 \times 10^{-34} Js$ (Planck's constant)
- Determine the energy of spectral lines using the above equation, using the wavelength to find v (recall $u = \lambda \times \nu$)

Photoelectric Effect

- Light at a certain **minimum frequency** (or threshold frequency) allows electrons from metal surfaces to break away.
- If the light energy exceeds the **binding energy** of the metal, then the ejected electrons will possess **kinetic energy**.
- Increasing the intensity of the electromagnetic waves increases the number of electrons ejected but does not alter the energies of the electrons.
- Mathematically: $h\nu = \Phi + \frac{1}{2}mu^2$ Where ½ mu^2 is the kinetic energy of the ejected electron.

Bohr Hydrogen Model

- Bohr established that the electron in an hydrogen atom is located in quantized orbitals
- 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 = 2.179x10^{-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
- Removing an electron from an orbital requires input of energy

For calculations with hydrogen: $\Delta E = R_H\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$

For calculations involving a "hydrogen-like" species: $\Delta E = Z^2 R_H\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$

Absorption and Emission Spectra

- An electron absorbs energy as it transitions to a higher orbital and emits EM radiation as it transitions to a lower orbital
- Orbitals are separated by defined amounts of energy, so the waves absorbed/emitted will have well-defined frequencies
- Each element has a characteristic spectrum of waves absorbed/emitted at certain wavelengths
- Characteristic line spectra of hydrogen:
    - **Lyman Series**: transition ending in **n=1** (UV)
    - **Balmer Series**: transition ending in **n=2** (Visible)
    - **Paschen Series**: transition ending in **n=3** (Infrared)

Heisenberg Uncertainty Principle

- It is impossible to know the precise location and momentum of an electron in orbit at the same time.
- The more you know about its momentum (p), the less you know about its position (x).
- Electrons do not travel in a defined path around the nucleus (Bohr model defect).
- $\Delta x \Delta p \geq \frac{h}{4\pi}$

Schrödinger's Equation

- Describes **particle behaviour** in terms of mass (m), and **wave behaviour** in terms of the wave function (ψ).
- Solutions to Schrödinger's Equation give wave equations to electrons in Hydrogen-like species.

Wave Function ψ

- Consists of a **radial** and an **angular** component.
- When $\Psi = 0$, there is a node.
- Ψ^2 gives the electron density probability (probability of finding an electron at a specific point).

Quantum Numbers

n: principle quantum number

- Energy of the orbital
- Represented by positive integer values
- Corresponds to the group on the periodic table

ℓ: angular momentum quantum number

- Takes on positive integers from 0 to n-1
- Determines the shape of the orbital
    - ℓ = 0 → s orbital
    - ℓ = 1 → p orbital
    - ℓ = 2 → d orbital

    - ℓ = 3 → f orbital

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 +½ or -½
- Electrons spinning clockwise or counter clockwise

- A principle shell contains n sub-shells and a total of 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
    - There are three degenerate p orbitals where n=2, ℓ=1

Orbitals

- Nodes contribute to the characteristic shapes of the orbitals
- Occur when there is a change from a positive lobe to a negative lobe
- Orbitals typically have n-1 nodes
    - There will be ℓ angular nodes and n-ℓ-1 radial nodes

Electron Filling Guidelines

- **Pauli-Exclusion Principle:** every electron in an atom has a unique set of quantum numbers (n,l,m_l,m_s)
- **Aufbau Principle:** electrons are placed in the lowest energy orbitals first until all suborbitals are filled
- **Hund's Rule:** electrons fill same energy orbitals singly before pairing up

3. Periodic Trends

Core Charge and Effective Nuclear Charge

- The effective nuclear charge or core charge refers to the net positive charge experienced by a valence electron in an atom
- Core charge is calculated by subtracting the number of core electrons (all non-valence electrons) from Z (the atomic number)
- The core charge will be consistent for all elements in a group on the periodic table and will increase as you move left to right across a period

Atomic and Ionic Radii

- Atomic radius refers to the radius of an atom, consisting of a nucleus surrounded by orbitals containing electrons
- An atom with more orbitals will have a greater atomic radius, hence an increase moving down a group

- An atom with more protons will pull electrons closer to the nucleus, hence a decrease moving across a period
- A negatively charged ion (anion) will have an increased radius due to electron repulsion
- A positively charged ion (cation) will have a decreased radius due to reduced electron repulsion

