

**DEPARTMENT OF CHEMISTRY
FOURAH BAY COLLEGE
UNIVERSITY OF SIERRA LEONE**

CHEM 121

INTRODUCTION TO ENERGETICS, THERMODYNAMICS AND KINETICS

CREDIT HOURS	2.0
MINIMUM REQUIREMENTS	C6 in WASSCE Chemistry or equivalent Pass in CHEM 111 <i>To be taken alongside CHEM 124</i>
REQUIRED FOR	CHEM 211

PART 1 – ENERGETICS, THERMODYNAMICS AND ELECTROCHEMISTRY

COURSE OUTLINE

What are the energy changes which take place in chemical reactions? What do we mean by exothermic and endothermic reactions? What is enthalpy? What are enthalpy profile diagrams? What is a molar enthalpy change? What do we mean by enthalpies of formation, combustion, solution and neutralisation?

What are mean bond enthalpies? What are atomisation energies? Why are these useful in estimating the enthalpy changes of chemical reactions? What is Hess' Law and how can we use it to find enthalpy changes indirectly? How can we use Hess' Law to analyse the energetics of the formation and solution of ionic compounds?

What is entropy and why is it important? How can we calculate entropy changes in chemical reactions?

What is free energy and how does it depend on enthalpy and entropy? How can we use free energy changes to predict reaction feasibility and its temperature dependence?

What is a Galvanic electrochemical cell? How much you predict how much energy can be obtained from electrochemical cells? What are standard electrode potentials? What is the electrochemical series and how can it be used to predict the feasibility of redox reactions? How is cell potential linked to free energy and equilibrium constants?

What happens in non-standard conditions and what is the Nernst equation? What is the difference between kinetic stability and thermodynamic stability?

CONTENTS

1.	<i>Exothermic and endothermic reactions, energy profile diagrams, molar enthalpy changes</i>
2.	<i>Thermochemistry ($q = mc\Delta T$), measuring enthalpy changes, enthalpies of formation, combustion, neutralisation and solution</i>
3.	Atomisation energies, mean bond enthalpies and calculation of approximate energy changes in covalent and molecular reactions
4.	Hess' Law; using enthalpies of combustion and formation to find enthalpy changes indirectly
5.	Born-Haber cycles: the energetics of the formation of ionic compounds
6.	Hess' Law: enthalpies of solution
7.	Introduction to entropy and degrees of disorder
8.	Free energy, reaction feasibility and critical temperature
9.	<i>Redox reactions, electrochemical cells and cell potential</i>
10.	The electrochemical series and feasibility of redox reactions; kinetic and thermodynamic stability
11.	Non-standard conditions and the Nernst equation
12.	Cell potential, K_c and free energy

items in italics are covered at senior secondary level

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

PART 2 – KINETICS

COURSE OUTLINE

What is meant by the term “rate of reaction”? What causes chemical reactions to take place? What is the Maxwell-Boltzmann distribution of molecular energies? What is a catalyst? What factors affect the rate of reaction? What do the terms collision frequency, collision energy and activation energy mean?

What is a rate equation? What are orders of reaction? How can orders of reaction and rate equations be deduced experimentally? How can the rates of reactions be measured? What is a concentration-time graph and how can it be used to deduce the half-life of a reaction and the order of reaction? What is a rate-concentration graph and how can it be used to deduce the order of a reaction?

Why do different reactants have different orders of reaction? What can we deduce about reaction mechanisms from rate equations?

CONTENTS

1.	Introduction to Rates of reaction, measuring rates of reaction
2.	<i>simple collision theory</i> , Maxwell-Boltzmann distribution of molecular energies
3.	<i>Factors affecting the rate of reaction</i> (qualitative treatment using Maxwell-Boltzmann distribution, quantitative treatment of effect of temperature and catalyst on rate of reaction)
4.	Quantitative treatment of effect of concentration on rate of reaction – orders of reaction and rate equations
5.	<i>concentration-time graphs</i> , reaction half-life
6.	Temperature Dependence of rate constants; Arrhenius equation, Molecularity, rate-determining steps and reaction mechanisms

items in italics are covered at senior secondary level

PART 1 – ENERGETICS and THERMODYNAMICS

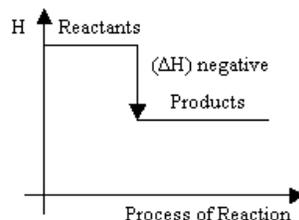
Lessons 1 and 2 – Introduction to Energetics

(a) Enthalpy changes

- **Potential energy** is a type of energy resulting from the attraction or repulsion between different particles:
 - particles which repel each other have a positive potential energy
 - as repelling particles are forced closer together, their potential energy increases
 - as repelling particles move further apart, their potential energy decreases until they are an infinite distance apart and they have zero potential energy
 - particles which are attracted to each other have a negative potential energy
 - as attracting particles get closer together, their potential energy becomes more negative (ie it decreases)
 - as attracting particles are pulled further apart, their potential energy becomes less negative (ie it increases) until they are pulled an infinite distance apart and they have zero potential energy
- All chemical substances are held together by the attraction between protons and electrons; all chemical substances therefore have a negative potential energy (called **chemical potential energy**); the stronger the attractive forces holding the substance together, the more negative (ie the lower) the potential energy of the substance and the more stable it is
- Chemical potential energy is also known as **enthalpy** and is given the symbol H
- When a chemical reaction takes place, the products and reactants have different enthalpies and thus there is a change in enthalpy; but since **total energy is always conserved**, any change in enthalpy must be balanced by an equal and opposite change in kinetic, or heat energy; the change in enthalpy during a chemical reaction is shown by the symbol ΔH

(b) Exothermic and Endothermic reactions

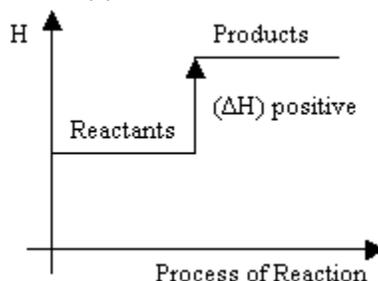
- In some reactions, the products are more stable than the reactants; the products therefore have a lower enthalpy than the reactants, and the enthalpy decreases; this can be shown in an **enthalpy level diagram**:



- In these reactions there is a negative enthalpy change ($\Delta H = -ve$); since the total energy is always conserved, the heat energy of the species must increase by an equal amount; the surrounding temperature therefore increases
- In these reactions, there is a transfer of energy from chemical potential energy to heat energy and an increase in temperature; such reactions **give out heat** and are said to be **EXOTHERMIC**
- In practice, not all of the energy will be transferred into heat (kinetic) energy; in some cases, sound energy will be produced as well; it is also possible in some cases to produce electrical energy rather than heat energy; but the loss in chemical potential energy will always be equal to the total gain in heat, kinetic, electrical or sound energy

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- In other reactions, the reactants are more stable than the products; the products therefore have a higher enthalpy than the reactants, and the enthalpy increases; this can be shown in an **enthalpy level diagram**:



- In these reactions there is a positive enthalpy change. ($\Delta H = +ve$); since the total energy is always conserved, the heat energy of the species must decrease by an equal amount; the surrounding temperature therefore decreases
- In these reactions, there is a transfer of energy from heat energy to chemical potential energy and a decrease in temperature; such reactions **absorb heat** and are said to be **ENDOTHERMIC**

(c) Molar Enthalpy Changes

- The quantity of heat energy absorbed or given out during a chemical reaction (q) depends on the amount of substance used; it is therefore necessary to specify the amount of reactants used when recording energy changes
- Enthalpy changes are generally measured per mole of reacting substance and typically have units of kJmol^{-1} ; this is known as the **molar enthalpy change** of a reaction; for example, in the reaction $A + 3B \rightarrow 2C + 4D$, the molar enthalpy change for this reaction, in kJmol^{-1} , is taken to be the enthalpy change when one mole of A reacts with three moles of B
- Heat change and molar enthalpy change can be interconverted using the following equation:

$$\Delta H = \frac{q}{n} \quad \text{or} \quad \Delta H \times n = q$$

Example: In the reaction $A + 3B \rightarrow 2C + 4D$, 200 kJ of energy are released when 0.2 moles of A reacts with 0.6 moles of B. What is the molar enthalpy change of the reaction?

