

DEPARTMENT OF CHEMISTRY
FOURAH BAY COLLEGE
UNIVERSITY OF SIERRA LEONE

CHEM 111

PRINCIPLES OF PHYSICAL AND INORGANIC CHEMISTRY

CREDIT HOURS	2.0
MINIMUM REQUIREMENTS	C6 in WASSCE Chemistry or equivalent To be taken alongside CHEM 114
REQUIRED FOR	CHEM 121

CHEM 111 – PRINCIPLES OF PHYSICAL AND INORGANIC CHEMISTRY

UNIT 1 – MOLES, FORMULAE AND EQUATIONS

COURSE OUTLINE

Moles, formulae and measurement: What is the meaning of relative atomic mass and how is it measured? What is a chemical formula and what is the difference between relative formula mass, relative molecular mass and molar mass? What is a mole and how is it related to mass, molar mass, aqueous volume, molar concentration (molarity), mass concentration and gaseous volume?

How should we record measurements? What is the difference between accuracy and precision? How can we calculate apparatus error and why is it important?

Chemical equations: What is a chemical equation? How do we balance equations? How can we use equations to predict the amount of substance needed or produced in a chemical reaction? What is a limiting reagent? What is the difference between yield and atom economy? What are the main types of chemical reaction and what are the differences between them? What are ionic equations? What is the pH scale? What is volumetric analysis? What is the meaning of chemical equivalency?

Principles of Scientific Enquiry: What is the difference between a theory, a theorem and a hypothesis? What is the difference between a rule and a law? What is the difference between deduction and induction? What is serendipity?

CONTENTS

1.	<i>atomic mass units, use of carbon-12, relative isotopic mass, relative atomic mass, principles of mass spectroscopy</i>
2.	<i>review of chemical structures: giant ionic, giant covalent, simple molecular, giant metallic structures; unit formula, molecular formula</i>
3.	<i>measuring amount of substance; the mole; molar mass; amount of substance in solution; ideal gas equation, empirical formula</i>
4.	principles of scientific measurement; accuracy and precision, appropriate degrees of accuracy, units and their interconversion; % error
5.	chemical equations; balancing equations; amount of substance calculations, <i>limiting reagents; simple volumetric analysis; atom economy and percentage yield</i>
6.	<i>acid-base reactions and the pH scale</i>
7.	<i>Solubility, precipitation and qualitative analysis</i>
8.	<i>oxidation and reduction, oxidation numbers, redox reactions, disproportionation, redox reactions in acidic and basic solution</i>
9.	Redox titrations; manganate, dichromate and iodine-thiosulphate titrations
10.	Chemical equivalency of elements; concept of normality; principles of scientific enquiry; induction, deduction, hypothesis, theory, serendipity

items in italics are covered at senior secondary level

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UNIT 2 – CHEMICAL EQUILIBRIUM

COURSE OUTLINE

What is chemical equilibrium? How can we write expressions for and deduce the values of K_c and K_p , and how can K_c and K_p be interconverted? What is Le Chatelier's principle and why is it useful?

What are heterogeneous equilibria? How can we write expressions for and deduce the values of K_{sp} , and how is this linked to solubility? What is the common ion effect?

What are acid-base equilibria? What is meant by the auto-ionisation, and ionic product, of water? How can we calculate the pH of strong and weak acids and bases from their molarity and vice versa? What is salt hydrolysis and how can we calculate the pH of salts from their molarity and vice versa? What are buffer solutions, how can we prepare them, how can we calculate their pH and why are they useful? What are acid-base indicators and how do they work? How can we choose suitable indicators for use in acid-alkali titrations?

CONTENTS

1.	<i>Principles of chemical equilibrium; dynamic equilibrium, K_c and reaction quotient</i>
2.	Gaseous equilibria, mole fraction, partial pressure and K_p , relationship between K_p and K_c
3.	<i>Le Chatelier's principle; effect of changing conditions on position of equilibrium and K_c</i>
4.	Heterogeneous equilibria, solubility constants and solubility
5.	Introduction to acid-base equilibria; acid-base pairs, auto-ionisation of water, acids and bases in water
6.	pH and pOH of strong and weak acids and bases
7.	Salt hydrolysis, Polyprotic acids and bases and very dilute solutions
8.	Buffer solutions
9.	Indicators and acid-base titrations

items in italics are covered at senior secondary level

UNIT 1 – MOLES, FORMULAE AND EQUATIONS

Lesson 1

1. Atomic Structure

- The basic properties of these three particles can be summarized in the following table:

Particle	Relative Charge	Relative Mass
Proton	+1 unit	Approx 1 unit
Neutron	No charge	Approx 1 unit
Electron	-1 unit	Approx 1/1840 units (very small)

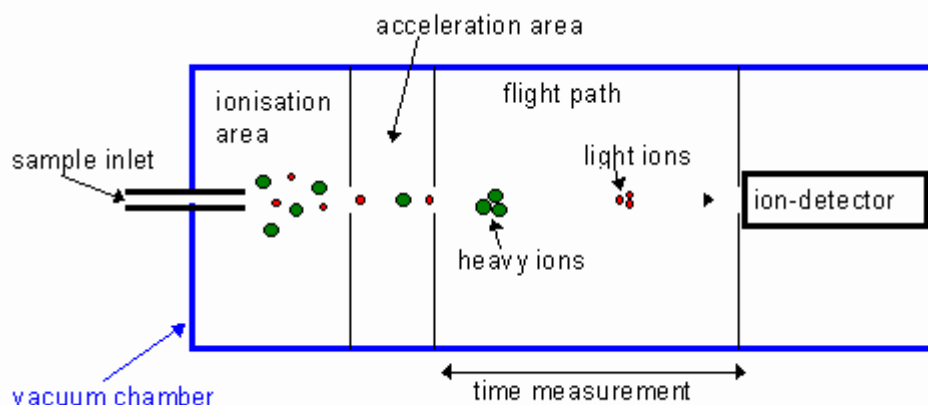
- All atoms have an **atomic number** (number of protons) and a **mass number** (number of nucleons); the chemical symbol and main identity of the atom is based on its atomic number; atoms with the same atomic number but different mass numbers are **isotopes**; they have the same chemical symbol; if a specific isotope is being referred to it can be identified by its mass number as a superscript prefix to the chemical symbol or separated by a hyphen after the name (eg ^{210}Po or polonium-210)
- One unit of charge is 1.602×10^{-19} coulombs; protons have a charge of +1 unit and electrons have a charge of -1 unit; all charges are measured in these units; the positive charge on a proton is exactly equal to the negative charge on an electron
- Protons and neutrons (nucleons) have a similar, but not identical, mass; furthermore, the mass of nucleons in one atom can vary from one atom to another (because of different binding energies); the mass of a nucleon is therefore not constant; the masses of protons and neutrons, and hence the masses of different atoms, are measured in **atomic mass units** (amu); 1 amu is 1.661×10^{-27} kg; this is $1/12^{\text{th}}$ of the mass of an atom of carbon-12, and is also therefore the average mass of a nucleon in carbon-12; a nucleus of carbon-12 therefore has a mass of 12.00000 atomic mass units by definition; the mass of any individual atom, or isotope, can be measured on this scale (ie in atomic mass units); the ratio of the mass of an atom to $1/12^{\text{th}}$ of the mass of an atom of carbon-12 is called the **relative isotopic mass** of an atom
- carbon-12 is chosen because its mass per nucleon neither unusually high nor unusually low, which means the all relative isotopic masses are usually very close to the value of the mass number; in most chemical calculations, the relative isotopic mass is taken to be equal to the mass number:

Isotope	Mass number	Relative isotopic mass
^1H	1	1.007825
^4He	4	4.002603
^9Be	9	9.012182
^{27}Al	27	26.981538
^{59}Co	59	58.933200

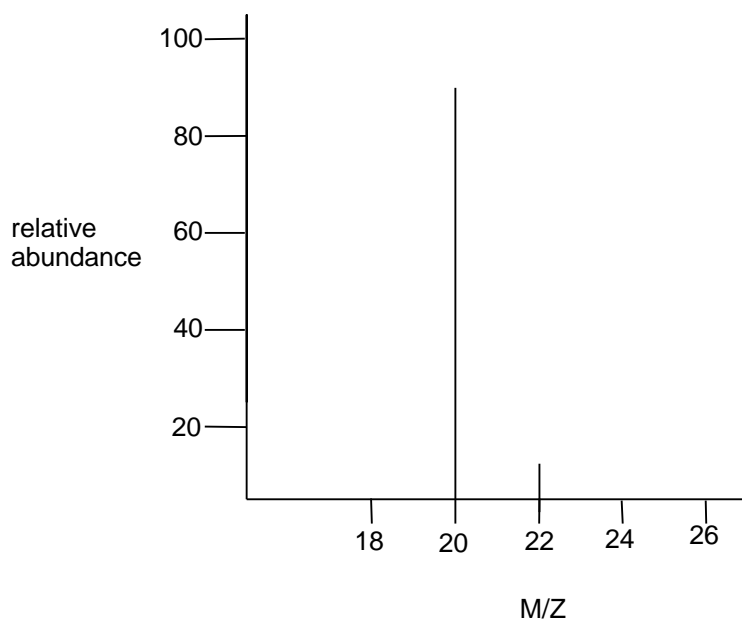
- The **relative atomic mass** of an atom is the ratio of the average mass of an atom to $1/12^{\text{th}}$ of the mass of one atom of carbon-12; it is the weighted average mass of the different isotopes of the atom; it can be found to 1 decimal place in the Periodic Table

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- The time of flight (TOF) mass spectrometer is an instrument used for measuring accurately the masses of atoms and molecules; it can also be used to measure the relative abundance of different isotopes and to predict the structure of more complex molecules; a TOF mass spectrometer has the following structure:



- first a sample is vaporized
 - then it is ionized
 - the ions are then accelerated to a uniform KE by an electric field
 - the ions are then allowed to drift towards the detector; heavier ions move more slowly
 - an electric current is detected each time an ion hits the detector
 - the mass of the ion can be deduced from the time it takes to reach the detector, and its abundance can be detected from the size of the current produced
- The relative atomic mass of the element can be calculated from its mass spectrum. An example of the mass spectrum produced by Ne is shown below:



- The peak at 20 is $^{20}\text{Ne}^+$, and the peak at 22 is $^{22}\text{Ne}^+$

Lesson 2

2. Review of chemical structures and formulae

- Pure substances can be classified as either elements or compounds:
 - An element is a substance containing only one type of atom
 - A compound is a substance containing two or different atoms bonded together with a fixed composition
- Atoms can combine to form elements or compounds in a number of different ways:
 - Atoms can exchange electrons and become oppositely charged ions; the attraction between oppositely charged ions is an **ionic bond**
 - Atoms can share one or more pairs of electrons; each shared pair of electrons is attracted to the nuclei of both atoms and is a **covalent bond**
 - Atoms can give up electrons into a delocalised sea, forming cations in the process; the collective attraction between the cations and the delocalised electrons is a **metallic bond**
- These bond types can give rise to a number of different chemical structures:
 - (i) **Giant ionic lattice structures (compounds only)**
 - Oppositely charged ions tend to arrange themselves in ordered 3D lattices, each ion is surrounded by several others of opposite charge and the lattice is held together by ionic bonds; this is known as a **giant ionic lattice structure**; compounds with this structure are often called **ionic compounds**.
 - The ions in ionic compounds can be monatomic or polyatomic; the bonding within polyatomic ions is covalent but they still form ionic bonds and giant ionic lattice structures with other ions
 - Ionic compounds are represented by a **unit formula**, which is the ratio of each ion present in the lattice, with the charges omitted
 - The **relative formula mass** of an ionic compound is the sum of the relative atomic masses in the unit formula
 - (ii) **Giant metallic lattice structures (usually elements)**
 - Atoms lose electrons to form positive ions and arrange themselves in ordered 3D lattices, held together by the attraction to the delocalised electrons (metallic bonds)
 - Elements which have giant metallic lattice structures are called **metals**
 - The formula of a metal is the symbol of the atom it is made from

(iii) **Simple molecular or simple atomic structures (elements and compounds)**

- When atoms form covalent bonds with other atoms, it usually takes only a few bonds to form before all atoms reach their bonding capacity; a small group of atoms held together by covalent bonds is called a molecule
- Different molecules are held together by intermolecular forces (Van der Waal's forces with or without hydrogen bonding), but these forces are much weaker than covalent bonds
- The resulting structure consists of discrete molecules held together by intermolecular forces; this is known as a **simple molecular structure** and is common in both elements and compounds
- Molecules are represented by a **molecular formula**, which is the total number of atoms of each element in one molecule of that substance
- The **relative molecular mass** of a molecule is the sum of the relative atomic masses in the molecular formula
- In noble gases, which form no bonds with each other at all, the individual atoms are held together by weak Van der Waal's forces; these are known as **simple atomic structures**; their formula is the symbol of the individual atom

(iv) **Giant covalent lattice structures (elements and compounds)**

- In some cases, when atoms form covalent bonds, it is not possible to satisfy the bonding requirements of each atom by the formation of a small molecule; in such cases the network of covalent bonds stretches over a large number of atoms in two or three dimensions and a giant lattice is formed; this is known as a **giant covalent lattice structure** and is found in both elements and compounds
- The giant lattice can be a 2D lattice or a 3D lattice
- The formula of elements with giant covalent structures is the symbol of the atom is made from; compounds with giant covalent structures are represented by a unit formula, which is the ratio of the number of each type of atom in the structure
- The **relative formula mass** of a giant covalent structure is the sum of the relative atomic masses in the unit formula

- The physical properties of elements and compounds depend on their chemical structure
- Analysis of any compound can give the composition of each element by mass; this can in turn give the **empirical formula** of a compound; this is the simplest whole number ratio of atoms of each element in a compound; this is not the same as the molecular formula (of molecules) or the unit formula (for ionic compounds) and further analysis is required to deduce the molecular formula of molecules and the unit formula of ionic compounds
- In some cases, the pure substance is not the most convenient form in which to use it; instead, substances are dissolved in a solvent to make a **solution**; this is common with molecules and ionic compounds; in most cases the solvent is water and the solution is called an **aqueous solution**