Ionization Energy

- The energy needed to expel an electron from the atom for atoms in the **gaseous** state
- **First ionization energy** - the energy needed to expel a ground state electron from an atom
  - First Ionization Energy + $X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$
- **Second ionization energy** – the energy needed to expel a second electron from the same atom
  - Second Ionization Energy + $X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-}$
- Ionization energy increases as you move upwards and to the right on the periodic table

Electronegativity

- The tendency for atoms to hold onto electrons
- Electronegativity increases as you move upwards and to the right on the periodic table,
  - Fluorine is the most electronegative atom
- Use the difference in electronegativity, ΔEN, between two bonded atoms to determine bond polarity
  - If **$\Delta EN \geq 2.0$** then the bond is **ionic**
  - If **$0.4 < \Delta EN < 2.0$** then the bond is **polar covalent**
  - If **$\Delta EN \leq 0.4$** then the bond is **covalent**

4. Molecular Structure

Lewis Structures

- Developed to visually represent the electron configuration of an atom
- Steps for drawing Lewis structures:
  - Start with the basic skeleton of the molecule (single bonds)
  - Complete octets for the outer atoms and then the central atom
  - Create double or triple bonds as necessary to complete the octet for the central atom
- **Ionic Charge** will affect the number of valence electrons to be accounted for
- **Formal Charge** of the atoms also affect the whole molecule (ideal structures have a lower formal charge on its atoms)
- Exceptions to the **Octet Rule**:
  - **Hydrogen** only needs $2e^{-}$ (1 bond) have a formal charge of 0
  - **Beryllium** only needs $4e^{-}$ (2 bonds) to have a formal charge of 0
  - **Boron** only needs $6e^{-}$ (3 bonds) to have a formal charge of 0
- **Expanded Octets**: elements in or below the **third period** on the periodic table can still form stable compounds with more than 8 electrons around it

- **Resonance**: bonds in resonant structures have fraction bond orders, as the electrons in the bonds are constantly shifting and being shared around the molecule

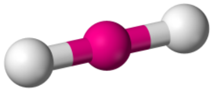
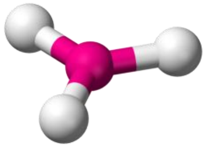
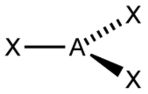
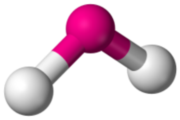
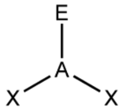
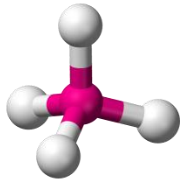
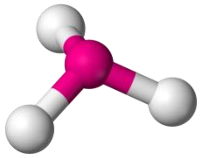
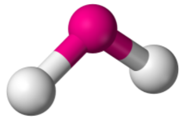
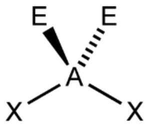
Hybridization

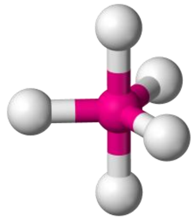
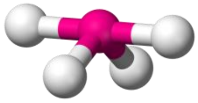
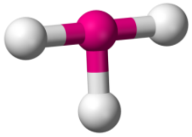
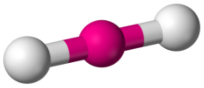
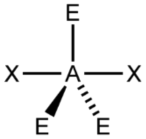
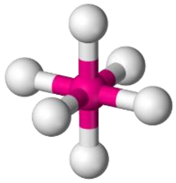
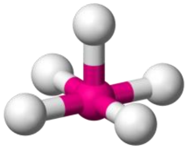
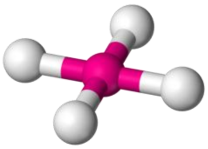
- A tool to help rationalize covalent bonding of non-equivalent orbitals
- Atomic orbitals are “combined” – 1 s and 3 p orbitals combine to form sp^3 orbitals
- **Note**: hybridization is not a physical occurrence (doesn’t actually happen)

VSEPR

- Used to determine the shape of molecules
- Single bonds, double bonds, lone pairs, etc. are all treated equally as “one electron group” when determining shape
- AXE convention – A is the central atom, X represents outer atoms, E represents electron lone pairs