Worked answer: 0.2 moles of A releases 200 kJ, so 1 mole must release $200/0.2 = 1000$ kJ

So the molar enthalpy change is -1000 kJmol^{-1}

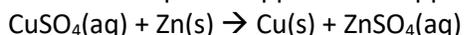
(d) Practical measurement of enthalpy changes

- Enthalpy changes are generally measured by carrying out a reaction under controlled conditions in a laboratory and measuring the temperature change; the amount of heat required to change the temperature of a system by 1K (or 1 °C) is known as the **heat capacity** of a system (H_c); it is measured in JK^{-1}
- The heat energy change (q) for a given reaction can therefore be calculated from the temperature change (ΔT) from the equation, if the heat capacity of the system is known: $q = \Delta T \times H_c$

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- The **specific heat capacity (c)** is the amount of heat required to heat 1 g of a substance by 1 K (or 1 °C)
 - therefore $H_c = c \times m$ and $q = m \times c \times \Delta T$
 - most enthalpy change experiments carried out in the laboratory either take place in aqueous solution or are used to heat a container containing water; it is therefore the water which is being heated or cooled; the specific heat capacity of water is known to be **4.18 JK⁻¹g⁻¹**; this value can be used for any aqueous solution
 - the mass of water can be calculated from its volume and its density; the density of water is 1 gcm⁻³ so its mass in grams is equal to its volume in cm³

Example: Zinc will displace copper from copper (II) sulphate solution according to the following equation:



If an excess of zinc powder is added to 50 cm³ of 1.0 moldm⁻³ copper(II) sulphate, the temperature increases by 6.3 °C. Calculate the molar enthalpy change for the reaction

Worked answer: mass of solution being heated = volume x density = 1 x 50 = 50 g, so heat change = 50 x 4.18 x 6.3 = 1317 J = 1.317 kJ; moles of CuSO₄ = 50/1000 x 1 = 0.05 so molar enthalpy change = 1317/0.05 = 26.3 kJmol⁻¹; temperature increased, so reaction exothermic, so sign should be -ve: **-26.3 kJmol⁻¹**

(e) Definitions of special enthalpy changes

The enthalpy changes of some reactions are frequently used in chemistry and so have been given special names:

- The **enthalpy of formation** of a substance is **the enthalpy change when one mole of that substance is formed from the most stable allotropes of its elements in their standard states**; its symbol is ΔH_f°
 - Eg $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$, $\Delta H = -74.8 \text{ kJmol}^{-1}$; the enthalpy of formation of methane is -74.8 kJmol^{-1}
 - Eg $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$, $\Delta H = -285.8 \text{ kJmol}^{-1}$; the enthalpy of formation of water is $-285.8 \text{ kJmol}^{-1}$
 - **the standard enthalpy of formation of all elements in their standard states is zero**
 - it is often not possible to measure enthalpies of formation directly
 - formation reactions can be exothermic or endothermic so enthalpies of formation can have negative or positive values
- The **enthalpy of combustion** of a substance is the **enthalpy change when one mole of that substance is burned in an excess of oxygen**
 - Eg $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$, $\Delta H = -285.8 \text{ kJmol}^{-1}$; the enthalpy of combustion of hydrogen is $-285.8 \text{ kJmol}^{-1}$
 - Eg $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$, $\Delta H = -890.3 \text{ kJmol}^{-1}$; the enthalpy of combustion of methane is $-890.3 \text{ kJmol}^{-1}$
 - burning a substance in oxygen is almost always exothermic, so standard enthalpies of combustion almost always have negative values
 - substances which do not support combustion, like water, carbon dioxide and most other oxides, have zero enthalpy of combustion
 - most enthalpies of combustion can be measured directly
- The **enthalpy of neutralisation** of an acid and a base is the **enthalpy change when one mole of water is formed by the reaction of that acid with that base**
 - Eg $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$, $\Delta H = -57.3 \text{ kJmol}^{-1}$; the enthalpy of neutralisation of HCl by NaOH is -57.3 kJmol^{-1}
 - it is usually possible to measure enthalpies of neutralisation directly
- The **enthalpy of solution** of a substance is the **enthalpy change when one mole of that substance dissolves in an excess of water**:
 - Eg $\text{NaOH}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$, $\Delta H = -44.5 \text{ kJmol}^{-1}$; the enthalpy of solution of NaOH is -44.5 kJmol^{-1}
 - it is possible to measure enthalpies of solution directly if the substance is soluble in water

Lesson 3 – Mean Bond Enthalpies and Atomisation Energies

(i) mean bond enthalpies

- During a chemical reaction, the bonds in the reactants are broken; this is an endothermic process; energy is required to do this; after the bonds have been broken, however, the bonds in the products are formed; this is an exothermic process; energy is released when this happens
- The enthalpy change for a chemical reaction can be deduced from consideration of the energy required to break bonds in the reactants and the energy released when the bonds in the products are formed; if the energy released when bonds are formed is greater than the energy required to break bonds, the reaction is exothermic; if the energy released when bonds are formed is less than the energy required to break bonds, the reaction is endothermic; the energy change can be calculated from the following equation:
 $\Delta H = \text{Energy required to break bonds in reactants} - \text{Energy released when bonds are made in the products}$

- The energy required to separate completely the atoms in one mole of covalent bonds is known as the **bond dissociation enthalpy** of that bond (ΔH_b); for a covalent bond A-B, the bond dissociation enthalpy is the energy required for the following change: $A-B(g) \rightarrow A(g) + B(g)$; the stronger the covalent bond, the larger the bond dissociation enthalpy; some common values are shown below:

Bond	$\Delta H / \text{kJmol}^{-1}$
C-H	+413
O-H	+464
C-C	+347
C=C	+612
C=O	+805
H-F	+568
H-Cl	+432
Cl-Cl	+243
Br-Br	+193
O=O	+498

- The precise strength of a covalent bond depends on its environment; even the strengths of the same type of bond in the same molecule may vary: in water, 502 kJmol^{-1} is required to separate the first H atom ($H-O-H(g) \rightarrow H-O(g) + H(g)$) but only 427 kJmol^{-1} is required to separate the second H atom ($H-O(g) \rightarrow H(g) + O(g)$; $H = +427 \text{ kJmol}^{-1}$); bond enthalpies are therefore generally expressed as **mean bond enthalpies** (the energy required to break one mole of a particular covalent bond averaged across a range of environments); the mean bond enthalpy of an O-H bond is generally given as $+464 \text{ kJmol}^{-1}$
- If mean bond enthalpies are used to predict enthalpy changes, they will only give an approximate value for the enthalpy change of a reaction, as the bond enthalpies used will be the average values and these may be different from those in the reaction being studied; **mean bond enthalpies thus only give you approximate values for enthalpy changes**
- Bond enthalpies apply only to the gaseous state and so do not consider any intermolecular forces which may exist between molecules

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

(ii) Atomisation Energies

- In giant covalent substances, all the covalent bonds have to be broken before free gaseous atoms can be formed; the energy required to produce one mole of free gaseous atoms of an element is known as the **atomisation energy** (ΔH_{at}); in other words, the atomisation energy for an element M is the energy change for the process $M(s) \rightarrow M(g)$; for compounds, the atomisation energy is the energy required to separate completely the atoms in one mole of that substance; so the atomisation energy for a compound A_xB_y is given by the equation $A_xB_y(s) \rightarrow xA(g) + yB(g)$; some atomisation energies are shown below:

Substance	$\Delta H_{at}/\text{kJmol}^{-1}$	
$C(s) \rightarrow C(g)$	+717	2 x C-C bond enthalpy
$Si(s) \rightarrow Si(g)$	+377	2 x Si-Si bond enthalpy
$SiO_2(s) \rightarrow Si(g) + 2O(g)$	+1864	4 x Si-O bond enthalpy