Lesson 3

3. The mole

- The mole is the SI unit for **amount of substance (n)**; one mole is equivalent to 6.02×10^{23} particles (**N**) this is known as **Avogadro's number (L)**; amount of substance has units of **mol**
- Avogadro's number is defined as the number of atoms in 12.000 g of carbon-12; this means that one mole of any atom must have a mass equal to its relative atomic mass in grams; this is known as the **molar mass (a_r)** of an atom and has units of **gmol⁻¹**
- The molar mass of any element or compound (**m_r**) is its relative formula mass, relative atomic mass or relative molecular mass in grams
- The amount of substance, in moles, can be determined directly by measurement in three ways:
 - of any pure substance, from a **mass (m)** measurement using a mass balance: $n = \frac{m}{m_r}$; because molar mass has units of gmol⁻¹, the mass should be measured in grams (g); the SI unit of mass is the kilogram (kg)
 - of any solution of known **molarity (C)**, from a **volume (V)** measurement using a measuring cylinder, pipette, burette or volumetric flask: $n = CV$; because molarity has units of moldm⁻³, the volume should be measured in dm³; the SI unit of volume is m³ and most instruments measure volume in cm³
 - of any gas, from a volume measurement using a gas syringe or inverted measuring cylinder, in addition to **temperature (T)** and **pressure (P)** measurements using the ideal gas equation: $n = \frac{PV}{RT}$; in most cases the pressure can be taken to be atmospheric pressure (1.01×10^5 Pa); SI units must be used for the ideal gas equation, so volume should be in m³, pressure in Pa and temperature in K

Lesson 4

4. Accuracy, Precision and measurement error

- Almost all quantities used in Chemistry are measurements, and are therefore subject to measurement error:
 - Graduated instruments such as measuring cylinders, gas syringes, burettes, mass balances and thermometers typically have an error equal to half of the smallest graduation
 - If instruments are used twice to obtain a single value (mass balances, thermometers, burettes) then the error per reading is doubled
 - Fixed measurement devices such as pipettes and volumetric flasks are individually labelled with the measurement error
 - Burettes have an additional error of 0.05 cm^3 per reading due to the individual drop on the tip
 - These errors can be expressed as percentage errors by dividing by the reading itself and expressing as a percentage
 - The total percentage error in an experiment can be calculated by summing the individual percentage errors from each instrument in the experiment
- Apparatus errors are a limiting factor in the **precision** and **accuracy** with which results can be obtained; measurements should reflect this limitation in the way they are recorded; the number of significant figures used in an answer is an indication of the confidence in the **accuracy** of the result; results must always be given to the number of significant figures than the apparatus error can justify; no more and no less
- The final answer resulting from calculations which use measurements should be given to the same number of significant figures as the least precise measurement
- Accuracy is a measure of the closeness of the result to the correct result; precision is a measure of the closeness of the results to each other; the number of significant figures used in an answer is an expression of the limits on precision, and hence the confidence in accuracy, with which the results have been obtained

Lesson 5

5. Equations and Chemical Reactions

- Chemical equations show the formulae (unit or molecular) of the reactants and products in a chemical reaction; due to the law of conservation of mass, the total numbers of each atom must be the same on both sides of the equation
- Chemical equations also show the molar ratio in which the reactants react together and produce products; the ratios are written in front of each formula and are known as stoichiometric coefficients; the stoichiometric coefficients can be deduced by balancing the equation
- The stoichiometric coefficients can be used to deduce the number of moles (and hence any mole-dependent quantities) of any reactant or product involved in the reaction once the number of moles of one reactant or product is known
- Unless the reactants are mixed together in the same mole ratio in which they react, one reactant will be used up before the others; this is known as the limiting reactant and the other reactants are said to be in excess
- The number of moles of product predicted by mole calculations should be regarded as a maximum; in practice, the amount of product obtained will be less than this; the reaction may not proceed to completion and other practical losses may occur as a result of the synthetic process; the amount of product obtained is called the yield; this can be expressed as the **percentage yield**, by expressing it as a percentage of the maximum product possible; the percentage yield will vary based on the conditions and the practical details of the synthesis
- In many reactions, only one of the products formed is useful; the other products are waste products; the sum of the molar masses of useful products in an equation can be expressed as a percentage of the sum of the molar masses of all of the products in an equation; this is known as the **percentage atom economy of the reaction**; atom economy is a property of the equation itself; it cannot be changed by changing the conditions and is unrelated to the percentage yield
- The vast majority of chemical reactions can be described as either acid-base, redox or precipitation reactions

Lesson 6

6. Acid-base reactions and pH

- Several definitions exist for acids and bases (Arrhenius, Bronsted-Lowry, Lewis)

(a) Arrhenius definition

- An Arrhenius acid is a species which gives H_3O^+ ions (often simplified as H^+ ions) in water; neither H^+ nor H_3O^+ ions exist in any form other than aqueous so the species must react with water to produce H_3O^+ ions: $\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$; this is often simplified to $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$; if the acid dissociates fully it is known as a strong acid (H_2SO_4 , HCl and HNO_3); most other acids only dissociate slightly and are known as weak acids; some acids can produce more than one H^+ ion (eg H_3PO_4 and H_3PO_4)
- An Arrhenius base is a species which gives OH^- ions in water; some bases are solutions of ionic hydroxides (eg NaOH); others dissociate in water to give OH^- ions (eg NH_3 , CO_3^{2-}); the Arrhenius definition of a base is very narrow and Arrhenius bases are more commonly referred to as alkalis; bases which fully dissociate in water to give OH^- are called strong bases (only soluble ionic hydroxides); bases which only partially dissociate are called weak bases; some bases can react with more than one H^+ ion
- a more useful definition of a base is a species which can react with H^+ ions to form a salt; this includes all alkalis as well as insoluble ionic oxides, hydroxides and carbonates; a salt is a species formed by the replacement of H^+ in an acid with a metal ion or ammonium ion; a neutralisation reaction is a reaction between an acid and a base to form a salt; acids and bases which can donate or accept more than one H^+ ion can form more than one salt; neutralisation reactions are most conveniently written as ionic equations, in which spectator ions are omitted
- Neutralisation reactions are often used in volumetric analysis (especially titrations) to analyse acids and bases; usually an acid is placed in the burette and added slowly to the alkali until the equivalence point is reached; if the acid or alkali being investigated is in solid form or very concentrated, a solution of it needs to be prepared in a volumetric flask; this solution can then be added to the burette (if it is an acid) or pipetted into a conical flask (if it is an alkali)
- the equivalence point in titrations is usually observed by using acid-base indicators although conductimetric titrations can also be used

(b) Bronsted-Lowry and Lewis definitions

- Bronsted-Lowry acid-base theory provides a general definition of acids and bases: acid = proton donor, base = proton acceptor; acid-base reaction = a reaction which involves the transfer of protons; Arrhenius acids and bases are just special cases of Bronsted-Lowry reactions in which water acts as the base and the acid respectively ($\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$, $\text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^-$)
- Lewis acid-base theory provides an even more general definition: acid = electron pair acceptor; base = electron pair donor; acid-base reaction = a reaction involving the transfer of electrons

(c) Acidic, alkaline and neutral solutions

- In practice, both H^+ and OH^- ions coexist in all aqueous solutions due to the auto-ionisation of water; aqueous solutions in which $[\text{H}^+] > [\text{OH}^-]$ are called acidic solutions; aqueous solutions in which $[\text{OH}^-] > [\text{H}^+]$ are called alkaline solutions; aqueous solutions in which $[\text{H}^+] = [\text{OH}^-]$ are called neutral solutions
- The value of $[\text{H}^+]$ is therefore taken as a measure of the acidity of a solution, often expressed as $\text{pH} = -\log_{10}[\text{H}^+]$; in neutral solutions $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ so the $\text{pH} = 7$; in acidic solutions $[\text{H}^+]$ is higher than this so $\text{pH} < 7$; in alkaline solutions $[\text{H}^+]$ is lower than this so $\text{pH} > 7$
- The expression $\text{pH} = -\log_{10}[\text{H}^+]$ can be used to calculate the pH of any solution if its $[\text{H}^+]$ is known and vice versa; in this way the pH of strong acids can be calculated as follows: if $\text{H}_x\text{A} \rightarrow x\text{H}^+ + \text{A}^{x-}$ and the molarity of the acid H_xA is C, then $[\text{H}^+] = xC$ so $\text{pH} = -\log_{10}(xC)$; similarly, the molarity of a strong acid can be deduced from its pH by applying the inverse formula: $C = \frac{10^{-\text{pH}}}{x}$

(d) Water of crystallisation

- In solid form, many acids, bases and salts contain water within their crystal structures. The water molecules are found in between the oppositely charged ions and are present in fixed molar proportions. Such substances are said to be **hydrated** and the water in the crystal is known as **water of crystallisation**.
- The water of crystallisation is separated from the chemical formula with a dot (eg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

Lesson 7

7. Precipitation reactions

- A precipitation reaction is one in which two ions in aqueous solution combine to form an insoluble solid; they occur when two different soluble salts are mixed – this mixing creates two new combinations of ions, and if either combination is insoluble then a precipitation reaction will take place
- Group I and ammonium cations, and nitrate anions, form no insoluble salts and are never involved in precipitation reactions; some other general rules for predicting precipitation are as follows:

Insoluble	Soluble
carbonates (other than with Group I and ammonium cations)	All Group I and ammonium salts
Hydroxides (other than with Group I, ammonium, strontium and barium ions)	All nitrates
Silver halides (except AgF)	AgF
BaSO ₄ and SrSO ₄ (and a few other sulphates)	Most other sulphates

- Precipitation reactions are best represented as ionic equations, with spectator ions omitted
- Precipitation reactions can be used in quantitative analysis, either in conductimetric titrations (because conductivity reaches a minimum) or in gravimetric analysis (the insoluble compound can be washed, dried and weighed)

Lesson 8

8. Redox reactions

- In inorganic chemistry, oxidation and reduction are usually defined in terms of electron transfer; oxidation is the loss of electrons - when a species loses electrons it is said to be oxidised; reduction is the gain of electrons - when a species gains electrons it is said to be reduced; processes which show the gain or loss of electrons by a species are known as half-equations or half-reactions
- The **oxidation number** of an atom is the charge that would exist on an individual atom if the bonding were completely ionic; in simple ions, the oxidation number of the atom is the charge on the ion; in molecules or compounds, the sum of the oxidation numbers on the atoms is zero; in polyatomic ions, the sum of the oxidation numbers on the atoms is equal to the overall charge on the ion; in all cases each individual atom is allocated a charge as if the bonding was completely ionic; in elements in their standard states, the oxidation number of each atom is zero.
- Many atoms can exist in a variety of oxidation states; the oxidation number of these atoms can be calculated by assuming that the oxidation number of the other atom is fixed:

Atom	Oxidation state in compounds or ions
Li, Na, K, Rb, Cs	+1
Be, Mg, Ca, Sr, Ba	+2
Al	+3
F	-1
H	+1 unless bonded to a metal, Si or B, in which case -1
O	-2 unless bonded to a Group I or Group II metal or H, in which case it can also exist as -1, or F, in which case it exists as +2

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- Oxidation numbers are used when naming compounds according to the internationally agreed IUPAC rules:
 - Binary ionic compounds are named by stating the cation followed by the anion
 - Binary covalent compounds are named by stating the atom with a positive oxidation number followed by the atom with a negative oxidation number
 - Simple cations (and atoms in a positive oxidation state in binary covalent compounds) are named using the name of the atom followed by its oxidation number in brackets and Roman numerals: (+1 = I, +2 = II, +3 = III, +4 = IV, +5 = V, +6 = VI, +7 = VII)
 - Simple anions (and atoms in a negative oxidation state in binary covalent compounds) are named by changing the final one or two syllables of the atom to -ide
 - In anions containing more than one atom, one of the atoms has a positive oxidation number and the other has a negative oxidation number; these anions are named by changing the last one or two syllables of the atom with a positive oxidation number to -ate, and then adding the oxidation state of that atom in brackets and Roman numerals; the presence and number of atoms with a negative oxidation state is indicated as a prefix with the final one or two syllables of the atom changed to -o, preceded by the number of atoms if more than one (two = di, three = tri, four = tetra, five = penta, six = hexa); in many cases the negative atom is oxygen and the prefix oxo- is usually omitted unless the number of oxygen atoms is unclear
 - It is common to leave out the Roman numeral if the atom has only one known oxidation number (such as sodium or magnesium)
 - In binary compounds, adding prefixes such as mono, di, tri to denote the number of atoms is unnecessary when oxidation numbers are being used but is sometimes used as an alternative to using oxidation numbers
- During oxidation and reduction, the oxidation numbers of atoms change; if an atom is oxidized, its oxidation number increases (ie it becomes more +ve or less -ve); if an atom is reduced, its oxidation number decreases (ie it becomes less +ve or more -ve)

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- Many oxidation and reduction processes involve polyatomic ions or molecules; the half-equations for these processes are more complex and are pH dependent, so can be written either using H^+ (if the conditions are acidic) or OH^- (if the conditions are alkali); there are two ways to construct balanced half-equations:

Method 1:

- Identify the atom being oxidised or reduced, and make sure there are the same number of that atom on both sides (by balancing)
- Insert the number of electrons being gained or lost (on the left if reduction, on the right if oxidation) using the equation: No of electrons gained/lost = change in oxidation number x number of atoms changing oxidation number
- balance O atoms by adding water
- balance H atoms by adding H^+

Method 2 (easier in more complex reactions):

- Identify the atom being oxidised or reduced, and make sure there are the same number of that atom on both sides (by balancing)
- balance O atoms by adding water
- balance H atoms by adding H^+
- add the necessary number of electrons to ensure the charge on both sides is the same

Both of the above methods give you equations for acidic conditions; to convert into alkaline conditions, add OH^- ions to both sides of the equation so that the number of OH^- and H^+ ions on one side are equal, then convert each pair into a water molecule and cancel out water molecules until they only appear on one side