VSEPR Theory – Molecular Shapes

2 Electron Pairs (sp hybridization)			
AX_2	Linear		X—A—X
3 Electron Pairs (sp^2 hybridization)			
AX_3	Trigonal Planar		
AX_2E	Bent/Angular		
4 Electron Pairs (sp^3 hybridization)			
AX_4	Tetrahedral		
AX_3E	Trigonal Pyramidal		
AX_2E_2	Bent/Angular		

5 Electron Pairs (sp^3d hybridization)			
AX_5	Trigonal Bipyramidal		
AX_4E	See-saw		
AX_3E_2	T-shaped		
AX_2E_3	Linear		
6 Electron Pairs (sp^3d^2 hybridization)			
AX_6	Octahedral		
AX_5E_1	Square Pyramidal		
AX_4E_2	Square Planar		

5. Molecular Orbital Theory

Atomic Orbitals vs. Molecular Orbitals

- Atomic orbitals aid in visualizing molecular shape (VSEPR theory) but does not explain the stability of certain structures, including H_2^+, CO, and NO, as well as paramagnetic properties
- Molecular orbital theory represents molecular orbitals associated with the **whole molecule** as opposed to single atoms

- The orbitals are mathematically calculated as the probability of finding electrons in specific areas of the molecule
- Each molecular orbital can accommodate up to **2** electrons
- Molecular orbitals illustrated using correlation diagrams to show placement of electrons in orbitals
- Sigma (σ) bonds form from combinations of s and p orbitals, while pi (π) bonds form only from combinations of p orbitals

Bonding Molecular Orbitals

- Formed by **constructive interference**
- Higher electron charge density is present between the nuclei of the atoms and promotes bonding
- Electrons in these molecular orbitals are **more stable** and **lower** in energy than the atomic orbitals in which they were formed
- Found at lower levels on correlation diagram

Anti-bonding Molecular Orbitals

- Formed by **destructive interference**
- Lower electron charge density between the nuclei of the atoms, which exposes nuclei and results in repulsion and a weakened bond
- Electrons in these molecular orbitals are **less stable** and **higher** in energy than the atomic orbitals in which they were formed
- Found at higher levels distinguished by a * on correlation diagram

Paramagnetism and Diamagnetism

- **Paramagnetism:** the substance has **unpaired** electrons in its correlation diagram
  - Exhibits magnetic properties (slightly attracted into magnet) since parallel electron spins reinforces one another
- **Diamagnetism:** the substance has no unpaired electrons in its correlation diagram
  - Substance slightly repels magnet since the antiparallel electron spins cancel out their magnetic effects

6. Gas Laws

Gases and Vapours

- Gases expand to fill the container they occupy
- Interactions between molecules are very weak due to the distance between them
- Gases are characterized by amount (moles), temperature (K), volume (L), and pressure (Pa)
- Vapours are the gaseous states of substances that would be liquid or solid at room temperature
- Oxygen, hydrogen, and nitrogen are gases, while evaporated water is a vapour

Gas Pressure

- Molecules of gas exert a force on the walls of their container

- Pressure is equal to force in Newtons divided by area in square meters
- Air pressure may be measured using a barometer
- $P = \rho gh$ ρ = density of the liquid, $g = 9.81\ m/s^2$,and h = height of the liquid
- Atmospheric pressure is 760 mmHg or 101.325 kPa

Gas Volume

- Measured in m^3 (SI unit), which is equivalent to 1000 L
- Often L is used in chemistry instead because the cubic meter is so large

Gas Temperature

- Absolute temperature scale (Kelvin scale) is used
- 0 K is theoretically the temperature at which gas molecules have no kinetic energy
- Real gases condense before absolute zero
- 0 K = -273.15 °C

Avogadro's Law

- Equal volumes of gases at fixed pressure and temperature will be equimolar
- Only true for high temperature and low pressure – such as at room temperature

Boyle's Law

- When temperature is fixed, the pressure of a gas is inversely proportional to its volume
- $P_1V_1 = P_2V_2$

Charles' Law

- The volume of a gas is directly proportional to its absolute temperature
- $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Admontons' Law

- Also called Gay-Lussac's Law
- The pressure of a gas is directly proportional to its absolute temperature
- $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

Combined Gas Law

- Obtained by combining Boyle's Law, Charles' Law, and Admontons' Law
- $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Ideal Gases