- Atomisation energies can also be used for simple molecular substances; the atomisation energy of Cl is the energy change for the process $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$; it has half the value of the bond dissociation energy of Cl-Cl; the atomisation; for all covalent substances, the atomisation energies are closely related to the bond enthalpies

(iii) Calculating approximate enthalpy changes

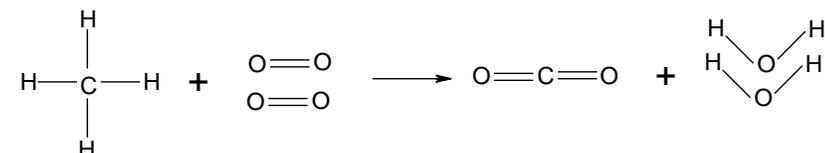
- The approximate enthalpy change for a reaction involving covalent bonds only can be calculated by considering the mean bond enthalpies of the bonds broken and bonds formed

Eg Use the mean bond enthalpies in the table above to estimate the enthalpy of combustion of methane

Solution: The enthalpy of combustion of methane is the energy change of the following reaction:



The bonds can be shown as follows:



Bonds to be broken in reactants: 4 C-H bonds, 2 O=O bonds: total energy = $(4 \times 413) + (2 \times 498) = +2648 \text{ kJmol}^{-1}$

Bonds to be broken in products: 2 C=O bonds, 4 O-H bonds: total energy = $(2 \times 805) + (4 \times 464) = +3466 \text{ kJmol}^{-1}$

So approximate $\Delta H = 2648 - 3466 = -818 \text{ kJmol}^{-1}$

(the correct value is -890 kJmol^{-1})

- If the enthalpy change for a reaction is known, and most of the bond enthalpies are known, it is possible to calculate the mean bond enthalpy of a particular bond:

Eg The enthalpy of formation of methane is known to be -76 kJmol^{-1} ; the bond enthalpy of a H-H bond is $+436 \text{ kJmol}^{-1}$, and the enthalpy of atomization of carbon ($C(s) \rightarrow C(g)$) is $+713 \text{ kJmol}^{-1}$; use this information to estimate the bond dissociation enthalpy of a C-H bond

Solution: The equation for the enthalpy of formation of methane is $C(s) + 2H_2(g) \rightarrow CH_4(g)$

The bonds broken in the reactants are the bonds in carbon ($C(s) \rightarrow C(g)$) and 2 H-H bonds; total energy required = $713 + 2(436) = 1585$

The bonds broken in the products are four C-H bonds; total energy = $4x$ (x = mean C-H bond enthalpy)

$\Delta H = \sum \Delta H_b$ (products) - $\sum \Delta H_b$ (reactants), so $1585 - 4x = -76$, so $4x = 1585 + 76 = 1661 \text{ kJmol}^{-1}$ so $x = 415 \text{ kJmol}^{-1}$

Lesson 4 – Hess's Law: Calculating Enthalpy Changes Indirectly

- **Hess' Law** states that "the enthalpy change for a chemical reaction depends only on the initial and final states and is independent of the path followed"; in other words whichever route, however direct or indirect, by which the reaction proceeds, the overall enthalpy change for the reaction will be same; it is an application of the principle of conservation of energy; Hess' Law can be used to calculate many enthalpy changes which cannot be measured directly; usually by using standard enthalpies of combustion or formation

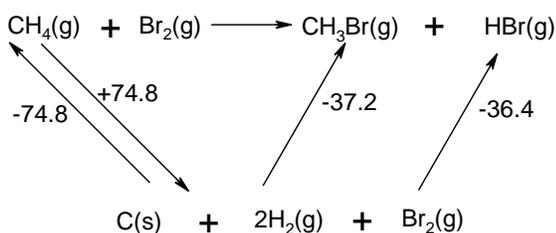
(i) Calculating enthalpy changes using enthalpies of formation

- Consider the reaction $AB + C \rightarrow DE + FG$; this reaction could proceed by converting all the reactants into their constituent elements in their standard states and then to convert the elements into products; in other words, reversing the formation of the reactants and then forming the products; according to Hess' Law the enthalpy change for any reaction should be related to the enthalpies of formation of its reactants and products as follows:

$$\Delta H = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

Eg Calculate the enthalpy change for the following reaction: $\text{CH}_4(\text{g}) + \text{Br}_2(\text{l}) \rightarrow \text{CH}_3\text{Br}(\text{g}) + \text{HBr}(\text{g})$, given that the enthalpies of formation of CH_4 , CH_3Br and HBr are -74.8 , -37.2 kJmol^{-1} and -36.4 kJmol^{-1} respectively

Solution: since the enthalpy of formation of CH_4 is -74.8 kJmol^{-1} then the enthalpy change when one mole of CH_4 is converted into its elements will be $+74.8$ kJmol^{-1} ; a cycle can be set up as follows:



The enthalpy change for the reaction is therefore $\Delta H = -(-74.8) + (-37.2) + (-36.4) = +1.2$ kJmol^{-1}

- The enthalpy change of any reaction can be calculated if the enthalpies of formation of all the reactants and products are known - **the enthalpy of formation of elements in their standard states is always zero**

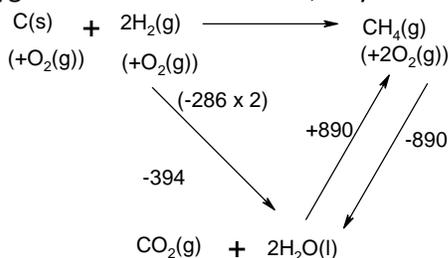
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(ii) Calculating enthalpy changes using enthalpies of combustion

- Consider the reaction $AB + C \rightarrow DE + FG$; this reaction could in theory proceed by burning all of the reactants in excess oxygen to give combustion products (often CO_2 and H_2O) and then reversing the combustion of the products; according to Hess' Law the enthalpy change for any reaction should be related to the enthalpies of combustion of its reactants and products as follows:

$$\Delta H = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$$

- Eg Calculate the enthalpy change for the following reaction: $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$, given that the enthalpies of combustion of CH_4 , C and H_2 are -890 , -394 kJmol^{-1} and -286 kJmol^{-1} respectively
Solution: since the enthalpy of combustion of CH_4 is -890 kJmol^{-1} then the enthalpy change when CO_2 and H_2O are converted into methane and oxygen must be $+890$ kJmol^{-1} ; a cycle can be set up as follows:



The enthalpy change for the reaction is therefore $\Delta H = -394 + (2 \times -286) - (-890) = -76$ kJmol^{-1}

- The enthalpy change for any reaction can be calculated if the enthalpy of combustion of reactants and products are known

Lesson 5 – Born-Haber cycles

(a) Enthalpy of Formation of Ionic Compounds

- The enthalpy changes during reactions involving covalent compounds can be explained in terms of simple bond breaking and bond making:

$$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$$

- Reactions involving ionic compounds, however, involve a more complex sequence of processes and must be treated by a different method; reactions involving the formation of ionic compounds from their elements can be broken down into three stages:
 - formation of free gaseous atoms from the elements in their standard states
 - addition or removal of electrons to form ions
 - attraction of the ions to form the ionic compound

Consider the reaction $\text{Na(s)} + 1/2\text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$

- Na(s) and $1/2\text{Cl}_2(\text{g})$ need to be converted into free gaseous atoms – Na(g) and Cl(g)
- The Na needs to be ionised to form Na^+ and an electron needs to be added to Cl to form Cl^-
- Na^+ and Cl^- will join to form an ionic lattice

(i) Atomisation and Bond Dissociation

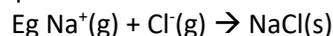
- The enthalpy changes required to form free gaseous atoms can be obtained from the **atomisation enthalpies** or the **bond dissociation enthalpies**:
 - the **atomisation enthalpy** of an atom is the energy required to produce one mole of free gaseous atoms of that atom (eg $1/2\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$, or $\text{Na(s)} \rightarrow \text{Na(g)}$)
 - the **bond dissociation enthalpy** is the enthalpy change when one mole of covalent bonds is broken homolytically in the gaseous state (eg $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl(g)}$)
 - atomisation energies are generally used instead of bond dissociation energies as they also consider the intermolecular forces between the molecules