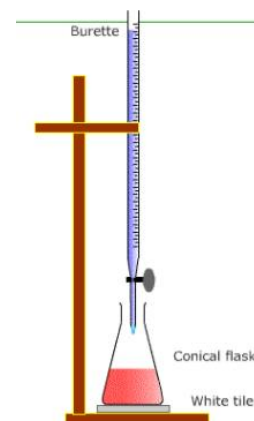
- Half-equations consider gain and loss of electrons, but in fact electrons cannot be created or destroyed; they can only be transferred from species to species; gain of electrons by one species necessarily involves loss of electrons by another; oxidation and reduction thus always occur simultaneously; an oxidation is always accompanied by a reduction and vice versa; any reaction consisting of the oxidation of one species and the reduction of another is known as a **redox** reaction
- A redox reaction can be derived by combining an oxidation half-equation with a reduction half-equation in such a way that the total number of electrons gained is equal to the total number of electrons lost
- In redox reactions, the species which is reduced is accepting electrons from the other species and thus causing it to be oxidised; it is thus an **oxidising agent**; the species which is oxidised is donating electrons to another species and thus causing it to be reduced. It is thus a **reducing agent**; a redox reaction can thus be described as a transfer of electrons from a reducing agent to an oxidising agent
- There are many substances which readily undergo both oxidation and reduction, and which can therefore behave as both oxidising agents and reducing agents; species such as these are capable of undergoing oxidation and reduction simultaneously; the simultaneous oxidation and reduction of the same species is known as **disproportionation**; a disproportionation reaction is a type of redox reaction

Lesson 9

9. Volumetric Analysis

- **Volumetric analysis** is the quantitative investigation of a solution using one or more measurements of volume
- The most common type of volumetric analysis is **titration**; during a titration, the volume of one solution required to react completely with another is measured; in most cases one solution is added gradually from a **burette** into another solution in a **conical flask** until the **equivalence point** is reached; the equivalence point of a titration is the point at which the volume of solution added from the burette is just enough to react completely with the solution in the conical flask.
- The phrase “solution A is titrated against solution B” means that a known volume of solution A should be placed in a conical flask and solution B placed in a burette; solution B should be added to solution A until the equivalence point is reached.
- The main purpose of titrations is to determine the **concentration** of a solution; this is known as **standardisation**. A solution whose concentration is known accurately is known as a standard solution; concentration can be expressed as **molarity, mass concentration** or **normality**
 - Molarity: moles of solute per dm^3 of solution (mol dm^{-3})
 - Mass concentration: mass of solute per dm^3 of solution (g dm^{-3})
 - Normality: equivalents of solute per dm^3 of solution (Eq dm^{-3})

Once one solution has been standardised, it can be used to standardise the solution it is reacting with.
- Titrations can also be used to determine the molar mass or percentage purity of a solid, if it is soluble in water; a standard solution of the substance should be prepared first, using a volumetric flask
- The main apparatus used in titrations are pipettes, burettes and conical flasks; volumetric flasks are also used if a standard solution needs to be prepared from a solid or from a concentrated solution



pipette



burette



volumetric flask

CHEM 111 – PRINCIPLES OF PHYSICAL AND INORGANIC CHEMISTRY

- A **pipette** is an apparatus used to deliver a known volume of solution accurately into another container; most pipettes have a single graduation mark and can therefore only be used to deliver a fixed volume of solution (usually 5 cm^3 , 10 cm^3 or 25 cm^3)
- A **burette** is an apparatus used to deliver a variable quantity of solution accurately into another container; the burette most widely used in laboratory chemistry can deliver volumes of up to 50 cm^3
- A **volumetric flask** is an apparatus designed to contain a specific amount of solution, usually 250 cm^3 ; it is used to prepare standard solutions from solids (by dissolving) or from concentrated solutions (by dilution)
- Titrations can be used in all three of the main types of inorganic reaction:
 - (a) **Acid-base** reactions
 - (b) **Precipitation** reactions
 - (c) **Redox** reactionsThe equivalence point needs to be clearly visible; in most cases, a suitable indicator is added to the conical flask, although some redox reactions are auto-indicating

(a) Acid-Base Titrations

- Most acids and bases are colourless; an indicator is therefore required to identify the equivalence point; during acid-base titrations, a large and sudden change in pH occurs at the equivalence point and this point can therefore be identified by using an indicator which changes colour over the same pH range
- The indicators most frequently used in titrations are methyl orange and phenolphthalein; each indicator has a characteristic **end-point** (equal to its pK_{In} value) which is the pH at which the indicator changes colour, most indicators change colour over a pH range approximately equal to $\text{pK}_{\text{In}} \pm 1$

Indicator	end-point (pK_{In})	pH range of colour change	Colour in acid	Colour in alkali	suitability
Methyl orange	3.7	3.1 – 4.4	Pink	yellow	Strong acids only
Phenolphthalein	9.3	8.3 – 10.0	Colourless	pink	Strong bases only

(b) Precipitation Titrations

- Precipitation titrations are very useful for the determination of chloride ions in solution; chloride ions react with silver ions to give the very insoluble precipitate of AgCl: $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$; in most cases the solution containing chloride ions is titrated against a solution of silver nitrate (AgNO_3) until all of the Cl^- has precipitated as AgCl
- The equivalence point of this reaction can be observed in two ways:
 - (i) The Mohr method: a small quantity of potassium chromate (K_2CrO_4) is added to the conical flask as an indicator; the CrO_4^{2-} ions in the solution form a red precipitate with Ag^+ ions (Ag_2CrO_4); but because AgCl is less soluble than Ag_2CrO_4 , AgCl precipitates first and the red precipitate of Ag_2CrO_4 is only observed when there are no Cl^- ions remaining in solution
 - (ii) The Fajans method: dichlorofluorescein is an organic compound which changes its colour to violet when it binds to Ag^+ ions, but since Ag^+ will instantly precipitate with Cl^- until there are no Cl^- ions remaining, the violet colour is only observed after the equivalence point; the violet colour is easier to see if starch is also added

(c) Redox Titrations

- Redox reactions can be used in quantitative analysis (especially titrations) to analyse oxidising and reducing agents:
 - (i) Reducing agents can be analysed by acidifying them and then titrating them against a standard solution of KMnO_4 , which behaves as an oxidising agent as follows: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$; the purple MnO_4^- is decolorised as it is added to the reducing agent until the reducing agent has been fully oxidised; any excess MnO_4^- will then turn the solution pink and this can be used to identify the equivalence point
 - (ii) Oxidising agents are generally analysed by reacting them with an excess of aqueous potassium iodide (KI); the iodide ion is oxidised to iodine as follows: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$; the resulting iodine is then titrated against a standard solution of sodium thiosulphate ($\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$) using starch indicator, which turns blue/black in the presence of excess iodine and hence disappears when the iodine has all been used up, which allows the equivalence point to be determined

Lesson 10

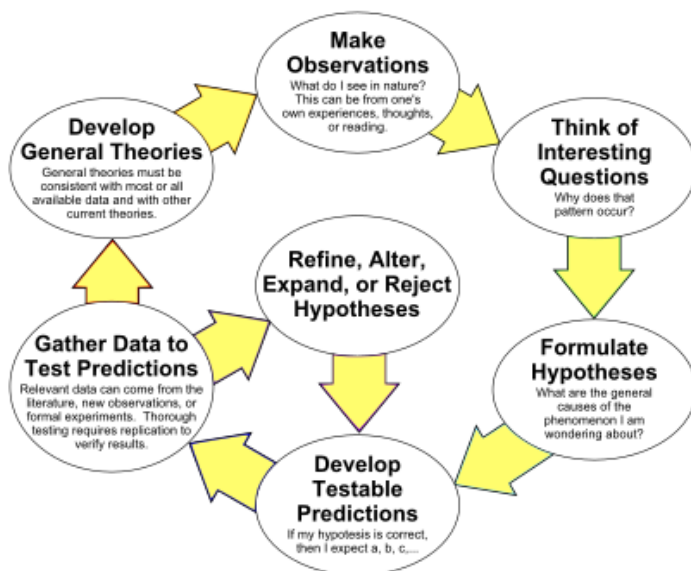
10. Normality and Equivalent Weights

- It is sometimes helpful to count elements and compounds in terms of “equivalents” rather than moles, especially during acid-base or redox reactions; one equivalent weight is the mass of substance required to completely react with 1 mole of H^+ or OH^- ions, or to gain or lose one mole of electrons
- For elements, the equivalent weight is the molar mass divided by the valency:
Eg the equivalent weight of O is 8.0 g; the equivalent weight of H is 1.0 g
- For monoprotic acids this is equal to the molar mass; for diprotic acids such as H_2SO_4 it is equal to 0.5 of the molar mass; for compounds and ions involved in redox reactions it is the molar mass divided by the number of electrons gained or lost
- In some cases the concentration of aqueous solutions is expressed in terms of normality (equivalent weights per dm^3) rather than molarity ($mol\,dm^{-3}$); for example $1\,N\,H_2SO_4 = 0.5\,M\,H_2SO_4$

11. Principles of Scientific Enquiry

- Scientific enquiry is a continuously repeating (iterative) process of developing and testing theories through the collection of experimental data (observation and measurement)

The Scientific Method as an Ongoing Process



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- The process of scientific enquiry can be summarised as follows:
 - observations are made about the natural world
 - attempts to explain these observations lead to the development of a hypothesis
 - the hypothesis leads to predictions which can be tested empirically (by observation)
 - based on the results of these tests, the original hypothesis may require refinement, alteration, expansion or even rejection
 - if a particular hypothesis becomes very well supported, a general [theory](#) or law may be developed, via a process of induction
- A Law is a descriptive principle of nature which holds in all circumstances covered by the wording of the law (it is experimental); a theory is a description of nature which encompasses more than one law
- A hypothesis is a law or theory which is not sufficiently supported to be considered universally true; a hypothesis may become a theory or law if it is repeatedly and extensively tested and supported by observations
- Inductive reasoning is a method of reasoning in which the evidence provides strong evidence for the truth of a conclusion, meaning that the truth of the conclusion is probable but not certain; in science it is the process of converting a series of particular observations into a general law or theorem
- Deduction is the process of arriving at a conclusion by logic
- A theorem is a statement that has been proved on the basis of previously established statements (it is deductive)
- Most scientific breakthroughs result from serendipity: an unsought and unexpected, but fortunate, observation

12. Molality

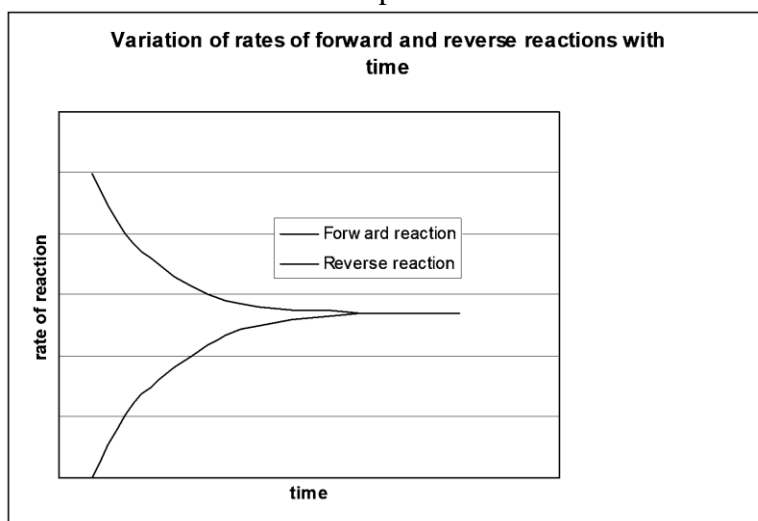
- Molality is the concentration of a solution expressed in moles of solute per kilogram of solvent; for aqueous solutions it is usually very similar to molarity

UNIT 2 – CHEMICAL EQUILIBRIA

Lesson 1

1. Principles of Chemical Equilibrium

- Reversible reactions are indicated by the sign \rightleftharpoons ; a reversible reaction is one in which the reverse reaction is able to take place to a significant extent
- Consider a reversible reaction $A + B \rightleftharpoons C + D$; initially the rate of the reverse reaction is zero as the concentration of products is zero; as the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases; eventually, the reaction will reach a stage where both forward and backward reactions are proceeding at the same rate; at this stage a dynamic equilibrium has been reached; the forward and reverse reactions are proceeding at the same rate and so there is no further change in the concentration of reactants and products:



- All reactions are reversible in theory; in some cases the reverse reaction is insignificant; in others, it is not allowed to take place because the product is removed as soon as it is formed; this is often the case in open systems, so dynamic chemical equilibria are most commonly found in closed systems

2. Equilibrium Constants

(a) Equilibrium constants at constant volume (K_c)

- If the following reaction: $wA + xB \rightleftharpoons yC + Zd$, the relative concentrations of reactants and products in the system can be given by:

$$\frac{[C]^y[D]^z}{[A]^w[B]^x} = K_c$$

K_c is a constant for a given equation at a given temperature and is known as the **equilibrium constant** of the reaction; if K_c and the initial amount of each reactant is known, the equilibrium concentration of each reactant and product can be calculated and vice versa, provided that the reaction is taking place at constant volume

- K_c does depend on the stoichiometric coefficients; if the equation $n(wA + xB \rightleftharpoons yC + Zd)$ were used, the equilibrium constant for the reaction $K_c^1 = (K_c)^n$; in addition, K_c for the reverse reaction (K_c^r) and the forward reaction (K_c^f) are related as follows: $(K_c^r) = (K_c^f)^{-1}$
- The units of the equilibrium constant vary, depending on the relative number of reactant and product species in the equation number of species involved; in general the units can be given by $(\text{mol dm}^{-3})^{\Delta n}$, where Δn is the change in the total number of species during the reaction

Lesson 2

(b) Equilibrium constants at constant pressure (K_p)