- Molecules have zero volume
- No attractions or repulsions between molecules
- Molecules only travel in straight lines and collide with the container walls
- Ideal gas law: $PV = nRT$ R is a constant = $8.3145\ m^3\ Pa\ mol^{-1}\ K^{-1}$

Dalton's Law of Partial Pressures

- The overall pressure of a mixture of gases is equal to the sum of the pressures of each of the component gases
- The pressure of each gas is proportional to the amount (moles) present
- $P_{total} = \frac{n_{total}RT}{V}$ $n_{total} = n_A + n_B \ldots$
- $P_A = X_A P_{total}$ $X_A = \frac{n_A}{n_{total}}$

7. Kinetic Molecular Theory

The Theory

- Concepts developed by Rudolf Clausius, James Maxwell, and Ludwig Boltzmann
- Helps with understanding properties of gases and why some conditions make them non-ideal
- Deviations from the theory are examined to explain some natural phenomena and the discrepancy
- Assumptions of the theory:
  - The particle is a point mass with no volume
  - Very large distance of separation
  - Constant, random motion in a straight path
  - Collisions are rapid and elastic (energy is conserved)

Kinetic Energy

- Directly proportional to temperature: $KE = \frac{3}{2}RT$
- From Boyle's Law: $KE = \frac{3}{2}PV$
- Depends on the number of molecules present, not the mass of the molecules

Molecular Speeds Distribution

- U_{rms} – root mean squared speed – fastest molecular speed
- $\bar{U}$ – mean speed
- U_{mp} – most probable speed
- $U_{rms} = \sqrt{\frac{3RT}{M}} > \bar{U} = \sqrt{\frac{8RT}{\pi M}} > U_{mp} = \sqrt{\frac{2RT}{M}}$
- Maxwell Boltzmann curve – mathematical function for speed distribution curve
- f(u) describes shape of the curve
- $f(u)\Delta u$ describes the fraction of molecules in a gaseous sample with speed between u and $(u + \Delta u)$

Diffusion and Effusion

- **Diffusion –** the tendency for gas molecules to move randomly and spread throughout a confined space
- **Effusion** – the leaking of gas molecules through a hole or pore in the barrier dividing the more concentrated area and the less concentrated area
  - Applicable when gas pressure is low and gas effuses through a tiny opening

    - Graham's Law: $\frac{(U_{rms})_A}{(U_{rms})_B} = \sqrt{\frac{M_B}{M_A}}$

Real Gases

- Have substantial volumes and intermolecular forces at high pressures and low temperatures
- **Compressibility factor** calculated by $\frac{PV}{nRT}$
    - Real gases – equal to 1
    - Substantial intermolecular forces – greater than 1
    - Substantial molecular volume – less than 1
- **Van der Waal's Equation**:

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

- Parameter "a" accounts for the intermolecular forces
- Parameter "b" accounts for the substantial volume of gases

8. Properties of Matter

Phases

- Solid, liquid, gas, or plasma
- Depends on the distance between molecules and the forces between them

Phase Transitions

- Changing between phases involves transfer of energy
- Temperature increases as the system gains energy
- Temperature remains constant at the melting and boiling points
- Energy is obtained to overcome intermolecular forces and increase entropy

Intermolecular Forces

- Typically weaker than ionic or covalent bonds
- Strength decreases rapidly as particles move apart
- Long range attractive, short range repulsive
- **Ion-ion**: attraction between atoms with a large difference in electronegativity
    - Coulomb forces: opposite charges attract
    - As strong as covalent bonds
- **Dipole-dipole**: attraction between polar molecules
    - Molecules arrange themselves so positive poles adjoin negative poles
- **Ion-dipole:** ions are surrounded by polar molecules
- **Induced dipole:** attraction between molecules with temporary dipoles
    - Also called London dispersion force
- Van der Waals forces comprise dipole-dipole and London dispersion forces
- From strongest to weakest: ion-ion, ion-dipole, dipole-dipole, induced-dipole

Hydrogen Bonding

- Type of dipole-dipole interaction
- Occurs between a δ^+ H bound to N, O, or F (high EN) and a lone pair

Phase Transitions – Boiling

- Occurs when vapour pressure of a liquid is equal to atmospheric pressure
- Increase temperature or decrease pressure to induce boiling
- Need to slightly exceed T_b to overcome intermolecular forces and produce sufficient excess vapour pressure to push through surroundings
- Greater intermolecular forces result in a higher T_b value