(ii) Ionisation and Electron Addition

- The **first ionisation energy** of an atom is the energy required to remove one electron from each of a mole of free gaseous atoms of that element: $\text{Eg } \text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}$
- The **first electron affinity** of an atom is the energy change when one electron is added to each of a mole of free gaseous atoms of that element: $\text{Eg } \text{Cl(g)} + \text{e} \rightarrow \text{Cl}^-(\text{g})$
- In cases where the ions have a charge of +2 or -2, other electrons must be transferred:
 - the second ionisation energy of an element is the energy required to remove one electron from each of a mole of free gaseous unipositive ions of that element: $\text{Eg } \text{Mg}^+(\text{g}) \rightarrow \text{Mg}^{2+}(\text{g}) + \text{e}$
 - the second electron affinity of an atom is the energy change when one electron is added to each of a mole of free gaseous uninegative ions of that element: $\text{Eg } \text{O}^-(\text{g}) + \text{e} \rightarrow \text{O}^{2-}(\text{g})$

(iii) Attraction of the ions to form an ionic compound

- The **enthalpy of lattice formation (or lattice energy)** of an ionic compound is the energy released when one mole of the compound is formed from its free gaseous ions under standard conditions:



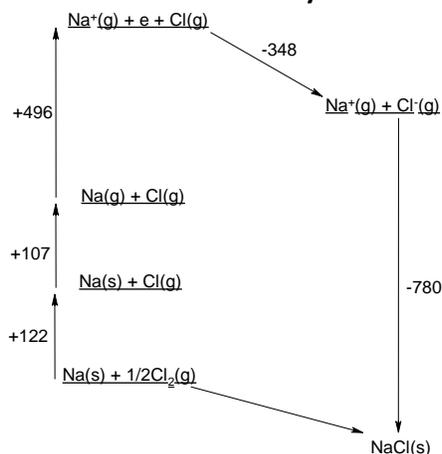
This process can sometimes be described in reverse: the **enthalpy of lattice dissociation** the energy required to convert one mole of an ionic compound into its free gaseous ions; the term “lattice enthalpy” can be used to describe both processes

(iv) Born-Haber cycles

- The formation of sodium chloride from sodium and chlorine thus consists of the following five processes:

Process	Equation	Enthalpy change/ kJmol^{-1}
Atomisation of sodium	$\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g})$	+107
Atomisation of chlorine	$1/2\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$	+122
First ionisation of sodium	$\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{e}$	+496
Electron addition to chlorine	$\text{Cl}(\text{g}) + \text{e} \rightarrow \text{Cl}^-(\text{g})$	-348
Lattice formation of sodium chloride	$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$	-780

- The energy changes can be qualitatively explained as follows:
 - Atomisation enthalpies are always endothermic as bonds need to be broken in the element (these can be metallic bonds (metals) or covalent bonds (non-metals); the stronger the bonding, the larger the atomization energy and bond dissociation enthalpy
 - Ionisation enthalpies are always positive (ie endothermic); second ionisation energies are always more endothermic than first ionisation energies as there is less repulsion between the remaining electrons so more energy is required to remove them
 - First electron affinities are usually exothermic as the incoming electron is attracted to the nucleus of the atom. Second electron affinities are always endothermic as the incoming electron is repelled by the overall negative charge on the ion
 - Enthalpies of lattice formation are negative (ie exothermic) as the ionic bonds are being formed; enthalpies of lattice dissociation are endothermic as the ionic bonds are being broken
- The sequence of processes making up the formation of an ionic compound can be shown as an energetic cycle known as a **Born-Haber cycle**:



- the enthalpy of formation of NaCl can be calculated from Hess' Law:

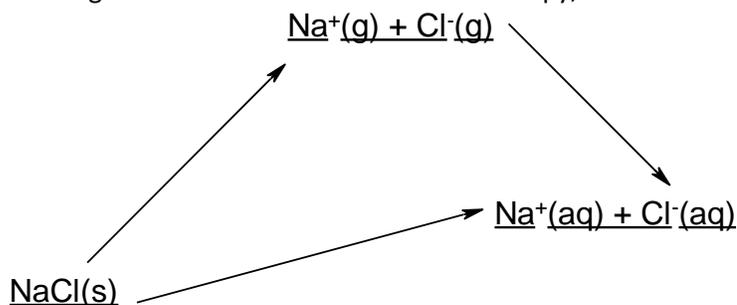
$$\Delta H_f(\text{NaCl}) = +107 + 122 + 496 + (-348) + (-780) = -403 \text{ kJmol}^{-1}$$

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- Born-Haber cycles can be used to calculate any of the above processes if all the others are known; in practice it is usually used to calculate the electron affinity or the lattice enthalpy, since these are difficult processes to measure directly
- The Born-Haber cycle for sodium chloride is relatively simple since there is one mole of both Na^+ and Cl^- ions, and only one electron is removed from Na and given to Cl; other ionic compounds are slightly more complicated:
 - In MgCl_2 , there are two moles of Cl^- ions and the Mg loses two electrons; an extra step is therefore required, to show the second ionisation energy of Mg; in addition, two moles of chlorine atoms must be made ($\Delta H_{\text{at}} \times 2$) and two moles of chloride ions must be made ($\Delta H_{\text{ea}} \times 2$)
 - In Na_2O , there are two moles of Na^+ ions and the O gains two electrons; an extra step is required, to show the second electron affinity of O; in addition, two moles of Na atoms must be made ($\Delta H_{\text{at}} \times 2$) and two moles of Na^+ ions must be made ($\Delta H_{\text{ie}} \times 2$)
 - In MgO , the Mg lose two electrons and the O gains two electrons; two extra steps are therefore required, to show the second ionisation energy of Mg second electron affinity of O

(b) Enthalpy of Solution of Ionic Compounds

- Ions are strongly attracted to water, since water is a polar molecule and so cations are attracted to the O atoms in water and anions are attracted to H atoms; the energy released when a gaseous ion is dissolved in water is known as the **hydration enthalpy** of the ion: $\text{M}^{x+}(\text{g}) \rightarrow \text{M}^{x+}(\text{aq})$
- Not all ionic compounds are soluble, however, since the ions in the solid state are also attracted to each other (cf lattice energy); the energy required to break up an ionic lattice is known as the **lattice dissociation enthalpy**
- The enthalpy change when one mole of an ionic compound dissolves in excess water is known as the **enthalpy of solution** (Eg $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{aq})$); the value of this energy change depends on the relative values of the hydration energies and the lattice dissociation enthalpy; this can be expressed in the form of a Hess' Law cycle:



The enthalpy of solution of an ionic compound can therefore be expressed in terms of the hydration energies and lattice enthalpies as follows:

$$\Delta H(\text{solution}) = \Sigma(\Delta H(\text{hydration})) - \Delta H(\text{lattice formation})$$

Or
$$\Delta H(\text{solution}) = \Sigma(\Delta H(\text{hydration})) + \Delta H(\text{lattice dissociation})$$

eg for sodium chloride:

lattice dissociation enthalpy of NaCl: $+780 \text{ kJmol}^{-1}$

hydration enthalpy of sodium ion: -406 kJmol^{-1}

hydration enthalpy of chloride ion: -364 kJmol^{-1}

so enthalpy of solution of NaCl = $780 - 406 - 364 = +10 \text{ kJmol}^{-1}$

- The hydration energy and the lattice energy depend on the charge and the size of the ions: the larger the charge and the smaller the size, the larger the hydration energy and the lattice enthalpy; trends in the enthalpy of solution therefore depend on which of the two energy processes changes by more; the more exothermic the enthalpy of solution, the more likely the compound is to dissolve

Lesson 6 – Entropy and Free Energy

(a) Entropy

- **Entropy (S)** is a measure of the degree of disorder of a system; the greater the degree of disorder in a system, the higher the entropy; entropy describes the number of ways in which that system can exist; a high degree of disorder, and hence a high entropy, makes a substance more stable; entropy increases solids < liquids < gases; metallic solids tend to have a higher entropy than giant covalent and ionic solids
- The units of entropy are $\text{Jmol}^{-1}\text{K}^{-1}$; the entropy values of some common substances are shown in the following table:

Substance	Entropy/ $\text{Jmol}^{-1}\text{K}^{-1}$
Diamond	2.4
Graphite	5.7
Aluminium	28.3
Water	69.9
Carbon monoxide	197.6
Carbon dioxide	213.6
Argon	154.7

- During a chemical reaction, the total entropy of the system will change; the entropy change for the following reaction can be calculated using the formula: $\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}}$

eg Calculate the entropy change for the reaction $\text{C(s)} + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$
 $\Delta S = 2(197.6) - 213.6 - 5.7 = +175.9 \text{ Jmol}^{-1}\text{K}^{-1}$

- If ΔS is +ve then the products are more stable (in terms of entropy) than the reactants and a reaction is likely; if ΔS is -ve then the products are less stable than the reactants (in terms of entropy) then a reaction is unlikely; chemical reactions are favoured if they are accompanied by an increase in entropy
- The Second Law of Thermodynamics states that the total entropy of the universe must increase as a result of every event ($\Delta S > 0$); in other words, a chemical reaction can only take place if the entropy of the universe increases as a result
- When considering the total entropy change, it is not sufficient just to consider the entropy change of the system; the change in entropy of the surroundings (the rest of the universe) must also be considered; the entropy change of the surroundings increases when the temperature increases (ie when exothermic reactions take place); the entropy change of the surroundings during chemical reactions can be calculated using the following equation: $\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$

eg The reaction $\text{C(s)} + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ has a ΔH of $+176 \text{ kJmol}^{-1}$ and a ΔS of $+176 \text{ Jmol}^{-1}\text{K}^{-1}$. What is the total entropy change for this reaction at 298 K?
 $\Delta S_{\text{sys}} = +176 \text{ Jmol}^{-1}\text{K}^{-1}$; $\Delta S_{\text{surr}} = -176000/298 = -591 \text{ Jmol}^{-1}\text{K}^{-1}$
 So $\Delta S_{\text{tot}} = +176 - 591 = -415 \text{ Jmol}^{-1}\text{K}^{-1}$

As the total entropy change is negative, this reaction cannot take place at 298 K, (although it may take place at higher temperatures)

- A reaction will be spontaneous (or feasible) if the total entropy change for the reaction is positive at that temperature; if the total entropy change is negative, the reaction will not take place

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

(b) Free Energy

- If $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = \Delta S_{\text{sys}} - \frac{\Delta H}{T}$, then $T\Delta S_{\text{tot}} = T\Delta S_{\text{sys}} - \Delta H$ and $-T\Delta S_{\text{tot}} = \Delta H - T\Delta S_{\text{sys}}$; the term $-T\Delta S_{\text{tot}}$ is known as the free energy change and is given the symbol ΔG ; $\Delta G = \Delta H - T\Delta S_{\text{sys}}$; ΔG has units of kJmol^{-1}

eg The reaction $\text{C(s)} + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ has a ΔH of $+176 \text{ kJmol}^{-1}$ and a ΔS of $+176 \text{ Jmol}^{-1}\text{K}^{-1}$. What is the free change for this reaction at 298 K?

$$\Delta G = \Delta H - T\Delta S = 176 - 298 (176/1000) = +124 \text{ kJmol}^{-1}$$

- A reaction will be spontaneous (or feasible) if the free energy change for the reaction is negative at that temperature; if the free energy change is positive, the reaction will not take place; in some cases the reaction may be very slow (ie the reactants have kinetic stability)
- The feasibility of a chemical reaction therefore depends on both the entropy change and the enthalpy change for the reaction

(c) The effect of temperature on reaction feasibility

- The entropy change of the surroundings ($-\frac{\Delta H}{T}$), and hence the value of the total entropy change and ΔG , both depend on the temperature: $\Delta G = \Delta H - T\Delta S_{\text{sys}}$ or $T\Delta S_{\text{tot}} = \Delta S_{\text{sys}} - \frac{\Delta H}{T}$; the higher the temperature, the greater the importance of ΔS_{sys} relative to ΔH ; in some cases, this can mean that the feasibility of the reaction depends on the temperature being above or below a certain critical value
- If ΔH is $-ve$ and ΔS is positive, the reaction will be spontaneous at all temperatures; if ΔH is $+ve$ and ΔS is negative, the reaction will not be spontaneous at any temperature
- In most reactions, however, ΔH and ΔS are either both positive or both negative; in these cases, the feasibility of the reaction will be temperature dependent:
 - If ΔH and ΔS are both $-ve$, the reaction will be spontaneous only below a certain temperature
 - If ΔH and ΔS are both $+ve$, the reaction will be spontaneous only above a certain temperature

Example: Consider the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$: $\Delta H = -290 \text{ kJmol}^{-1}$, $\Delta S = -305 \text{ Jmol}^{-1}\text{K}^{-1}$

Calculate the ΔG of this reaction at 300 K and at 1500 K:

Answer: $\Delta G = \Delta H - T\Delta S_{\text{sys}} = -290 - 300(-0.305) = -199 \text{ kJmol}^{-1}$ at 300 K, $-290 - 1500(-0.305) = +168 \text{ kJmol}^{-1}$ at 1500 K

Example: Consider the reaction $\text{CaCO}(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$: $\Delta H = +178 \text{ kJmol}^{-1}$, $\Delta S = +160 \text{ Jmol}^{-1}\text{K}^{-1}$

Calculate the ΔG of this reaction at 300 K and at 1500 K:

Answer: $\Delta G = \Delta H - T\Delta S_{\text{sys}} = 178 - 300(0.160) = +130 \text{ kJmol}^{-1}$ at 300 K, $178 - 1500(0.160) = -62 \text{ kJmol}^{-1}$ at 1500 K

- Reactions in which ΔH and ΔS are either both positive or both negative have a critical temperature, at which the system is in perfect equilibrium and the reaction has no tendency to move in either direction; at this temperature $\Delta G = 0$, so $\Delta H = T\Delta S$ and $T = \frac{\Delta H}{\Delta S}$

PART 2 - KINETICS

Lesson 1 – Introduction to Rates of Reaction

(a) rate of reaction definition

- During a chemical reaction, the concentration of the reactants decreases and the concentration of the products increases; the **rate of a reaction** is the decrease in concentration of reactants per unit time, or the increase in concentration of products per unit time; the units of rate of reaction are $\text{mol dm}^{-3} \text{s}^{-1}$
- The rate of increase or decrease of concentration depends on the stoichiometric coefficients; in the reaction:

$$A + 3B \rightarrow 2C + 4D$$

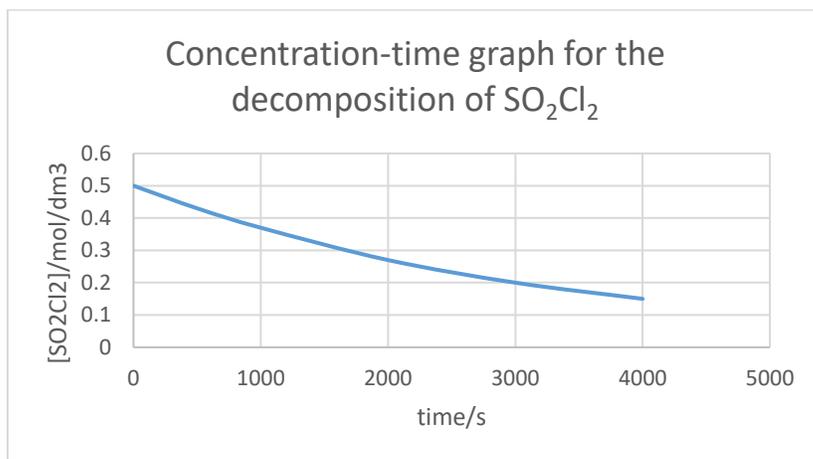
The rate of increase in the concentration of C will be double the rate of decrease in the concentration of A