- In some cases, reactions take place at constant pressure, rather than at constant volume; in such cases the equilibrium constant at constant pressure (K_p) should be used instead:
 - $K_p = \frac{p_C^y p_D^z}{p_A^w p_B^x}$ where $p_A =$ partial pressure of A $= \frac{n_A}{n_T} P$, where P is the total pressure and n_T is the total number of moles
 - So $K_p = \frac{\left(\frac{n_C P}{n_T}\right)^y \left(\frac{n_D P}{n_T}\right)^z}{\left(\frac{n_A P}{n_T}\right)^w \left(\frac{n_B P}{n_T}\right)^x}$ but $P = \frac{n_T R T}{V}$ from the ideal gas equation (R = molar gas constant, T = temperature)
 - So $K_p = \frac{\left(\frac{n_C R T}{V}\right)^y \left(\frac{n_D R T}{V}\right)^z}{\left(\frac{n_A R T}{V}\right)^w \left(\frac{n_B R T}{V}\right)^x} = \frac{[C]^y [D]^z}{[A]^w [B]^x} R T^{(y+z-w-x)} = K_c R T^{(y+z-w-x)}$
 - $y + z - x - w$ is the total change in the number of particles during the reaction, or Δn
 - so $K_p = K_c R T^{\Delta n}$
- If K_c or K_p is close to 1, it means that the position of equilibrium lies close to the middle of the reaction, which means that the equilibrium mixture contains similar quantities of reactants and products; if K_c or $K_p \gg 1$, it means that the position of equilibrium lies to the right of the reaction, which means that the equilibrium mixture contains significantly more products than reactants; if K_c or $K_p \ll 1$, it means that the position of equilibrium lies to the left of the reaction, which means that the equilibrium mixture contains significantly more reactants than products

(c) Reaction Quotients

- If K_c or K_p is close to 1, it means that the position of equilibrium lies close to the middle of the reaction, which means that the equilibrium mixture contains similar quantities of reactants and products; if K_c or $K_p \gg 1$, it means that the position of equilibrium lies to the right of the reaction, which means that the equilibrium mixture contains significantly more products than reactants; if K_c or $K_p \ll 1$, it means that the position of equilibrium lies to the left of the reaction, which means that the equilibrium mixture contains significantly more reactants than products
- For reactions which are not at equilibrium, the value of $\frac{[C]^y [D]^z}{[A]^w [B]^x}$ or $\frac{p_C^y p_D^z}{p_A^w p_B^x}$ is called the reaction quotient Q_c or Q_p
- If $Q < K$, Q needs to increase before equilibrium is reached and the reaction will move to the right to reach equilibrium; if $Q > K$, Q needs to decrease before equilibrium is reached and the reaction will move to the left to reach equilibrium

Lesson 3

3. Le Chatelier's Principle

- If the conditions are changed after equilibrium has been established, the system may no longer be at equilibrium and may move in one direction or another to re-establish equilibrium; the direction in which the system will move to re-establish equilibrium can be predicted by Le Chatelier's principle: "If a constraint is imposed on a system at equilibrium, then the system will respond in such a way as to counteract the effect of that constraint"; such constraints can be the addition or removal of one of the reactants or products, a change in pressure, a change in temperature or the addition of a catalyst.
- If a reactant or product is added to or removed from a system at equilibrium, the system will no longer be at equilibrium and the concentrations will change until equilibrium is restored; Le Chatelier's principle predicts that if a reactant's concentration in a system is increased, the system will move to the right in order to decrease the concentration of that reactant, and vice versa; this can also be deduced by considering the effect on the reaction quotient Q of adding or removing a species; at equilibrium, $K = Q$, but if a change is then made which increases Q , the reaction will move to the left until Q has decreased back to the value of K , but if but if a change is then made which decreases Q , the reaction will move to the right until Q has increased back to the value of K
- If the pressure is changed when a system is at equilibrium, the system may no longer be at equilibrium and the concentrations will change until equilibrium is restored; Le Chatelier's principle predicts that if the pressure in a system is increased, the system will move to decrease the pressure by moving in whichever direction reduces the total number of gas molecules, and vice versa; this can also be deduced by considering the effect on the reaction quotient Q of changing the pressure; if V in the K_c term is replaced by nRT/P , then P will appear in the equilibrium expression as $P^{\Delta n}$, so an increase in pressure will increase Q if Δn is positive and decrease Q if Δn is negative; the reaction will respond accordingly
- If the temperature is changed when a system is at equilibrium, the system may no longer be at equilibrium and the concentrations will change until equilibrium is restored; if the forward reaction is exothermic, then the temperature of the system will rise if the forward reaction takes place; the reverse reaction will therefore be endothermic, and the temperature of the system will fall if the reverse reaction takes place; Le Chatelier's principle therefore predicts that an increase in temperature will favour the endothermic reaction, and that a decrease in temperature will favour the exothermic reaction; if the forward reaction is exothermic, then an increase in temperature will cause the system to shift to the left, and a decrease in temperature will cause the system to shift to the right, and vice versa; changes in Q cannot be used to predict the effect of a change in temperature because K itself varies with temperature
- The addition of a catalyst will have no effect on the position of equilibrium; it will increase the rate of the forward and reverse reactions, but by the same amount. The position of equilibrium will thus be unchanged

Lesson 4

4. Heterogeneous Equilibria

- A heterogeneous equilibrium is one in which the reactants and products are not all in the same phase; this can be a gaseous mixture with some solid or liquid species, or an aqueous or liquid mixture with some solid species
- In aqueous and liquid equilibria, the concentration terms for solids can be considered to be independent of the quantity of solid present; they can therefore be included in the value of the equilibrium constant and are not included in the equilibrium expression
- This is significant when considering the solubility of sparingly soluble ionic compounds, which set up an equilibrium with the aqueous solution as follows: $A_xB_y(s) \rightarrow xA^{m+}(aq) + yB^{n-}(aq)$; the equilibrium constant for such an equilibrium system would be given by $K_{sp} = [A^{m+}]^x[B^{n-}]^y$; K_{sp} is known as the solubility product of the compound; this can be used to predict the solubility of different ionic compounds under different circumstances
- It can be concluded from the K_{sp} expression that the solubility of a compound in aqueous solution will be significantly reduced if one or other of the ions is already present in solution; this is known as the common ion effect
- In gaseous equilibria, the concentration terms for both solids and gases can be considered to be independent of the quantity of those substances present; they can therefore be included in the value of the equilibrium constant and are not included in the equilibrium expression; the K_p expression for heterogeneous reactions should therefore include the partial pressures of the gaseous terms only

Lesson 5

5. Acid-base equilibria

(a) Bronsted-Lowry theory

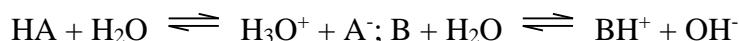
- Bronsted-Lowry definition for acids and bases is the most useful one for considering reversible reactions between acids and bases; an acid is a substance which can behave as a proton (H^+) donor - any species containing H attached to an electronegative atom can behave as an acid; $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$; **a base is a substance which can behave as a proton acceptor**; any species which has a lone pair of electrons can thus behave as a base; $\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+$

- The species formed when an acid gives up a proton can accept a proton and thus behave as a base, and the species formed when a base accepts a proton can give up a proton and behave as an acid:



HA and A^- , and BH^+ and B , are conjugate acid-base pairs; HA and BH^+ are the conjugate acids of A^- and B respectively; A^- and B are the conjugate bases of HA and BH^+ respectively; thus every acid-base reaction can be considered to reach an equilibrium with one acid and one base on each side; and the conjugate acids and bases on the other side: $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{BH}^+$

- Not all acids are equally good proton donors; in fact some give up their protons very reluctantly; conversely, some bases accept protons readily whereas others accept protons very reluctantly; acids and bases can be classified as strong or weak based on their ability to donate and accept protons respectively; the stronger the acid, the weaker its conjugate base and vice versa
- Most common acid-base reactions take place in aqueous solution, and thus acids and bases are generally defined by the way in which they react with water; the Arrhenius definition of acids and bases can be considered a special case of the Bronsted-Lowry definition – when Arrhenius acids react with water, water behaves as a base; when Arrhenius bases react with water, water behaves as an acid:



In strong acids and bases, this dissociation is complete; in weak acids and bases, this dissociation is partial; the dissociation of Arrhenius acids in water is often simplified to $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$;

- Water is an example of a species which can behave as an acid and a base; such species are said to be **amphoteric**; amphoteric species have a conjugate acid and a conjugate base and can undergo acid base reactions with themselves: $\text{AH} + \text{AH} \rightleftharpoons \text{A}^- + \text{AH}_2^+$

Water reacts with itself as follows: $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$; this is known as the auto-ionisation of water and is a feature of every aqueous solution, including pure water

(b) Auto-ionisation of water

- The equilibrium constant for this dissociation can be written as follows: $K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$; the concentration of water in aqueous solution (55 mol dm^{-3}) is not changed significantly by this dissociation, since the proportion of water which dissociates into its ions is small; the water concentration can thus be assumed to be constant and it can be incorporated into K_c as follows:

$$K_c[\text{H}_2\text{O}] = K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

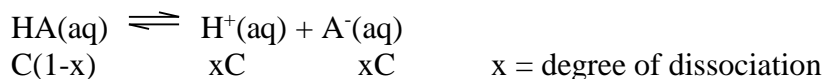
This expression is known as the **ionic product of water** and has a value of $1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$ at 25°C ; this value is a constant at a given temperature; the ionic product of water is slightly higher at higher temperatures, suggesting that the dissociation is endothermic; $[\text{H}_3\text{O}^+]$ is often simplified to $[\text{H}^+]$

- The pH of pure water can be calculated from this expression:
in pure water $[\text{H}^+] = [\text{OH}^-]$ so $K_w = [\text{H}^+][\text{OH}^-] = [\text{H}^+]^2$ so $[\text{H}^+] = \sqrt{K_w} = 1 \times 10^{-7} \text{ mol dm}^{-3}$ and $\text{pH} = 7.0$
- The value of K_w can be used to calculate $[\text{OH}^-]$ if $[\text{H}^+]$ is known, and the value of $[\text{H}^+]$, and hence the pH, if $[\text{OH}^-]$ is known; this can be used to calculate the pH of strong bases

Lesson 6

(c) Dissociation constants for weak acids and bases

- Weak acids dissociate partially in water and reach an equilibrium as follows:



The equilibrium expression for the dissociation of a weak acid is as follows: $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$

K_a is known as the **acid dissociation constant** for the acid and has units of mol dm^{-3} ; it is often quoted as $\text{p}K_a = -\log_{10}K_a$; the larger the K_a , the greater the degree to which the acid dissociates into its ions and the stronger the acid

- The pH of weak acids can be calculated if the K_a and molarity of the acid are known; the calculation can be simplified by ignoring the auto-ionisation of water, and hence assuming that all of the H^+ has come from the acid; this means that $K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$; the calculation can be further simplified by assuming that x is small and hence $\text{C}(1-x) \approx \text{C}$; substituting C and xC into the K_a expression gives $K_a = \text{x}^2\text{C}$; therefore $\text{x} = \sqrt{\frac{K_a}{\text{C}}}$; note that x decreases as C increases – this is consistent with Le Chatelier's principle; $[\text{H}^+] = \text{xC} = \text{C}\sqrt{\frac{K_a}{\text{C}}} = \sqrt{K_a\text{C}}$; this expression means that if any two of $[\text{H}^+]$, K_a and C are known, the other can be calculated, as well as the pH; these calculations can be done without making the $\text{C}(1-x) \approx \text{C}$ approximation but it is then necessary to solve a quadratic; this is necessary if x is appreciable

- Weak bases can be analysed in a very similar way:

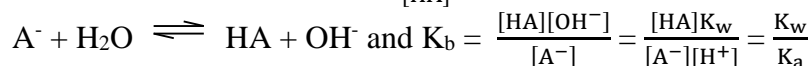
$\text{B(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq}); K_c = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]}$ but because $[\text{H}_2\text{O}]$ is constant in aqueous solutions, this can be simplified to: $K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$

$[\text{OH}^-] = \text{xC} = \text{C}\sqrt{\frac{K_b}{\text{C}}} = \sqrt{K_b\text{C}}$; this expression means that if any two of $[\text{OH}^-]$, K_b and C are known, the other can be calculated, as well as the pH

Lesson 7

(d) Salt hydrolysis

- The K_a of a weak acid can be directly related to the K_b of its conjugate base by considering the following equations: $HA \rightleftharpoons H^+ + A^-$ and $K_a = \frac{[H^+][A^-]}{[HA]}$



This means that if the K_a of weak acid is known, K_b of its conjugate base can be deduced and vice versa

- Salts are composed of the conjugate acid and base of the base and acid which were neutralised to make them
 - Salts which are made from strong acids and strong bases have no significant acid-base properties of their own; this is because the K_a and K_b values of the strong acid and the strong base respectively are so high that the K_a and K_b values of the conjugate acid and base respectively extremely small and can be ignored; such salts can be considered neutral
 - If a salt is made from a weak acid; the conjugate base of the weak acid will have a K_b value sufficiently large to cause a significant reaction with water; such salts are alkaline and have pH values greater than 7; similarly is the salt is made from a weak base, the conjugate acid of the weak base will have a K_a value sufficiently large to cause a significant reaction with water; such salts are acidic and have pH values lower than 7; the tendency of cations or anions in salts to react with water resulting in acidic or alkaline solutions is known as **salt hydrolysis**; in salts of weak acids and weak bases, both cation and anion will hydrolyse; the resulting pH of the solution will depend on the relative magnitude of K_a and K_b of the cation and the anion in the salt

(e) Very dilute solutions

- In all the calculations considered so far, the H_3O^+ present due to the auto-ionisation of water has been ignored. This is normally a reasonable assumption, since water only ionises very slightly ($[H^+] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ in pure water); in very dilute solutions, however, the H^+ present due to the auto-ionisation of water is significant and cannot be ignored; in strong acids and bases it is relatively easy to calculate the effect of the dissociation of water: consider a strong acid of molarity C , which will dissociate to give H^+ ions of concentration C ; consider also the dissociation of water to give $[H^+] = [OH^-] = x$
In total, $[H^+] = C + x$ and $[OH^-] = x$, so $[H^+][OH^-] = K_w = x(C + x)$, so $x^2 + Cx - K_w = 0$