Phase Transitions – Melting/Freezing

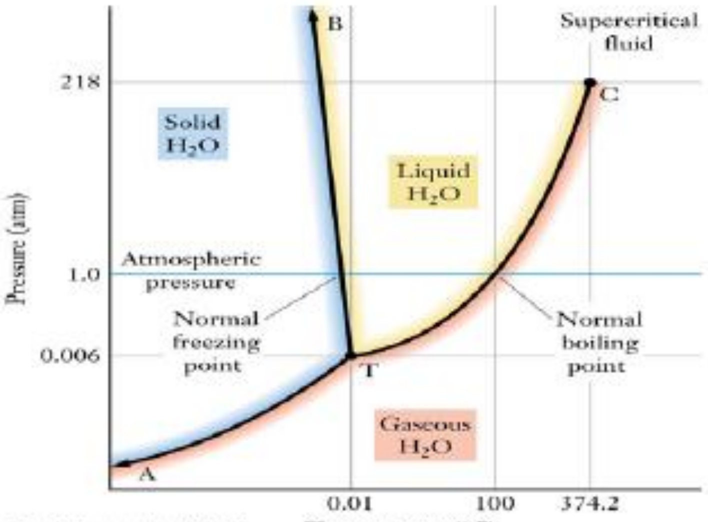
- Little change to intermolecular forces
- Energy change mainly due to "unpacking"
- Unpacked molecules are more randomly arranged – increase entropy

Entropy

- 2nd Law of Thermodynamics
- Measure of randomness or disorder in a system
- Increases from solid → liquid → gas

Phase Diagrams

- Constructed for any pure substance
- Indicates phase of a substance at various temperature and pressure values
- Coexistence lines indicate phase transitions, two phases exist in equilibrium
  - All points on the solid/liquid line are melting/freezing points
  - All points on the liquid/gas line are boiling/condensation points



© 2003 Thomson-Brooks/Cole

- Normal boiling point and melting point are the points on the liquid/gas and solid/liquid lines where pressure = 1 atm
- Triple point (T): temperature and pressure where all 3 phases coexist
- Critical point (C): temperature and pressure at which liquid/gas interface disappears, phases become indistinguishable

Vapour Pressure

- A liquid in an evacuated flask partially evaporates
- Pressure of the vapour increases from 0 as more molecules transition to the gaseous state
- Eventually the rates of condensation and evaporation reach an equilibrium, the pressure of the vapour at this point is defined as the vapour pressure (P*)
- As temperature increases, P* also increases according to the Clausius-Clapeyron equation
- $\ln \frac{P_2^*}{P_1^*} = -\frac{\Delta H_V^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ ΔH°_V = enthalpy of vaporization of the liquid

Relative Humidity

- Ratio of actual pressure of water vapour to its theoretical vapour pressure
- RH = $\frac{P(H_2O)}{P^*(H_2O)}$ x 100%
- As temperature increases, P* also increases and relative humidity would decrease
- As temperature decreases, P* also decreases and relative humidity would increase
- The dew point occurs when relative humidity is 100%, $P(H_2O) = P^*(H_2O)$
- If temperature decreases after the dew point is reached, condensation and fog will form

9. Liquid Solutions

Solutions and Mixtures

- Homogenous mixture – 1 phase, uniform composition and properties
- Components are miscible in each other
- Intermolecular forces are vital in liquid solutions
- “Like dissolves like” – applies to polar and non-polar solutions

Enthalpy of Solution

- Dissolving requires several steps
    - Bonds between component A (**solvent**) are broken
        - **Endo**thermic process ($\Delta H_A>0$)
    - Bonds between component B (**solute**) are broken
        - **Endo**thermic process ($\Delta H_B>0$)
    - Connections between component A and component B are formed
        - **Exo**thermic process ($\Delta H_C<0$)
    - Therefore $\Delta H_{soln} = \Delta H_A + \Delta H_B + \Delta H_C$
- Quantify composition of solutions in terms of **percent mass** or **percent moles**
    - **Molarity** – moles of solute divided by volume of solution
    - **Molality** – moles of solute over mass of solvent

Vapour Pressure and Raoult's Law

- **Vapour pressure** is exerted by vapour phase onto the liquid below at equilibrium
- Vapour will continue to form until the gaseous region above the liquid is saturated with vapour
- **Raoult's Law –** the vapour pressure of a component above a solution is directly dependent on the mole fraction of the component in the liquid solution.
- $P_A = X_A P°_A$