The rate of decrease in the concentration of B will be three times the rate of decrease in the concentration of A

The rate of reaction is defined as the change in concentration per unit time for a species with a stoichiometric coefficient of 1

(b) Measuring Rates of Reaction

- The rate of a reaction is not constant over time; as the reaction proceeds, the concentration of reactants decrease and so the collision frequency decreases, slowing down the reaction; it is possible to measure the rate of reaction at any point during a reaction by measuring the change in concentration of the reactants over time and plotting a **concentration-time** graph:
- A typical concentration-time graph would look like this:
 (Eg for the reaction $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$)



- the rate of reaction is the change in concentration per unit time and can therefore be calculated from the **gradient** of the line at a particular time
- As the graph is a curve (its gradient is steadily decreasing with time), the gradient of the line at a particular point must be calculated by drawing a tangent to that line at a particular point and calculating the gradient of that tangent
- the initial rate of reaction is the gradient of the tangent to the curve at $t = 0$.
- the rate of reaction at a particular time is the gradient of the tangent to the curve at that particular time

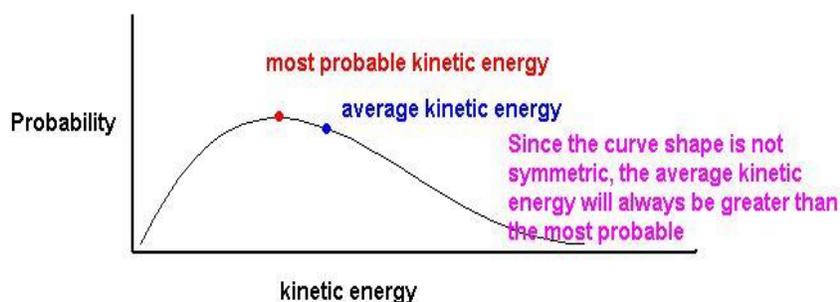
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- In some reactions, it is not easy to measure the concentration of a reactant over a time period; it is often easier to mention the time taken for a particular stage in the reaction to be reached; since rate is the change in concentration per unit time, it follows that the rate of reaction is inversely proportional to the time taken for that stage to be reached; examples of such measurements could be:
 - time taken for fixed amount of gas to be produced
 - time taken for absorbance to change by a certain amount
 - use of a **clock reaction**: the appearance of a certain coloured product is delayed by adding a fixed amount of another species:
Eg $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$
Iodine is produced in this reaction; if starch was added to the original mixture, a blue-black colour would appear immediately
however if a fixed amount (ie 0.02 moles) of sodium thiosulphate is also added to the mixture, it reacts with the iodine and a blue-black colour is only seen when all the thiosulphate has been used up
it is possible to measure the time taken for the blue-black colour to appear

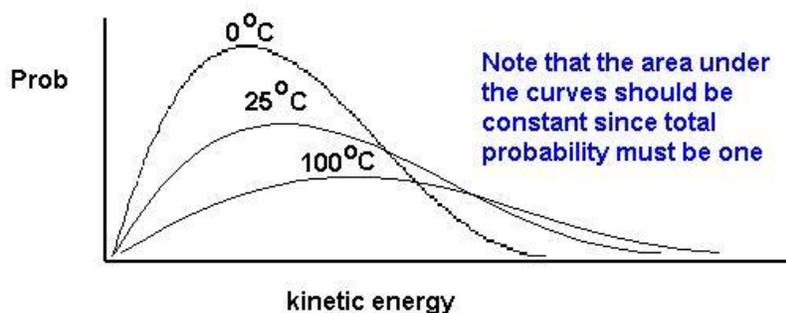
Lesson 2 - Simple Collision Theory

- Substances in the liquid, aqueous and gaseous phase consist of particles in rapid and constant motion; the rate of a chemical reaction depends on three factors:
 - Collision frequency:** a chemical reaction is to take place between two particles, they must first collide; the number of collisions between particles per unit time in a system is known as the **collision frequency** of the system; the collision frequency of a system can be altered by changing the concentration of the reactants, by changing the total pressure, by changing the temperature or by changing the size of the reacting particles
 - Collision energy:** not all collisions result in a chemical reaction; most collisions just result in the colliding particles bouncing off each other; collisions which do not result in a reaction are known as **unsuccessful collisions**; unsuccessful collisions happen when the colliding species do not have enough energy to break the necessary bonds in the reacting particles; if the colliding species do have sufficient energy, they will react and the collision will be **successful**; the combined energy of the colliding particles is known as the **collision energy**

Not all the particles in a given system have the same energy; they have a broad distribution of different energies; the shape of the distribution of energies depends on the temperature of the system: the higher the temperature, the greater the mean kinetic energy of the particles; the distribution of molecular energies at a characteristic temperature T_1 can be represented graphically - it is known as a **Maxwell-Boltzmann distribution**:



At a higher temperature T_2 the distribution of energies will be different; the mean energy will be higher and the distribution will be broader:



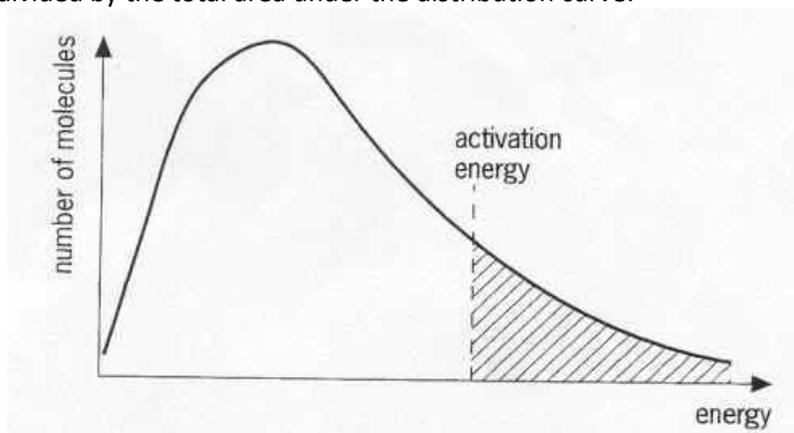
The greater the mean kinetic energy of the particles, the greater the collision energy

- Activation energy:** the minimum energy the colliding particles need in order to react is known as the **activation energy**; if the collision energy of the colliding particles is less than the activation energy, the collision will be unsuccessful; if the collision energy is equal to or greater than the activation energy, the collision will be successful and a reaction will take place; the activation energy can be changed by the addition of a catalyst

- In summary:

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- in reactions that do not happen instantaneously, most collisions are unsuccessful
 - such reactions can be made faster by increasing the **collision frequency** (*the more frequently the particles collide, the faster the reaction will be*)
 - such reactions can also be made faster by increasing the **fraction of successful collisions** (*the greater the fraction of collisions that result in a chemical reaction, the faster the reaction will be*); this can be achieved either by increasing the **collision energy** or by reducing the **activation energy**
- The fraction of successful collisions can be shown graphically as the area under the curve to the right of the activation energy divided by the total area under the distribution curve:



This fraction can be expressed mathematically as $e^{-\frac{E_a}{RT}}$; as the activation energy increases, the fraction of successful collisions decreases; as the temperature increases, the fraction of successful collisions increases

Lesson 3 - Factors affecting the rate of a chemical reaction

- The rate of a chemical reaction can be changed in a number of ways:
 - by changing the concentration of the reacting particles
 - by changing the pressure of the system (if some of the reacting particles are in the gas phase)
 - by changing the temperature of the system
 - by adding a catalyst