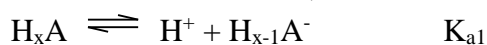
So $x = \frac{\sqrt{(C^2 + 4K_w)} - C}{2}$; if C is significant, $C^2 + 4K_w \approx C^2$ and $x \approx 0$; if $C = 0$, $x = \sqrt{K_w}$; if C is small but not 0, x can be calculated and the pH calculated from $[H^+] = C + x$

(f) Polyprotic acids and bases

- Some acids are capable of donating more than one proton and some bases are capable of accepting more than one proton; these are known as polyprotic acids and bases respectively:



- In such acids and bases, each successive dissociation will have its own K_a or K_b value:



K_{a1} is always greater than K_{a2} , which is always greater than K_{a3} ; furthermore, the dissociations are not independent of each other but the H^+ from the first dissociation suppresses the subsequent dissociations, so in many cases only the first dissociation is significant; an analogous situation occurs in polyprotic bases

- Polyprotic acids and bases form more than one salt, depending on how many protons have been accepted or lost; salts formed from the partial neutralisation of polyprotic acids are called acid salts; they still have available protons and their own K_a value (K_{a2} or K_{a3}); they will also have a K_b value resulting from the K_{a1} or K_{a2} of their conjugate acid; they are thus amphoteric and will set up a variety of equilibria in water; their net behaviour will depend on the relative magnitude of K_a and K_b ; salts formed from the partial neutralisation of polyprotic bases are called base salts; they will have their own K_b value but also a K_a value resulting from the K_b of the conjugate base; salts formed from the complete neutralisation of polyprotic acids will be polybasic and vice versa; most salts formed from polyprotic acids and bases are likely to undergo some form of salt hydrolysis
- Polyprotic acids, bases and their salts form several equilibria simultaneously with water and their pH calculations are complex

Lesson 8

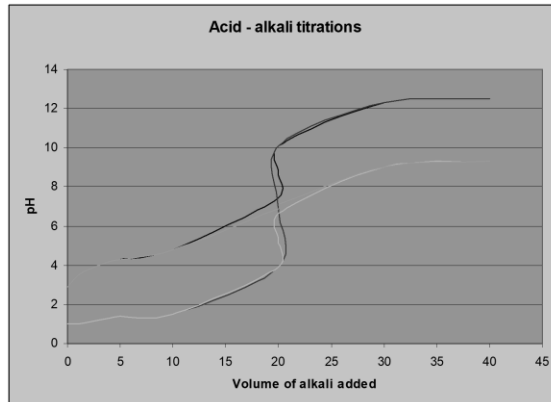
(g) Buffer Solutions

- A buffer solution is a solution which can resist changes in pH on addition of small quantities of acid or alkali or on dilution; buffer solutions are a mixture of a weak acid and a weak base; the weak acid neutralises any OH^- added and the weak base neutralises any H^+ , but the acid and the base must both be sufficiently weak not to react significantly with each other; most buffer solutions are mixtures of weak acids and their conjugate bases (HA and A^-) or weak bases and their conjugate acids (B and BH^+); these mixtures are easy to analyse because they only form a single equilibrium
- Buffer solutions form the following equilibrium in water: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
 - $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$, $[\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$, $\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$ (Henderson-Hasselbalch equation)
 - For basic buffers, $K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$, $[\text{OH}^-] = \frac{K_b[\text{B}]}{[\text{BH}^+]}$, $\text{pOH} = \text{p}K_b + \log \frac{[\text{BH}^+]}{[\text{B}]}$ so $\text{pH} = \text{p}K_w - \text{p}K_b - \log \frac{[\text{BH}^+]}{[\text{B}]}$
 - unlike in weak acids, both $[\text{HA}]$ and $[\text{A}^-]$ are similar and much larger than $[\text{H}^+]$; the simplification $[\text{H}^+][\text{A}^-] = [\text{H}^+]^2$ therefore no longer applies, the same is true with $[\text{B}]$ and $[\text{BH}^+]$ in basic buffers
- The reaction is therefore able to proceed in both directions to a significant extent; on addition of H^+ , the reaction moves left to reduce $[\text{H}^+]$, $[\text{HA}]$ will increase slightly and $[\text{A}^-]$ will decrease slightly, causing only a slight decrease in pH; the addition of OH^- removes H^+ so the reaction moves right to replace H^+ , $[\text{HA}]$ will decrease slightly and $[\text{A}^-]$ will increase slightly, causing only a slight increase in pH
 - this works until the amount of H^+ added exceeds the amount of A^- present, or the amount of OH^- added exceeds the amount of HA present, in which case the buffering capacity of the solution has been exceeded and the solution is no longer able to behave as a buffer
 - basic buffers work in a very similar way
- On dilution, the pH does not change significantly because the ratio $\frac{[\text{A}^-]}{[\text{HA}]}$ does not change; both A^- and HA dissociate more to compensate for the dilution
- A buffer does not have to be a mixture of a weak acid and its conjugate base; any mixture of a weak acid and a weak base will have the same effect; any amphoteric substance with significant values of both K_a and K_b can behave as a buffer
- Buffers are extremely useful whenever the pH needs to be kept within certain limits, as is the case with many biochemical processes; blood is buffered within pH limits of 6.8 – 7.4 by a mixture of dissolved CO_2 (H_2CO_3) and its conjugate base HCO_3^- ; the precise pH can be set by choosing an acid with a $\text{p}K_a$ value close to the desired pH and mixing it with its conjugate base in the ratio required to achieve the required pH
- Buffer solutions can be prepared either by mixing the weak acid with the weak base, or by partial neutralisation of the weak acid or base

Lesson 9

(h) Titrations and Indicators

- During titrations between acids and alkalis, the pH of the solution changes very sharply within two drops on either side of the equivalence point as the solution changes from acidic to alkaline (or vice versa); the equivalence point of the titration is the mid-point of the steep section of the titration curve
- The pH of the mixture can be calculated at any point during a titration; how this is done depends on whether the acid and base are strong or weak:
 - If both acid and alkali are strong, then the pH can be deduced by considering the number of moles of H^+ or OH^- remaining, assuming that they react completely until one runs out; this method should also be used when a strong acid or base is in excess
 - If a strong acid is added to a weak base, or a strong base is added to a weak acid, so that the weak base or weak acid are in excess and therefore only partially neutralised, a buffer solution is established and its pH can be calculated by considering the relative amounts of HA and A^- (or B and BH^+) in the mixture; a particularly useful situation occurs at half-neutralisation, when $[\text{HA}] = [\text{A}^-]$ and therefore $\text{pH} = \text{pK}_a$; this means that the pK_a of the acid can be directly read from the pH titration curve
 - The pH at the equivalence point can be deduced from consideration of any salt hydrolysis taking place
 - Weak acid-weak base titrations result in multiple equilibria existing simultaneously and are not easily analysed
- The titration curves for all the different possible titrations can be sketched on the same graph as follows:



Type of titration	pH at equivalence point	pH change at equivalence point
Strong acid - strong base	7.0	4 to 10
Weak acid - strong base	Approx 8.5	7 to 10
Strong acid - weak base	Approx 5.5	4 to 7
Weak acid - weak base	Approx 7	No sudden change

- The pH and the pH changes at the equivalence point are guidelines only; for strong acids and strong bases, the pH depends on the molarities; for weak acids and weak bases, the pH depends on the molarities and the dissociation constants

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- An acid-base indicator is a weak acid which dissociates to give an anion of a different colour; consider a weak acid HIn:
$$\text{HIn(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{In}^-(\text{aq})$$

Colour 1 Colour 2

HIn and its conjugate base In⁻ are different colours; the colour of the indicator depends on the relative concentrations of the two species, which in turn depends on the pH; if the solution is strongly acidic, the above equilibrium will be shifted to the left and HIn (colour 1) will dominate; if the solution is strongly alkaline, the above equilibrium will shift to the right and In⁻ (colour 2) will dominate

- The pH at which HIn and In⁻ are present in equal amounts is called the end-point of the indicator; it depends on the indicator dissociation constant K_{In} as follows:

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \text{ so } [\text{H}^+] = [\text{H}^+] = \frac{K_{\text{In}}[\text{HIn}]}{[\text{In}^-]}, \text{ so when } [\text{HIn}] = [\text{In}^-], [\text{H}^+] = K_{\text{In}} \text{ and } \text{pH} = \text{p}K_{\text{In}}$$

Typically, one colour will dominate the other if its concentration is more than 10 times the other, which would happen if $\text{pH} < \text{p}K_{\text{In}} - 1$ (Colour 1) or $\text{pH} > \text{p}K_{\text{In}} + 1$ (Colour 2); in between these pH values, when $\text{pH} = \text{p}K_{\text{In}} \pm 1$, an intermediate colour would appear; this serves as a general rule only; the exact pH range over which an indicator changes colour depends on the relative intensity of the two colours and varies from indicator to indicator

- Indicators are used in acid - alkali titrations in order to find the equivalence point of the titration; if they are to determine the equivalence point accurately, they must undergo a complete colour change at the equivalence point; this means that the pH range of the colour change (ie the end-point of the indicator) must fall completely within the pH range of the equivalence point; not all indicators can therefore be used for all titrations, and indicators must be chosen carefully so that the end-point of the indicator matches the pH range at the equivalence point

CHEM 111 PRACTICE QUESTIONS

Unit 1 – Moles, Formulae and Equations

Lesson 1

1. (a) Deduce the number of protons, neutrons and electrons in the following species:
- $^{37}\text{Cl}^-$
 - $^1\text{H}^+$
 - $^{45}\text{Sc}^{3+}$
- (b) Write symbols for the following species:
- 8 protons, 8 neutrons, 10 electrons
 - 82 protons, 126 neutrons, 80 electrons
 - 1 proton, 2 neutrons, 1 electron
2. (a) Define the terms relative atomic mass and relative isotopic mass; explain why ^9Be and ^9B have slightly different masses
- (b) Deduce the relative atomic mass of silicon to 2 decimal places, given that it has the following isotopes: ^{28}Si 92.21%, ^{29}Si 4.70%, ^{30}Si 3.09%
- (c) Use the mass spectrum of zirconium below to deduce the relative atomic mass of zirconium to 1 decimal place:
-
- | m/z | Relative Abundance (%) |
|-----|------------------------|
| 90 | 100 |
| 91 | ~10 |
| 92 | ~15 |
| 94 | ~15 |
| 96 | ~5 |
- (d) Most argon atoms have a mass number 40. How many neutrons does this isotope have? The relative isotopic mass of this isotope is 39.961, but the relative atomic mass of argon is 39.948. What can you deduce about the other isotopes of argon?
3. State and explain the five processes taking place in a mass spectrometer

Lesson 2

4. (a) Classify the following substances as: A – giant ionic; B – giant metallic; C – simple molecular; D – simple atomic; E – giant covalent
- (i) silicon dioxide
 - (ii) ammonia
 - (iii) potassium
 - (iv) magnesium chloride
 - (v) chlorine
 - (vi) water
 - (vii) copper sulphate
 - (viii) neon
 - (ix) graphite
- (b) Deduce the unit formula for the following compounds:
- (i) sodium oxide
 - (ii) magnesium oxide
 - (iii) calcium iodide
 - (iv) potassium sulphide
 - (v) magnesium sulphate
 - (vi) ammonium nitrate
 - (vii) calcium carbonate
 - (viii) aluminium oxide
 - (ix) strontium hydroxide
 - (x) ammonium sulphate
- (c) State the molecular formula of the following molecules:
- (i) water
 - (ii) ammonia
 - (iii) carbon dioxide
 - (iv) carbon monoxide
 - (v) chlorine
- (d) (i) A compound containing 85.71% C and 14.29% H has a relative molecular mass of 56. Find its molecular formula.
- (ii) Analysis of a hydrocarbon showed that 7.8 g of the hydrocarbon contained 0.6 g of hydrogen and that the relative molecular mass was 78. Find the molecular formula of the hydrocarbon.
- (iii) An ionic compound is analysed and found to contain 48.4% oxygen, 24.3% sulphur, 21.2% nitrogen and 6.1% hydrogen. Calculate its empirical formula and deduce its unit formula.