Henry's Law

- As the pressure of gas above a liquid increases, there will be a subsequent increase in the amount of dissolved gas in the solution
- $C = K_H P_{gas}$ where C is solubility of the gas in solvent, K_H is Henry's Law parameter

Pressure-Composition Diagrams

- **Ideal solution** – vapour pressure lines depicted as straight
  - Solute-solute, solvent-solvent, solute-solvent forces are all equal
- **Positive deviation** – vapour pressure lines curved upwards compared to the ideal solution lines
  - Solute-solute and solvent-solvent bonding are stronger than solute-solvent forces
- **Negative deviation** – vapour pressure lines curved downwards compared to the ideal solution lines
  - Solute-solute and solvent-solvent bonding are weaker than solute-solvent forces

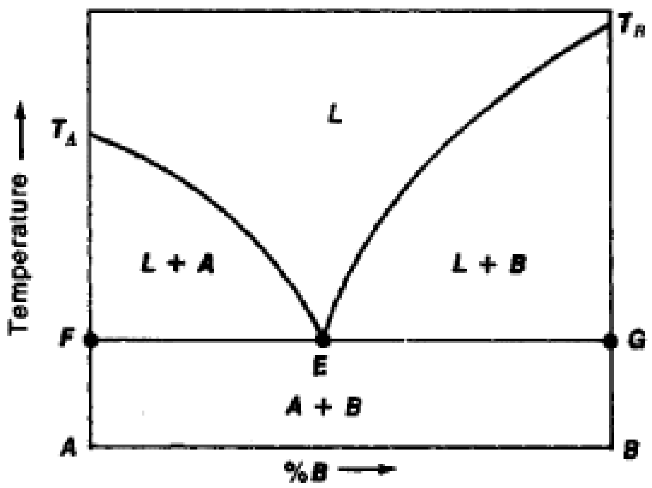
Temperature-Composition Diagrams

- Liquid-liquid diagram
- Gives information about boiling point of both components of the mixture
- Important for **distillation**
  1. Find the liquid composition on the horizontal axis and draw a vertical line up to the liquid boundary
  2. Draw a horizontal line (tie-line) across to the vapour boundary line
  3. Draw a vertical line down to obtain composition of the distilled liquid
- Typically boiling point of a mixture is between the boiling points of the individual components
- **Azeotropes** are mixtures that have a boiling point below (minimum-boiling) or above (maximum-boiling) the individual boiling points of the components
  - **Minimum-boiling** – average intermolecular forces in the mixture is less than in the individual liquids
  - **Maximum-boiling** – average intermolecular forces in the mixture is more than in the individual liquids

Solid-Liquid Phase Diagrams

- Indicate composition of a mixture of liquid and solid components
  - Bottom - equilibrium mixture of the two component solids
  - Middle left - mixture of solid component A and liquid from both components

  - Middle right - mixture of solid component B and liquid from both components
  - Top - liquid of both components
  - **Eutetic point (E)** – lowest possible melting point of the mixture



10. Thermodynamics: Introduction and 1st Law

System

- The area of interest, where a reaction or process occurs
- **Open system –** exchange of matter and energy with surroundings
- **Closed system** – only exchange of energy possible
- **Isolated system** – no contact with surroundings at all

Work and Energy

- **Work** is resulting movement against an opposing force
  - W = Fd, (Joules)
- **Energy** is capacity of a system to do work
- Internal Energy (U) cannot be measured directly
- **ΔU** can be measured after energy leaves system through physical work or heat
- **Irreversible expansion –** process can only go one way
  - $w = -P_{ex}\Delta V$
- **Reversible expansion –** process that is very close to equilibrium state and can therefore go either way
  - $w = -nRT\ln\frac{V_f}{V_i}$
- **Free expansion** – expansion into a vacuum
  - No work done

Heat

- Not a state function
- Extensive property – less energy needed to raise the temperature of a small sample compared to a large sample

- **Adiabatic reaction** – does not allow the transfer of heat between system and surroundings
  - $\Delta H = 0$
- **Diathermic reaction** – only allows the flow of heat, no loss of energy from physical work
  - $\Delta V = 0$ and therefore $\Delta U = q$
- **Isothermal reaction** – system does not allow a change in temperature
  - $\Delta T = 0$ and therefore $\Delta U = 0$
- **Heat capacity –** measurement of heat
  - **Specific heat capacity –** $q = mC_s\Delta T$
  - **Molar heat capacity** – $q = nC_m\Delta T$