(i) **concentration:**

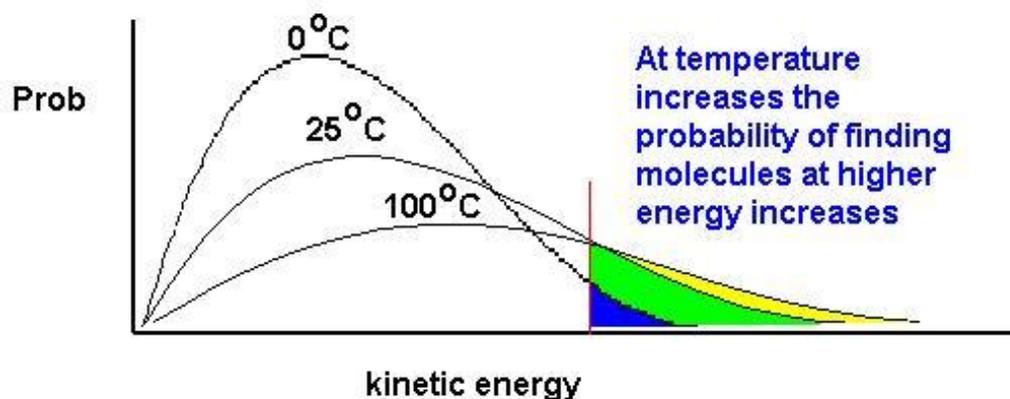
- the greater the concentration of the species in a liquid or gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide; hence an increase in concentration causes the rate of reaction to increase by increasing the collision frequency
- changing the concentration has no effect on the collision energy or the activation energy, and hence no effect the fraction of successful collisions
- so an increase in concentration increases the rate of reaction because **the number of particles per unit volume increases so the collision frequency increases**

(ii) **pressure**

- the greater the pressure in a gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide; hence an increase in pressure causes the rate of reaction to increase by increasing the collision frequency; the pressure of a system is generally increased by reducing its volume
- changing the pressure has no effect on the collision energy or the activation energy, and hence no effect the fraction of successful collisions
- so an increase in pressure increases the rate of reaction because **the number of particles per unit volume increases so the collision frequency increases**

(iii) **temperature**

- an increase in temperature changes the distribution of molecular energies in such a way as to increase the mean kinetic energy of the particles and thus increase the collision energy
- for a given activation energy, it follows that an increase in temperature will increase the number of colliding particles with an energy equal to or greater than the activation energy (ie the shaded area under the graph to the right of the activation energy):



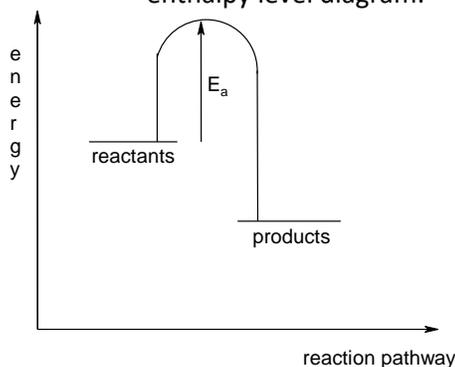
it is clear that at a higher temperature, the fraction of particles with enough energy to react increases significantly and therefore the fraction of collisions which are successful thus also increases

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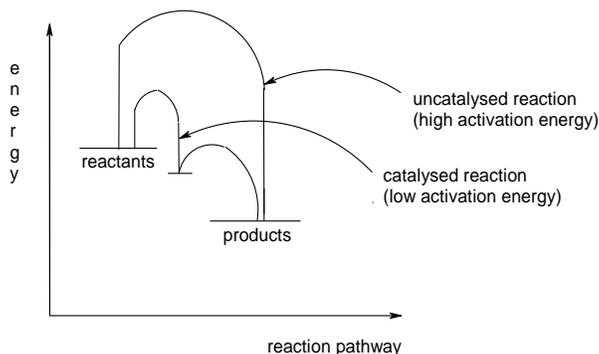
- an increase in temperature also increases the collision frequency, because they are moving faster; this also increases the rate of reaction
- in summary, the rate of reaction increases when the temperature is increased because the collision frequency and the collision energy both increase; of these two reasons, the increase in collision energy is the most important and accounts for about 95% of the increase in rate for a given reaction
- increasing the temperature has no effect on the activation energy
- an increase in temperature increases the rate of reaction because **the mean collision energy of the particles increases, so more of the particles have a collision energy greater than the activation energy, so the fraction of successful collisions increases; also the particles are moving faster so the collision frequency increases**

(iv) catalysts

- a catalyst is a substance which changes the rate of a chemical reaction without itself being chemically altered at the end of the reaction
- catalysts provide an alternative reaction pathway, usually by introducing an extra step into the reaction, which has a lower activation energy than the uncatalysed reaction; this effect can be illustrated with an enthalpy level diagram:



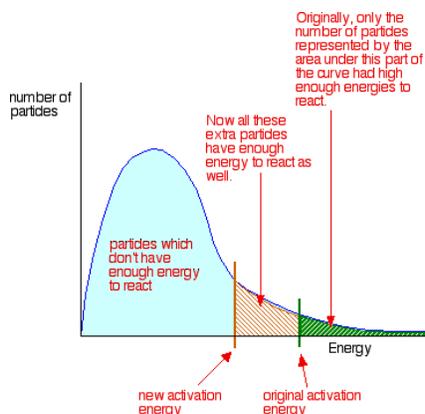
This energy diagram shows a simple one-step exothermic reaction. The activation energy E_a is the energy needed to break the bonds in the colliding particles and cause a successful collision.



This energy diagram shows a reaction taking place with and without a catalyst. The uncatalysed reaction has a high activation energy. The catalysed reaction proceeds via an alternative reaction pathway and has a lower activation energy.

- since catalysts reduce the activation energy of a chemical reaction, the number of particles which have sufficient energy to react will therefore increase; this can be shown graphically by considering the Maxwell-Boltzmann distribution of molecular energies:

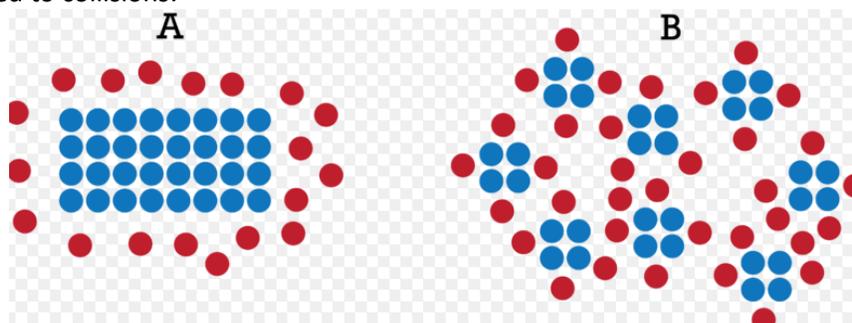
CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS



- a catalyst increases the rate of reaction because **the activation energy of the particles decreases, so more of the particles have a collision energy greater than the activation energy, so the fraction of successful collisions increases**
- a catalyst has no effect on the collision frequency or the collision energy

(v) physical states of reactants

- if reactants are gaseous, or well mixed in liquid or aqueous form, then all of the particles in the sample are able to react
- particles in the solid state, however, are not free to move, so only the particles at the **surface** of the solid are able to collide with other particles; this reduces the collision frequency and reduces the rate of reaction
- the rate of reaction in solids can be increased by reducing the particle size, and hence increasing the **surface area** exposed to collisions:



A – large particle size, fewer of the blue solid particles can collide with the red particles, slower reaction

B – small particle size, more of the blue solid particles can collide with the red particles, faster reaction

• Factors affecting rate of reaction – summary

Effect:	On collision frequency	On collision energy	On activation energy	On fraction of successful collisions	On rate
Increase concentration (liquids and gases)	Increases	No effect	No effect	No effect	Increases
Increase pressure (gases)	Increases	No effect	No effect	No effect	Increases
Increase temperature	Increases	Increases	No effect	Increases	Increases
Add a catalyst	No effect	No effect	Decreases	Increases	Increases

Lesson 4 – Orders of Reaction and Rate Equations

(a) Introducing Rate Equations

- The relationship between the rate of a chemical reaction and the concentration of the reactants is shown by the **rate equation** of the reaction

Consider the reaction $A + 3B \rightarrow 2C + 4D$

The rate of this chemical reaction is given by the equation: $\text{rate} = k[A]^x[B]^y$

- [A] is the concentration of A, and [B] is the concentration of B.
- x and y are the **orders of reaction** with respect to A and B respectively.