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Lesson 3

5. (a) If you have 2.5×10^{21} atoms of magnesium, how many moles of magnesium do you have?
(b) If you have 0.25 moles of carbon dioxide, how many molecules of carbon dioxide do you have?
6. (a) Deduce the relative masses of:
(i) CO_2
(ii) Na_2CO_3
(iii) MgCl_2
(iv) CH_4
(v) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
(vi) $\text{Mg}(\text{OH})_2$
(vii) $\text{Al}_2(\text{SO}_4)_3$
(b) In each case, indicate whether your answer is a relative formula mass or a relative molecular mass
7. (a) Calculate the number of moles present in:
(i) 2.5 g of O_2
(ii) 40 cm^3 of 0.2 mol dm^{-3} HNO_3
(b) Calculate the molarity and the mass concentration of an aqueous solution containing:
(i) 0.002 moles of H_2SO_4 in 16.5 cm^3
(ii) 0.1 moles of NH_3 in 50 cm^3
(iii) 8 g of NaOH in 250 cm^3
(c) What mass of $\text{C}_6\text{H}_{12}\text{O}_6$ should be added to a 250 cm^3 volumetric flask to make a 0.10 mol dm^{-3} solution when the flask is filled to its mark with water?
(d) What volume of 2.0 mol dm^{-3} hydrogen peroxide should be added to a 100 cm^3 volumetric flask to make a $0.050 \text{ mol dm}^{-3}$ solution when the flask is filled to its mark with water?
(e) Concentrated HCl contains 36% HCl by mass (the rest is water). What mass of concentrated HCl should be added to a 250 cm^3 volumetric flask to make a 0.10 mol dm^{-3} solution when the flask is filled to its mark with water?
8. (a) According to the ideal gas equation, $PV = nRT$ ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)
Use the ideal gas equation to show that the **molar gas volume** at room temperature (298 K) and standard atmospheric pressure (101.3 kPa) is 24.4 dm^3
(b) Assuming room temperature and standard atmospheric pressure, calculate:
(i) the number of moles in 4.88 dm^3 of O_2
(ii) the volume occupied by 20 g of NO_2
(iii) the mass of 200 cm^3 of N_2
9. Deduce which sample (A, B or C) contains the most ammonia (NH_3):
Sample A contains 2.0 g of NH_3
Sample B contains 50 cm^3 of a 2 mol dm^{-3} aqueous solution of NH_3
Sample C contains 2.8 dm^3 of NH_3 at room temperature and standard atmospheric pressure

Lesson 4

10. (a) Deduce the apparatus errors in the following measurements:
- (i) mass using a 2 dp mass balance
 - (ii) temperature change using a thermometer with graduation marks every 1°C
 - (iii) titre volume using a typical burette
 - (iv) volume of solution using a measuring cylinder with graduation marks every 1 cm³
- (b) Deduce the percentage errors in the following measurements using the apparatus from Q11a unless otherwise stated:
- (i) A mass of 2.34 g
 - (ii) A temperature change 6.5 °C
 - (iii) A titre volume of 22.35 cm³
 - (iv) A volume of 25 cm³ measured using a measuring cylinder
 - (v) A volume of 25.0 cm³ measured using a pipette with apparatus error 0.05 cm³
 - (vii) A volume of 250 cm³ measured using a volumetric flask with apparatus error 0.2 cm³
- (c) Arrange the seven measurements in Q11b in order of increasing accuracy (ie from least accurate to most accurate)
- (d) A student uses the measurements of 2.34 g, 6.5 °C and 25 cm³ (using the measuring cylinder) to calculate an enthalpy change. Deduce the total percentage apparatus error in the answer.
- (e) A student uses measurements of 2.34 g, 250 cm³ (using the volumetric flask), 25.0 cm³ (using the pipette) and the titre volume of 22.35 cm³ to calculate a molar mass. Deduce the total percentage apparatus error in the answer.
11. (a) What is the difference between accuracy and precision?
- (b) Explain the range of possible values represented by the following measurements:
- (i) 21 cm³
 - (ii) 21.0 cm³
 - (iii) 21.00 cm³
- (c) A student gets a calculator value of 0.02576281 moldm⁻³ when calculating a concentration. The measurements used in the calculation created a total apparatus error of 2.1%. Express the concentration to a suitable number of significant figures.

Lesson 5

12. Consider the combustion equation: $C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$
- How many moles of oxygen gas are required for the complete combustion of 0.2 moles of pentane (C_5H_{12})?
 - How many moles of carbon dioxide are produced during the complete combustion of 0.2 moles of pentane?
 - How many moles of water are produced during the complete combustion of 0.2 moles of pentane?
 - 0.15 moles of pentane are mixed with 0.80 moles of oxygen and allowed to react completely.
 - Which is the limiting reactant?
 - Which reactant is in excess and how many moles of it will be left after the reaction?
 - How many moles of carbon dioxide will be produced?
 - How many moles of water will be produced?
 - If all reactants and products are in the gaseous state, what is the total number of gas moles remaining after the reaction is complete?
13. 0.52 g of sodium was added to 100 cm³ of water and the following reaction took place:
 $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
Calculate:
- The volume of hydrogen evolved at 298 K and 100 kPa
 - The concentration of the sodium hydroxide solution produced, assuming the volume of water does not change.
14. 0.10 g of magnesium was dissolved in 5.0 cm³ of 2.0 mol dm⁻³ hydrochloric acid. The following reaction takes place: $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
- Deduce which of the two reactants is in excess.
 - Hence calculate the volume of hydrogen gas produced (the molar gas volume under the conditions of the experiment was 24.4 dm³)
15. Ethanol can be produced commercially either by the fermentation of glucose or by the hydration of ethene:
Fermentation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
Hydration: $C_2H_4 + H_2O \rightarrow C_2H_5OH$
- Calculate the percentage atom economy of both reactions. Suggest how the percentage atom economy of the fermentation process could be improved.
 - 100 g of glucose was fermented and 45 g of ethanol was obtained. Calculate the percentage yield of ethanol in this experiment.
 - 100 g of ethene was hydrated in excess steam and 80 g of ethanol was obtained. Calculate the percentage yield of ethanol in this experiment.

Lesson 6

16. Classify the following substances as acids, bases or salts:
- | | |
|-------------------------------------|-------------------------------------|
| (a) HCl | (f) BaO |
| (b) Ca(OH) ₂ | (g) H ₂ SO ₄ |
| (c) MgCO ₃ | (h) MgCl ₂ |
| (d) Na ₂ SO ₄ | (i) Na ₂ CO ₃ |
| (e) HNO ₃ | (j) NH ₃ |
17. Write balanced symbol equations for the following reactions:
- sulphuric acid and sodium hydroxide
 - nitric acid and calcium carbonate
 - hydrochloric acid and magnesium oxide
 - nitric acid and ammonia
 - hydrochloric acid and potassium carbonate
 - sulphuric acid and ammonia
18.
 - Give the formula of all three salts formed when H₃PO₄ reacts with NaOH.
 - Give the equation for the most likely reaction when H₃PO₄ is mixed with NaOH in a 1:2 ratio
 - Write an equation for the reaction occurring when aqueous carbon dioxide reacts with HCl
 - in a 1:1 ratio
 - in a 1:2 ratio
 - Write an equation for the reaction occurring when NaHCO₃ reacts with:
 - HCl
 - NaOH
 - Itself
19. Explain the meaning of the terms “strong acid”, “weak acid”, “strong base” and “weak base”. Give an example of each, writing an equation to show how each reacts with water.
20. Explain what is meant by the terms “acidic solution”, “alkaline solution” and “neutral solution”.
21.
 - Calculate the pH of the following solutions:
 - 0.015 mol dm⁻³ HCl
 - 6.0 mol dm⁻³ HNO₃
 - 0.20 mol dm⁻³ H₂SO₄
 - The mixture formed when 10 cm³ of 0.1 mol dm⁻³ NaOH is added to 25 cm³ of 0.1 mol dm⁻³ HCl
 - Calculate the molarity of the following solutions:
 - A solution of HNO₃ with a pH of 2.5
 - A solution of H₂SO₄ with a pH of 0.5
22. A 25.0 cm³ sample of 0.0850 mol dm⁻³ hydrochloric acid was placed in a beaker. Distilled water was added until the pH of the solution was 1.25. Calculate the total volume of the solution formed..

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23. Succinic acid has the formula $(\text{CH}_2)_n(\text{COOH})_2$ and reacts with dilute sodium hydroxide as follows:
$$(\text{CH}_2)_n(\text{COOH})_2 + 2\text{NaOH} \rightarrow (\text{CH}_2)_n(\text{COONa})_2 + 2\text{H}_2\text{O}$$
2.0 g of succinic acid were dissolved in water and the solution made up to 250 cm^3 . This solution was placed in a burette and 18.4 cm^3 was required to neutralise 25 cm^3 of 0.1 mol dm^{-3} NaOH. Deduce the molecular formula of the acid and hence the value of n.
24. A sample of hydrated calcium sulphate, $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$, has a relative formula mass of 172. What is the value of x?
25. A hydrated salt is found to have the empirical formula $\text{CaN}_2\text{H}_8\text{O}_{10}$. What is its dot formula?
26. A sample of hydrated magnesium sulphate, $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$, is found to contain 51.1% water. What is the value of x?
27. 13.2 g of a sample of zinc sulphate, $\text{ZnSO}_4 \cdot x\text{H}_2\text{O}$, was strongly heated until no further change in mass was recorded. On heating, all the water of crystallisation evaporated as follows: $\text{ZnSO}_4 \cdot x\text{H}_2\text{O} \rightarrow \text{ZnSO}_4 + x\text{H}_2\text{O}$. Calculate the number of moles of water of crystallisation in the zinc sulphate sample given that 7.4 g of solid remained after strong heating.
28. Sodium carbonate exists in hydrated form, $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$, in the solid state. 3.5 g of a sodium carbonate sample was dissolved in water and the volume made up to 250 cm^3 . 25.0 cm^3 of this solution was titrated against 0.1 mol dm^{-3} HCl and 24.5 cm^3 of the acid were required. Calculate the value of x given the equation:
$$\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$$
29. 25 cm^3 of a sample of vinegar (CH_3COOH) was pipetted into a volumetric flask and the volume was made up to 250 cm^3 . This solution was placed in a burette and 13.9 cm^3 were required to neutralise 25 cm^3 of 0.1 mol dm^{-3} NaOH. Calculate the molarity of the original vinegar solution and its concentration in g dm^{-3} , given that it reacts with NaOH in a 1:1 ratio.
30. 2.5 g of a sample of impure ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, was dissolved in water and the solution made up to 250 cm^3 . This solution was placed in a burette and 21.3 cm^3 were required to neutralise 25 cm^3 of 0.1 mol dm^{-3} NaOH. Given that ethanedioic acid reacts with NaOH in a 1:2 ratio, calculate the percentage purity of the sample.
31. When silicon tetrachloride is added to water, the following reaction occurs:
$$\text{SiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}(\text{aq})$$
1.2 g of impure silicon tetrachloride was dissolved in excess water, and the resulting solution was made up to 250 cm^3 . A 25 cm^3 portion of the solution was then titrated against 0.10 mol dm^{-3} sodium hydroxide, and 18.7 cm^3 of the alkali were required. What was the percentage purity of the silicon tetrachloride?

Lesson 7

32. Write ionic equations for the following reactions:
- When aqueous magnesium chloride is added to aqueous silver nitrate, a white precipitate is formed.
 - When aqueous sodium hydroxide is added to aqueous aluminium sulphate, a white precipitate is formed.
 - When aqueous barium chloride is treated with dilute sodium sulphate, a white precipitate is formed.
 - A pale blue precipitate is formed on slow addition of potassium hydroxide solution to copper (II) sulphate solution.
 - A white precipitate is formed when dilute hydrochloric acid is added to a solution of lead (II) nitrate.
 - When dilute calcium chloride is mixed with sulphuric acid, a white precipitate is formed.
 - When aqueous calcium chloride is mixed with aqueous sodium carbonate, a white precipitate is formed.
33. Predict whether a precipitate will form when the following solutions are mixed, and if so, write the ionic equation for the reaction occurring:
- ammonium chloride and sulphuric acid
 - silver nitrate and sodium bromide
 - barium chloride and sulphuric acid
 - sodium chloride and copper sulphate
 - magnesium chloride and sodium hydroxide
34. 1.25 g of a metal chloride with formula MCl_3 was dissolved in water and an excess of silver nitrate solution was added to it. The resulting precipitate was washed, dried, weighed and found to have a mass of 3.42 g. Determine the relative atomic mass of M and hence suggest its identity.

Lesson 8

35. Deduce the oxidation numbers of the following atoms:

- | | |
|--------------------------------------|--|
| (a) Si in SiF_4 | (k) O in H_2O_2 |
| (b) S in H_2S | (l) Mn in MnO_4^- |
| (c) Pb in PbO_2 | (m) Cr in $\text{Cr}_2\text{O}_7^{2-}$ |
| (d) S in H_2SO_4 | (n) C in $\text{C}_2\text{O}_4^{2-}$ |
| (e) N in NO_3^- | (o) I in IO_3^- |
| (f) N in NO_2^- | (p) S in SO_2 |
| (g) I in I_2 | (q) O in OF_2 |
| (h) S in $\text{S}_2\text{O}_3^{2-}$ | (r) Fe in Fe_3O_4 |
| (i) Cl in ClO^- | (s) S in $\text{S}_4\text{O}_6^{2-}$ |
| (j) Cl in ClO_3^- | (t) C in HCN |

36. Turn the following chemical changes into balanced redox reactions by writing half equations for each change and then combining them (assume acidic conditions when the half-equation is pH-dependent)

- $\text{PbO}_2 \rightarrow \text{Pb}^{2+}$, $\text{Cl}^- \rightarrow \text{Cl}_2$
- $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$
- $\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-}$, $\text{I}_2 \rightarrow 2\text{I}^-$
- $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$, $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$
- $\text{IO}_3^- \rightarrow \text{I}_2$, $\text{I}^- \rightarrow \text{I}_2$
- $\text{ClO}^- \rightarrow \text{ClO}_3^-$, $\text{ClO}^- \rightarrow \text{Cl}^-$
- $\text{H}^+ \rightarrow \text{H}_2$, $\text{OH}^- \rightarrow \text{O}_2$
- $\text{ClO}^- \rightarrow \text{Cl}^-$, $\text{I}^- \rightarrow \text{I}_2$
- $\text{PbO}_2 \rightarrow \text{Pb}^{2+}$, $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$
- $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$