First Law of Thermodynamics

- The internal energy of an isolated system is constant
- Change in internal energy is made up of the two components of energy transfer
  - $\Delta U = q + w$

Enthalpy

- A state function
- Assumes reaction conditions where $\Delta P = 0$ or $P_{ex} = P_{system}$
- Mathematically, $\Delta H = \Delta U + P\Delta V$ or $\Delta H = q_p$
- Enthalpies of physical changes:
  - **Enthalpy of Vaporization** (ΔH_{vap}), always positive
    - Involved with evaporation (endothermic)
    - $\Delta H_{vap} = H_m(\text{vapour}) - H_m(\text{liquid})$
  - **Enthalpy of Fusion** (ΔH_{fus}), always positive
    - Involved with melting (endothermic)
    - $\Delta H_{fus} = H_m(\text{liquid}) - H_m(\text{solid})$
  - **Enthalpy of Freezing** is ($-\Delta H_{fus}$) and exothermic
  - **Enthalpy of Sublimation** (ΔH_{sub})
    - Combine ΔH_{vap} and ΔH_{fus}
  - **Lattice Energy** – the difference in molar enthalpy between the solid and a gas of widely separated ions
    - $\Delta H_L = H_m(\text{ions, g}) - H_m(\text{solid})$

Heating Curves

- Steeper line indicates lower heat capacity value
  - Constant pressure – $C_P = \frac{\Delta H}{\Delta T}$
  - Constant volume – $C_V = \frac{\Delta U}{\Delta T}$
- Longer plateau of phase transition indicates higher enthalpy of process

Reaction Enthalpies and Hess's Law

- For reactions involving gases, the following is applied – $\Delta H = \Delta U + \Delta n_{gas}RT$
  - If there is no gas evolved from a reaction ($\Delta n = 0$), then $\Delta H = \Delta U$
- Standard reaction enthalpies are compiled under standard conditions

- **Hess's Law** – the overall reaction enthalpy is the sum of the enthalpies of the intermediate reactions
- Bond enthalpies are amount of energy needed to break a specific type of bond
  - ΔH_B only applies to situations where it is dissociation of a species in the **gas** phase
- **Kirchhoff's Law** helps to explain situations where reaction enthalpies are varied with temperature differences

Standard Enthalpies of Formation

- Standard data that represents the enthalpies evolved from the formation of substances from a more stable form
- The data is presented as in terms of enthalpy per mole of formation of the substance
- ΔH_f° of pure substances in their element form = 0
- $\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$

11. Thermodynamics: 2nd and 3rd Laws

Entropy

- Entropy (S) is the thermodynamic measure of disorder
  - Measured in Joules per Kelvin
- Spontaneous changes, such as cooling to room temperature and gas expansion, increase entropy of a system
- **2nd Law of Thermodynamics**: a system and its surroundings naturally progress from order to disorder
- Changes in entropy can involve thermal or positional disorder
  - Thermal disorder – the system is heated
  - Positional disorder – the molecules become more randomly arranged
- **3rd Law of Thermodynamics:** entropy approaches 0 as temperature approaches 0.

Calculating Changes in Entropy

- Changes in entropy can occur due to input of heat energy at a fixed temperature, or changes in temperature, pressure , or volume
- Select appropriate equation based on the variable which changes
- Standard entropies of vaporization and fusion are calculated for P = 1 bar and the substances in their standard states
- Standard entropy of reaction: $\Delta S^\circ = \sum nS_m^\circ(\text{products}) - \sum nS_m^\circ(\text{reactants})$

Clausius Inequality

- Recall that $\Delta U = w + q$
- $q_{rev} > q_{irrev}$ since $w_{irrev} > w_{rev}$
- w_{rev} is more negative because maximum work is achieved through reversible expansion
- $\Delta S \geq \frac{q}{T}$ is a general expression which applies to q_{rev} or q_{irrev}

System and Surroundings

- Total entropy is entropy of the system combined with entropy of the surroundings

- $\Delta S_{total} = \Delta S + \Delta S_{surr}$
  - If $\Delta S > 0$, the forward reaction is spontaneous
  - If $\Delta S < 0$, the reverse reaction is spontaneous
  - If $\Delta S = 0$, the system is in equilibrium and no change occurs in either direction

Equilibrium

- No tendency of the system to change in either direction
- Dynamic equilibrium – rates of forward and reverse reactions are equal
- Mechanical equilibrium – pressure of a gas is equal to the external pressure

Gibb's Free Energy

- Calculated to assess spontaneity of reaction and potential of to deliver work
- Determines composition of reaction mixture at equilibrium
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G < 0$, spontaneous change occurs
- $\Delta G = 0$ at equilibrium
- Standard Gibb's energy of reaction:
  - $\Delta G° = \sum nG_m°(\text{products}) - \sum nG_m°(\text{reactants})$
  - $\Delta G° = \sum nG_f°(\text{products}) - \sum nG_f°(\text{reactants})$
- Gibb's energy of formation ($G_f°$) is calculated for formation of a compound from elements in their most stable form
- If $(G_f°) < 0$, compound is thermodynamically stable
- If $(G_f°) > 0$, compound is thermodynamically stable and may decompose
  - Labile compounds decompose rapidly, while inert substances survive over time

12. Colligative Properties

Vapour Pressure Lowering

- Presence of a solute disrupts intermolecular interactions between solvent molecules
- $P_A = X_A P°_A$

Boiling Point Elevation and Freezing Point Depression

- Presence of non-volatile solute increases the entropy of the liquid solvent
- Greater change in temperature required before phase change is favourable
- Depends on molality (b), measured in mol/kg
  - Molality = $\frac{n_{solute}}{m_{solvent}}$
- $\Delta T_b = k_b b_{solute}$ and $\Delta T_f = k_f b_{solute}$
  - k values determined experimentally, unique for each solvent

Osmotic Pressure

- Solvent tends to flow toward areas of higher concentration
- Osmotic pressure is equal to the force require to prevent flow of solvent
- Calculated using van't Hoff equation: $\Pi = iRTc_{solute}$
  - i is the van't Hoff factor, experimentally determined

Practice Questions

1. 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

2. 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

3. 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

4. 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

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

6. 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) $1s^22s^22p^63s^23p^6$

7. 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

8. 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

9. 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) $n=3$, $l=2$, $m_l=3$, $m_s=1/2$

10. 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) $n=5$, $l=0$, $m_l=0$, $m_s=1/2$

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

   a) -1
   b) 0
   c) +7

d) +8
e) +17

12. Which of the following molecules is non-polar?

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

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

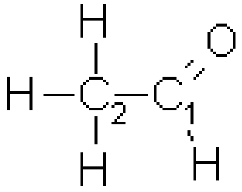
a) I_2
b) ICl
c) HI
d) KI
e) NH_3

15. 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

16. 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



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

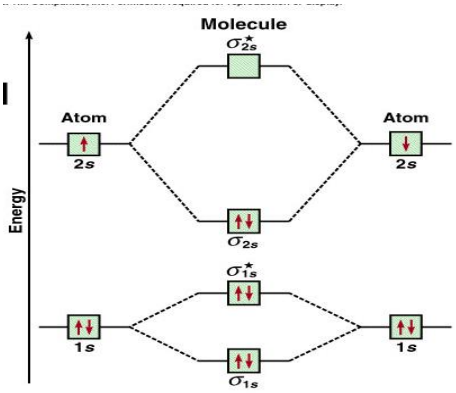
19. Atom A has 3 electrons in its valence shell and atom B has 6 electrons in its valence shell. The formula expected for a compound of A and B is:

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

20. 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

21. 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

22. The molar mass of a gas which 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

23. 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

24. The "nb" term in the van der Waals equation 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

25. Which of the following molecules is non-polar?

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

26. 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

27. The normal boiling point of chloroform ($CHCl_3$) is 61.2°C. At a pressure of 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

28. 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

29. 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

30. Calculate the value of ΔH° for the reaction $CuCl_{2(s)} + Cu_{(s)} = 2\ CuCl_{(s)}$:

$Cu_{(s)} + Cl_{2(g)} = CuCl_{2(s)}$ ΔHf = -206 kJ/mol
$2\ Cu_{(s)} + Cl_{2(g)} = 2\ CuCl_{(s)}$ ΔHf = -36 kJ/mol

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