37. Write half-equations to show the following processes in alkaline conditions:

- O_2 to OH^-
- Cr^{3+} to CrO_4^{2-}
- H_2O_2 to OH^-
- MnO_4^- to MnO_2

Lesson 9

38. Ammonium iron (II) sulphate crystals have the following formula: $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot n\text{H}_2\text{O}$. In an experiment to determine n , 8.492 g of the salt were dissolved and made up to 250 cm^3 of solution with distilled water and dilute sulphuric acid. A 25 cm^3 portion of the solution was further acidified and titrated against potassium manganate (VII) solution of concentration $0.0150 \text{ mol dm}^{-3}$. A volume of 22.5 cm^3 was required. Determine n .
39. A solution of hydrogen peroxide of volume 25 cm^3 was diluted to 500 cm^3 . A 25.0 cm^3 portion of the diluted solution was acidified and titrated against $0.0150 \text{ mol dm}^{-3}$ potassium permanganate solution, and 45.7 cm^3 were required. Calculate the concentration of the original hydrogen peroxide solution before dilution, given that hydrogen peroxide is oxidized according to the following equation:
 $\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + \text{O}_2(\text{g}) + 2\text{e}$
40. The ethanedioate ion, $\text{C}_2\text{O}_4^{2-}(\text{aq})$ is a reducing agent: $\text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{e}$
 A sample of ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, weighing 2.24 g was dissolved in water and the solution made up to 250 cm^3 . 25 cm^3 samples of the solution were taken and the ethanedioate in the solution required 35.6 cm^3 of 0.020M potassium manganate (VII) for reaction.
 Calculate the value of x .
41. 25.0 cm^3 of a 0.1 mol dm^{-3} solution of KNO_2 is completely oxidized by 50.0 cm^3 of $0.0200 \text{ mol dm}^{-3}$ potassium manganate (VII) solution. To what oxidation number was the N oxidized?
42. The active ingredient in bleach is sodium chlorate (I). It can be reduced by iodide ions to make iodine:
 $\text{ClO}^- + 2\text{H}^+ + 2\text{I}^- \rightarrow \text{Cl}^- + \text{I}_2 + \text{H}_2\text{O}$
 In an experiment to determine the concentration of sodium chlorate (I) in a bleach, 5 cm^3 of the bleach was pipetted into a volumetric flask and made up to 250 cm^3 .
 25 cm^3 portions of this solution were then added to a conical flask and an excess of potassium iodide was then added. The resulting solution was titrated against 0.1 mol dm^{-3} sodium thiosulphate, and 22.3 cm^3 was required.
 (a) Write an equation for the reaction between sodium thiosulphate and iodine
 (b) Hence determine the concentration of sodium chlorate (I) in the original bleach sample
43. In an experiment to determine the percentage by mass of copper in a 1 pence coin weighing 1.24 g, the coin was completely dissolved in concentrated nitric acid until all of the copper had been oxidised to copper (II) ions. The excess nitric acid was then neutralised and the volume made up to 250 cm^3 in a volumetric flask. 25 cm^3 portions of this solution were then added to a conical flask and an excess of potassium iodide was then added. Cu^{2+} ions react with iodide ions as follows:
 $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$
 The resulting solution was titrated against 0.1 mol dm^{-3} sodium thiosulphate, and 18.4 cm^3 was required. Determine the percentage of copper in the coin.
44. Potassium iodate (V), KIO_3 , reacts with iodide ions to produce iodine as follows:
 $\text{IO}_3^- + 6\text{H}^+ + 5\text{I}^- \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$
 0.75 g of an impure sample of KIO_3 was dissolved in water and made up to 250 cm^3 in a volumetric flask. 25 cm^3 portions of this solution were then added to a conical flask and an excess of potassium iodide and dilute sulphuric acid were then added. The resulting solution was titrated against 0.1 mol dm^{-3} sodium thiosulphate, and 17.1 cm^3 was required. Determine the percentage purity of the sample of potassium iodate (V).

Lesson 10

45. (a) Deduce the equivalent weight of the following elements:
(i) Copper
(ii) Aluminium
(iii) Chlorine
- (b) Calculate the normality of the following solutions:
(i) $0.02 \text{ mol dm}^{-3} \text{ KMnO}_4$
(ii) $0.05 \text{ mol dm}^{-3} \text{ Ca(OH)}_2$
(iii) $0.10 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$
46. A solution of sodium chloride of molarity 5.0 mol dm^{-3} is found to have a density of 1.186 g cm^{-3} . Calculate the molality of the solution.
47. (a) Describe briefly the cycle of scientific enquiry.
(b) Explain the difference between a hypothesis and a law.
(c) Explain the difference between a law and a theory.
(d) Explain the difference between a theorem and a theory.
(e) Explain the difference between induction and deduction.
(f) Explain what is meant by the term serendipity.

Unit 2 – Chemical Equilibrium

K_c and Le Chatelier's principle

- The reaction for the formation of hydrogen iodide does not go to completion but reaches an equilibrium: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
A mixture of 1.9 mol of H_2 and 1.9 mol of I_2 was prepared and allowed to reach equilibrium in a closed vessel on 250 cm³ capacity. The resulting equilibrium mixture was found to contain 3.0 mol of HI. Calculate the value of K_c .
- Consider the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.
1 mol of dinitrogen tetroxide, N_2O_4 , was introduced into a vessel of volume 10 dm³. At equilibrium 50% had dissociated. Calculate K_c for the reaction.
- In an experiment, 9.0 moles of nitrogen and 27 moles of hydrogen were placed into a vessel of volume 10 dm³ and allowed to reach equilibrium. It was found that two thirds of the nitrogen and hydrogen were converted into ammonia. Calculate K_c for the reaction.
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- Hydrogen chloride can be oxidised to chlorine by the Deacon process:
 $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
0.800 mol of hydrogen chloride was mixed with 0.200 mol of oxygen in a vessel of volume 10 dm³. At equilibrium it was found that the mixture contained 0.200 mol of hydrogen chloride. Calculate K_c for the reaction.
- A 0.04 sample of SO_3 is introduced into a 3.04 dm³ vessel and allowed to reach equilibrium. The amount of SO_3 present at equilibrium is found to be 0.0284 mole. Calculate the value of K_c for the reaction $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$.
- At 723K, hydrogen and iodine react together and the following equilibrium is established:
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
The value of K_c for this equilibrium is 64. In an experiment, equal amounts of hydrogen and iodine were mixed together, and the equilibrium mixture of the three gases in a container of volume 1 dm³ at 723K was found to contain 1.5 moles of iodine. Calculate the concentration of hydrogen iodide in the mixture at 723K.
- The expression for an equilibrium constant, K_c , for a homogeneous equilibrium reaction is given below.
$$K_c = \frac{[\text{A}]^2[\text{B}]}{[\text{C}][\text{D}]^3}$$
 - Write an equation for the forward reaction and deduce the units of K_c
 - State what can be deduced from the fact that the value of K_c is larger when the equilibrium is established at a lower temperature.

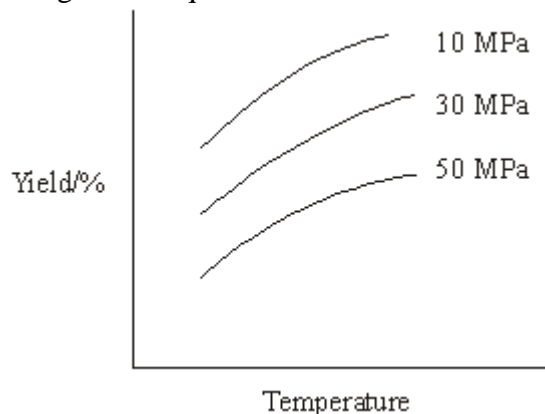
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8. A 36.8 g sample of N_2O_4 was heated in a closed flask of volume 16.0 dm^3 . An equilibrium was established at a constant temperature according to the following equation.



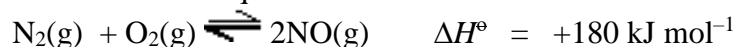
The equilibrium mixture was found to contain 0.180 mol of N_2O_4

- Write an expression for K_c and calculate its value under these conditions.
 - Another 36.8 g sample of N_2O_4 was heated to the same temperature as in the original experiment, but in a larger flask. State the effect, if any, of this change on the position of equilibrium and on the value of K_c compared with the original experiment.
9. The diagram below shows the effect of temperature and pressure on the equilibrium yield of the product in a gaseous equilibrium.



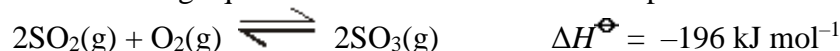
- Use the diagram to deduce whether the forward reaction involves an increase or a decrease in the number of moles of gas. Explain your answer.
 - Use the diagram to deduce whether the forward reaction is exothermic or endothermic. Explain your answer.
10. When a 0.218 mol sample of hydrogen iodide was heated in a flask of volume $V \text{ dm}^3$, the following equilibrium was established at 700 K.
- $$2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$$
- The equilibrium mixture was found to contain 0.023 mol of hydrogen.
- Write an expression for K_c for the equilibrium and calculate its value at 700 K
 - Explain why the volume of the flask need not be known when calculating a value for K_c .
 - Calculate the value of K_c at 700 K for the equilibrium
- $$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$
11. A mixture was prepared using 1.00 mol of propanoic acid, 2.00 mol of ethanol and 5.00 mol of water. At a given temperature, the mixture was left to reach equilibrium according to the following equation.
- $$\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \quad \Delta H^\ominus = -22 \text{ kJ mol}^{-1}$$
- The equilibrium mixture contained 0.54 mol of the ester ethyl propanoate.
- Write an expression for the equilibrium constant, K_c , for this equilibrium. Calculate its value at this temperature and explain why this value has no units.
 - For this equilibrium, predict the effect of an increase in temperature on each of the following.
 - the amount, in moles, of ester at equilibrium
 - the time taken to reach equilibrium
 - the value of K_c

12. At high temperatures, nitrogen is oxidised by oxygen to form nitrogen monoxide in a reversible reaction as shown in the equation below.



State and explain the effect of an increase in pressure, and the effect of an increase in temperature, on the yield of nitrogen monoxide in the above equilibrium.

13. Sulphur dioxide and oxygen were mixed in a 2:1 mol ratio and sealed in a flask with a catalyst. The following equilibrium was established at temperature T_1



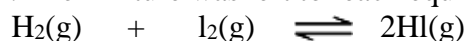
- (a) When equilibrium was established at a different temperature, T_2 , the value of K_p was found to have increased. State which of T_1 and T_2 is the lower temperature and explain your answer.
- (b) In a further experiment, the amounts of sulphur dioxide and oxygen used, the catalyst and the temperature, T_1 , were all unchanged, but a flask of smaller volume was used. Deduce the effect of this change on the yield of sulphur trioxide and on the value of K_c .
14. When heated above 100°C , nitrosyl chloride (NOCl) partly decomposes to form nitrogen monoxide and chlorine as shown in the equation.



- (a) A 2.50 mol sample of NOCl was heated in a sealed container of volume 5 dm^3 and equilibrium was established at a given temperature. The equilibrium mixture formed contained 0.80 mol of NO. Calculate the value of K_c for this equilibrium mixture.
- (b) A different mixture of NOCl, NO and Cl_2 reached equilibrium in a sealed container of volume 15.0 dm^3 . The equilibrium mixture formed contained 1.90 mol of NOCl and 0.86 mol of NO at temperature T . The value of K_c for the equilibrium at temperature T was $7.4 \times 10^{-3} \text{ mol dm}^{-3}$. Calculate the amount, in moles, of Cl_2 in this equilibrium mixture.
- (c) Consider this alternative equation for the equilibrium at temperature T .

$$\text{NOCl}(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g})$$
 Calculate a value for the different equilibrium constant K_c for the equilibrium as shown in this alternative equation. Deduce the units of this K_c

15. A mixture of 1.50 mol of hydrogen and 1.20 mol of gaseous iodine was sealed in a container of volume $V \text{ dm}^3$. The mixture was left to reach equilibrium as shown by the following equation.



At a given temperature, the equilibrium mixture contained 2.06 mol of hydrogen iodide. Calculate the value of K_c for this reaction at this temperature.

K_p

16. Consider the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.
1 mol of dinitrogen tetroxide, N_2O_4 , was introduced into a vessel. At equilibrium at a constant pressure of 100 kPa, 50% had dissociated. Calculate K_p for the reaction.
17. Hydrogen chloride can be oxidised to chlorine by the Deacon process:
$$4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$$
0.800 mol of hydrogen chloride was mixed with 0.200 mol of oxygen at a constant pressure of 100 kPa. At equilibrium it was found that the mixture contained 0.200 mol of hydrogen chloride. Calculate K_p for the reaction.
18. In an experiment, 9.0 moles of nitrogen and 27 moles of hydrogen were p and allowed to reach equilibrium at a constant pressure of 25 Mpa. It was found that two thirds of the nitrogen and hydrogen were converted into ammonia. Calculate K_p for the reaction.
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
19. A 0.04 sample of SO_3 is allowed to reach equilibrium at a constant pressure of 200 kPa. The amount of SO_3 present at equilibrium is found to be 0.0284 mole. Calculate the value of K_p for the reaction
$$2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$$
.
20. The reaction between carbon monoxide and hydrogen proceeds according to the equilibrium $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$ A vessel contains 0.1 mole of carbon monoxide. After 0.3 mole of hydrogen is added, 0.06 mol of methanol are formed. The pressure was kept constant at 300 kPa. Calculate the equilibrium constant K_p .
21. For the general reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, derive an expression for K_p in terms of K_c , R, T and Δn ($c + d - a - b$)
22. A sealed flask containing gases **X** and **Y** in the mole ratio 1:3 was maintained at 600 K until the following equilibrium was established: $\text{X}(\text{g}) + 3\text{Y}(\text{g}) \rightleftharpoons 2\text{Z}(\text{g})$
The partial pressure of **Z** in the equilibrium mixture was 6.0 MPa when the total pressure was 22.0 MPa. Calculate the value of K_p for the reaction.
23. Sulphur dioxide and oxygen were mixed in a 2:1 mol ratio and sealed in a flask with a catalyst. The following equilibrium was established at temperature T_1 :
$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H^\ominus = -196 \text{ kJ mol}^{-1}$$
- The partial pressure of sulphur dioxide in the equilibrium mixture was 24 kPa and the total pressure in the flask was 104 kPa. Calculate the value of K_p for the reaction.
 - When equilibrium was established at a different temperature, T_2 , the value of K_p was found to have increased. State which of T_1 and T_2 is the lower temperature and explain your answer.
 - In a further experiment, the amounts of sulphur dioxide and oxygen used, the catalyst and the temperature, T_1 , were all unchanged, but a flask of smaller volume was used. Deduce the effect of this change on the yield of sulphur trioxide and on the value of K_p .

Heterogeneous equilibria and K_{sp}

24. Consider the following equilibrium: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. At 1073 K, the partial pressure of CO_2 is found to be 23.6 kPa. Calculate K_p and K_c for the reaction at this temperature.
25. Consider the following equilibrium: $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$. At 295 K, the partial pressure of each gas is 26.5 kPa. Calculate K_p and K_c for the reaction at this temperature.
26. Consider the following equilibrium: $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$. A solid sample of $\text{NH}_4\text{CO}_2\text{NH}_2$ was allowed to decompose to equilibrium in an evacuated container. The total gas pressure was found to be 36.3 kPa. Calculate K_p for the reaction.
27. (a) Calculate the value of K_{sp} for calcium sulphate (CaSO_4) given that its solubility at 25 °C is 0.67 g dm^{-3} .
 (b) Calculate the value of K_{sp} for PbCl_2 given that its solubility is $0.011 \text{ mol dm}^{-3}$.
 (c) The K_{sp} of silver bromide (AgBr) is $7.7 \times 10^{-13} \text{ mol}^2\text{dm}^{-6}$. Deduce the molar solubility of silver bromide.
 (d) The K_{sp} of copper hydroxide $\text{Cu}(\text{OH})_2$ is $2.2 \times 10^{-20} \text{ mol}^3\text{dm}^{-9}$. Deduce the molar solubility of copper hydroxide.
28. (a) The K_{sp} of barium sulphate (BaSO_4) is $1.1 \times 10^{-10} \text{ mol}^2\text{dm}^{-6}$. Deduce whether or not a precipitate will form if 200 cm^3 of $0.0040 \text{ mol dm}^{-3} \text{ BaCl}_2$ is mixed with 600 cm^3 of $0.0080 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$.
 (b) The K_{sp} of calcium hydroxide $\text{Ca}(\text{OH})_2$ is $8.0 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$. Deduce whether or not a precipitate will form if 2.0 cm^3 of $0.20 \text{ mol dm}^{-3} \text{ NaOH}$ is mixed with 1.0 cm^3 of $0.10 \text{ mol dm}^{-3} \text{ CaCl}_2$.
29. Silver nitrate is slowly added to a solution that contains $0.020 \text{ mol dm}^{-3} \text{ Cl}^-$ and Br^- . K_{sp} of $\text{AgCl} = 1.6 \times 10^{-10} \text{ mol}^2\text{dm}^{-6}$ and K_{sp} of $\text{AgBr} = 7.7 \times 10^{-13} \text{ mol}^2\text{dm}^{-6}$.
 (a) Calculate the concentration range of Ag^+ ions which could separate Br^- and Cl^- in solution by precipitating AgBr but not AgCl .
 (b) What is the concentration of Br^- ions in the solution just before AgCl begins to precipitate?
30. (a) Calculate the solubility of AgCl in a $6.5 \times 10^{-3} \text{ mol dm}^{-3}$ solution of AgNO_3 . The K_{sp} of $\text{AgCl} = 1.6 \times 10^{-10} \text{ mol}^2\text{dm}^{-6}$.
 (b) Calculate the solubility of AgBr in a $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ solution of NaBr . The K_{sp} of AgBr is $7.7 \times 10^{-13} \text{ mol}^2\text{dm}^{-6}$.
31. 75 cm^3 of $0.060 \text{ mol dm}^{-3} \text{ NaF}$ is added to 25 cm^3 of $0.15 \text{ mol dm}^{-3} \text{ Sr}(\text{NO}_3)_2$. The solubility product of SrF_2 is $2.0 \times 10^{-10} \text{ mol}^3\text{dm}^{-9}$. Deduce the concentration of Na^+ , F^- , Sr^{2+} and NO_3^- in the resulting solution.
32. Ba^{2+} ions are highly toxic. Barium compounds, however, are very useful for medical X-ray analysis. Patients are typically given 20 g of BaSO_4 ($K_{sp} = 1.1 \times 10^{-10} \text{ mol}^2\text{dm}^{-6}$). Calculate the concentration of Ba^{2+} ions when this is mixed with 5.0 dm^3 of a patient's blood.

Acid-Base Equilibria and pH ($K_w = 1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$)

33. For each of the following equilibria, identify the conjugate acid base pairs by labelling each species as Acid 1, Base 1, Acid 2 or Base 2
- (a) $\text{H}_2\text{O}(\text{l}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
- (b) $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- (c) $\text{H}_2\text{SO}_4(\text{aq}) + \text{HNO}_3(\text{aq}) \rightleftharpoons \text{HSO}_4^-(\text{aq}) + \text{H}_2\text{NO}_3^+(\text{aq})$
- (d) $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- (e) $\text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l})$
34. (a) Calculate the pH of the following solutions:
 (i) $0.10 \text{ mol dm}^{-3} \text{ C}_6\text{H}_5\text{COOH}$ (K_a of benzoic acid = $6.3 \times 10^{-5} \text{ mol dm}^{-3}$)
 (ii) $0.05 \text{ mol dm}^{-3} \text{ NaHSO}_4$ (K_a of $\text{HSO}_4^- = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$)
- (b) Calculate the molarity of a solution of HCOOH ($K_a = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$) which has a pH of 3.0
- (c) The pH of a 0.10 mol dm^{-3} solution of a weak monoprotic acid, HA is 2.85. Determine the K_a of the acid.
- (d) A 500 cm^3 solution containing 1.9g of a weak acid HA has a pH of 3.5. Calculate the molar mass of the acid, given that it has a K_a of $2.0 \times 10^{-6} \text{ mol dm}^{-3}$.
35. Pure water at 40°C has a pH of 6.7
- (a) Calculate the ionic product of water at 40°C
- (b) Deduce whether the auto-ionisation of water is endothermic or exothermic
36. Calculate the pH of the following solutions:
- (a) $0.02 \text{ mol dm}^{-3} \text{ Ba}(\text{OH})_2$.
- (b) $0.1 \text{ mol dm}^{-3} \text{ NH}_3$ (K_b of $\text{NH}_3 = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$)
- (c) The solution formed after the addition of 50.0 cm^3 of $0.150 \text{ mol dm}^{-3} \text{ NaOH}$ to 25.0 cm^3 of $0.06 \text{ mol dm}^{-3} \text{ HCl}$.
37. (a) Given that the K_b for NH_3 is $1.8 \times 10^{-5} \text{ mol dm}^{-3}$, calculate the pH of $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$.
- (b) Given that the K_a for CH_3COOH is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$, calculate the pH of $0.25 \text{ mol dm}^{-3} \text{ CH}_3\text{COONa}$.
- (c) Calculate the molarity of a solution of KCN which has a pH of 11.0, given that the K_a for HCN is $4.9 \times 10^{-10} \text{ mol dm}^{-3}$
38. (a) Calculate the pH of $2 \times 10^{-8} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$
- (b) Calculate the pH of the solution formed when 0.1 g of NaOH is dropped into a tank containing 5 m^3 of water.

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- 39.** 0.500 g of an impure sample of salicylic acid was tipped into a beaker and 100 cm³ of distilled water were added. The solution was poured into a 250 cm³ graduated flask and made up to the mark with distilled water. The pH of this solution was measured and a value of 2.50 was obtained.
- Calculate the concentration of salicylic acid in this solution. The K_a for salicylic acid is $1.07 \times 10^{-3} \text{ mol dm}^{-3}$. Assume that salicylic acid is the only acid in this solution. You may represent salicylic acid as HA.
 - Use your answer to part (a) to calculate the mass of salicylic acid ($M_r = 138.0$) present in the original sample.
 - Use your answer to part (a) to calculate the percentage purity of the salicylic acid used to make the solution.
- 40.** Calculate the pH of the solution formed when 25.0 cm³ of 0.150 mol dm⁻³ aqueous sulfuric acid are added to 30.0 cm³ of 0.200 mol dm⁻³ aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.
- 41.**
- A saturated solution of calcium hydroxide (limewater) at 25 °C has a pH of 11.5. Calculate the solubility product for calcium hydroxide at 25 °C.
 - Calculate the molar solubility of Fe(OH)₂ ($K_{sp} = 1.6 \times 10^{-14} \text{ mol}^3\text{dm}^{-9}$) in a solution at a fixed pH of
 - 5.0
 - 8.0
 - 10.0
 - The K_{sp} for Mg(OH)₂ is $1.2 \times 10^{-11} \text{ mol}^3\text{dm}^{-9}$. What is the highest pH at which 1.0 g of magnesium hydroxide can be dissolved in 500 cm³ of a solution containing no other Mg²⁺ ions?
- 42.** In a 0.25 M solution, a different acid HY is 95% dissociated.
- Calculate the pH of this solution.
 - Calculate the value of K_a for the acid HY.
- 43.** A solution of phenol in water has a concentration of 4.7 g dm⁻³. Calculate the pH of this solution of phenol. (K_a of phenol = $1.28 \times 10^{-10} \text{ mol dm}^{-3}$)
- A $1.50 \times 10^{-2} \text{ mol dm}^{-3}$ solution of HCOOH has $[\text{H}^+] = 1.55 \times 10^{-3} \text{ mol dm}^{-3}$
 - Calculate the values of K_a and $\text{p}K_a$ for methanoic acid.
 - Estimate the percentage of HCOOH molecules that have dissociated in this aqueous solution of methanoic acid.
- 44.** An excess of magnesium was added to 100 cm³ of 0.0450 mol dm⁻³ hydrochloric acid. The same mass of magnesium was added to 100 cm³ of 0.0450 mol dm⁻³ ethanoic acid. Both reactions produced the same volume of hydrogen gas, measured at room temperature and pressure, but the reaction with ethanoic acid took much longer to produce this gas volume.
- Write equations for both reactions and show that both reactions should have produced 54 cm³ of hydrogen gas.
 - Explain why the reaction with ethanoic acid took much longer.

Buffer Solutions

45. (a) What is meant by the term "buffer solution"?
- (b) Calculate the pH of a buffer solution which contains the weak monoprotic acid, propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$), in concentration 0.10 mol dm^{-3} and sodium propanoate in concentration 0.05 mol dm^{-3} . K_a of propanoic acid is $1.26 \times 10^{-5} \text{ mol dm}^{-3}$.
- (c) Give equations to show how the above solution fulfills its buffer function
- (d) Calculate the pH of the solution after 0.01 moles of NaOH are added to 500 cm^3 of the solution
- (e) Calculate the pH of the solution after 0.01 moles of HCl are added to 500 cm^3 of the solution
- (f) Calculate the pH after 0.01 moles of NaOH is added to 500 cm^3 of water
- (g) Comment on your answers to (d) and (f).
46. (a) Calculate the pH of 0.12 mol dm^{-3} ethanoic acid ($K_a = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$).
- (b) Calculate the mass of sodium ethanoate (CH_3COONa) which must be added to 500 cm^3 this solution to give a buffer solution of $\text{pH} = 4.60$
- (c) Calculate the pH after 0.01 moles of HCl are added to this solution
- (d) Calculate the pH after 0.01 moles of NaOH are added to this solution
47. Calculate the pH of a buffer which is 0.20 mol dm^{-3} with respect to ammonium sulphate and 0.10 mol dm^{-3} with respect to ammonia. (K_a of $\text{NH}_4^+ = 5.6 \times 10^{-10} \text{ mol dm}^{-3}$)
48. Methanoic acid, HCOOH , has a K_a value of $1.58 \times 10^{-4} \text{ mol dm}^{-3}$. What ratio of methanoic acid and sodium methanoate would give a buffer of $\text{pH} = 4.00$?
49. (a) Calculate the pH of a buffer solution which is 0.1 mol dm^{-3} with respect to HCN ($K_a = 4.9 \times 10^{-10} \text{ mol dm}^{-3}$) and 0.8 mol dm^{-3} with respect to sodium cyanide
- (b) Calculate the pH after 0.05 moles of HCl are added to 1 dm^3 of this buffer
- (c) Calculate the pH after 0.05 moles of NaOH are added to 1 dm^3 of this buffer
- (d) Calculate the pH after 0.2 moles of NaOH are added to 1 dm^3 of this buffer
- (e) Comment on your answer to (d)
50. An acidic buffer solution is formed when 10.0 cm^3 of $0.125 \text{ mol dm}^{-3}$ aqueous sodium hydroxide are added to 15.0 cm^3 of $0.174 \text{ mol dm}^{-3}$ aqueous HX. The value of K_a for the weak acid HX is $3.01 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the pH of this buffer solution at 298 K. Give your answer to 2 decimal places.
51. A $0.210 \text{ mol dm}^{-3}$ solution of potassium hydroxide was added from a burette to 25.0 cm^3 of a $0.160 \text{ mol dm}^{-3}$ solution of ethanoic acid in a conical flask. Given that the value of the acid dissociation constant, K_a , for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$, calculate the pH at 25°C of the solution in the conical flask at the following three points:
- (a) Before any potassium hydroxide had been added
- (b) After 8 cm^3 of potassium hydroxide had been added
- (c) After 40 cm^3 of potassium hydroxide had been added
52. The pH of blood must remain between 6.8 and 7.4 and is blood is therefore buffered by the presence of carbonic acid (H_2CO_3 , $K_a = 4.5 \times 10^{-7} \text{ mol dm}^{-3}$) and hydrogencarbonate ions (HCO_3^-); calculate the maximum and minimum ratio of $\text{HCO}_3^- : \text{H}_2\text{CO}_3$ required to maintain the pH of blood between 6.8 and 7.4

Indicators and Titrations

53. Most acid-base indicators are weak acids, of which the colour of the conjugate acid (HIn) and the colour of the conjugate base (In⁻) are different; as a result the colour of the indicator depends on its degree of dissociation, which in turn depends on the pH. The end-point of an indicator is the pH at which [HIn] = [In⁻]
- Show that the end-point pH of an indicator is equal to its pK_{In} value
 - Indicators are generally believed to show the acid colour only when [HIn] > 10[In⁻], the alkali colour only when [In⁻] > 10[HIn] and an hence an intermediate colour when 10[In⁻] > [HIn] > 0.1[In⁻]; show that a typical indicator changes colour over the pH range pK_{In} ± 1
 - Hence suggest the end-point pH range for the following indicators:
Phenolphthalein (pK_{In} = 9.3)
Methyl orange (pK_{In} = 3.7)
54. (a) Sketch pH curves for the following titrations:
 20 cm³ 1.0 moldm⁻³ NH₃ against 1.0 moldm⁻³ HCl
 20 cm³ 1.0 moldm⁻³ NaOH against 2.0 moldm⁻³ HCl
 20 cm³ 1.0 moldm⁻³ CH₃COOH against 0.6 moldm⁻³ NaOH
 20 cm³ 1.0 moldm⁻³ CH₃COOH against 1.5 moldm⁻³ NH₃
- (b) Use you answers to 52 (c) to suggest whether methyl orange and phenolphthalein would be suitable indicators for each titration.