The **order of reaction** with respect to a given reactant is the power of that reactant's concentration in the rate equation.

The sum of these powers, in this case $x + y$, is known as the overall order of reaction:

The **overall order of reaction** is the sum of the powers of the reactant concentrations in the rate equation

k is the **rate constant** of the reaction.

The **rate constant** is the constant of proportionality in the rate equation

(b) Determining orders of reaction from initial rate measurements

- The orders of reaction with respect to each reactant in the reaction can be determined by carrying out the reaction with various different initial concentrations and measuring the change in initial rate of reaction; the orders of reaction can be determined arithmetically or graphically
- If the order of reaction with respect to one reactant is being determined, the concentration of one reactant only should change; the others should remain constant so that the change in rate can be attributed to the change in concentration of that reactant alone; if the overall order is being determined, the concentration of all reactants should change by the same factor

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

(i) Method 1 – the Arithmetic Method

- (change in concentration)^{order of reaction} = change in rate
- If the reaction is first order, then if the concentration doubles the rate will also double; if the concentration triples the rate will also triple, etc
- If the reaction is second order, then if the concentration doubles the rate will quadruple. If the concentration triples the rate will increase ninefold, etc
- If the reaction is zero order, then the change in concentration will have no effect on the rate of reaction

Worked Example:

Consider the reaction $\text{RX} + \text{OH}^- \rightarrow \text{ROH} + \text{X}^-$

The following rate data were obtained at constant temperature; what is the rate equation and what is the rate constant?

Initial concentration of RX/ mol dm ⁻³	Initial concentration of OH/ mol dm ⁻³	Initial rate/ mol dm ⁻³ s ⁻¹
0.01	0.04	8×10^{-3}
0.01	0.02	4×10^{-3}
0.005	0.04	4×10^{-3}

Solution:

- From expt 2 to expt 1, the concentration of hydroxide ions doubles and the concentration of RX is unchanged; the rate also doubles, so the order of reaction with respect to OH⁻ is 1
- From expt 3 to expt 1, the concentration of RX doubles and the concentration of hydroxide ions is unchanged; the rate also doubles, so the order of reaction with respect to RX is also 1.

The rate equation can thus be written as follows: rate = k[RX][OH⁻]

Having deduced the rate equation, the rate constant can be calculated using the data in one of the experiments:

Eq in expt 1, $k = \text{rate}/([\text{RX}][\text{OH}^-]) = 8 \times 10^{-3}/(0.04 \times 0.01) = 20 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$.

Worked example:

Consider the reaction $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$

The following rate data were obtained at constant temperature; what is the rate equation and what is the rate constant?

Initial concentration of PCl ₃ / mol dm ⁻³	Initial concentration of Cl ₂ / mol dm ⁻³	Initial rate/ mol dm ⁻³ s ⁻¹
0.2	0.1	0.0004
0.4	0.1	0.0008
0.8	0.2	0.0064

Solution:

- From expt 1 to expt 2, the concentration of PCl₃ doubles and the concentration of Cl₂ is unchanged; the rate also doubles, so the order of reaction with respect to PCl₃ is 1
- From expt 2 to expt 3, the concentration of both reactants doubles; the rate increases eightfold, so the overall order of reaction is 3
- The order of reaction with respect to chlorine is therefore 3 – 1 = 2

The rate equation can thus be written as follows: rate = k[PCl₃][Cl₂]²

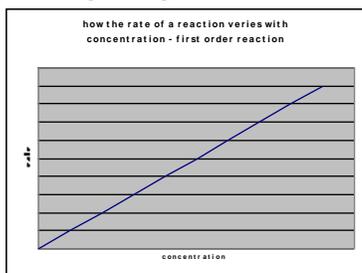
So using Expt 1, $k = \text{rate}/[\text{PCl}_3][\text{Cl}_2]^2 = 0.0004/(0.2 \times 0.1^2) = 0.2 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

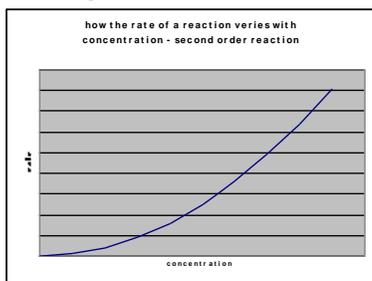
(ii) Method 2 – the Graphical Method (Initial Rate – Concentration Graphs)

- If the concentrations in the different experiments are not simple whole number ratios of each other, it is not easy to compare the concentrations and rates; the order of reaction with respect to each reactant can be deduced by plotting a graph of concentration vs initial rate (an **initial rate-concentration graph**)

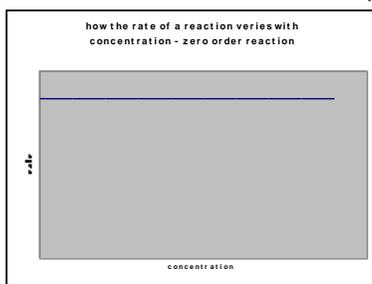
- first-order reactions; if $\text{Rate} = k[A]$, then a plot of initial rate against initial concentration will be a straight line through the origin of gradient k :



- second-order reactions; if $\text{rate} = k[A]^2$, then a plot of initial rate against initial concentration will be a curve through the origin:



- zero order reactions; if $\text{rate} = k$, then a plot of initial rate against initial concentration will be a horizontal line:



- An even better method is to plot $\log(\text{rate of reaction})$ against $\log(\text{concentration})$; this should always give a straight line, the gradient of which is the order of reaction

Lesson 5 – Determining orders of reaction from concentration-time graphs

(i) Method 1 – The gradient method

- By measuring the gradients of the tangents at different points on a concentration-time graph, it is possible to deduce the order of reaction by the arithmetic method

Using the concentration-time graph for the decomposition of SO_2Cl_2 (above):

- the initial concentration of SO_2Cl_2 is 0.5 mol dm^{-3} ; the gradient of the tangent to the curve at this point is $1.6 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
 - After 2200 s, the concentration of SO_2Cl_2 is 0.25 mol dm^{-3} ; the gradient of the tangent to the curve at this point is $8.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
 - It is clear that when the concentration of SO_2Cl_2 halves, the rate of reaction also halves; this shows that the order of reaction with respect to SO_2Cl_2 is 1 and that the rate equation is therefore $\text{rate} = k[\text{SO}_2\text{Cl}_2]$
 - If the rate of reaction has fallen by a factor of 4 when the concentration had halved, it would show that the reaction was second order
 - If the rate of reaction had not fallen at all when the concentration had halved, it would show that the reaction was zero order
 - The rate constant can be determined by rearranging the rate equation: $k = \text{rate}/[\text{SO}_2\text{Cl}_2]$
- A better a more reliable technique is to use the graph to determine the **half-life** of the reaction

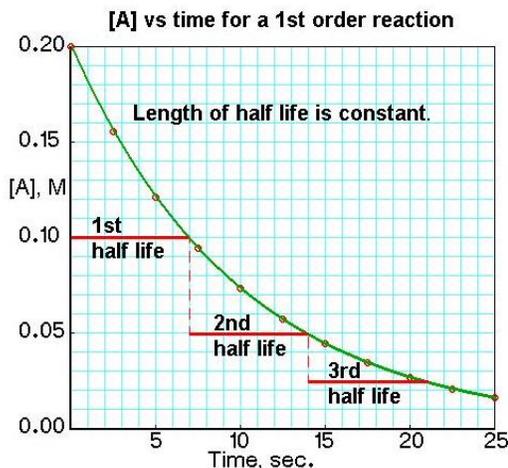
The half-life of a chemical reaction is the time taken for the concentration of a reactant to fall to half of its previous value

(ii) Method 2 – The half-life method

- Consider a first order reaction
 - rate = $k[A]$, so $-\frac{d[A]}{dt} = k[A]$, so $\frac{d[A]}{[A]} = -kdt$, so $\ln[A] = -kt + c$
 - c is the value of $\ln[A]$ when $t = 0$; this can be written as $\ln[A]_0$, so $\ln[A] = \ln[A]_0 - kt$
 - The half-life $t_{1/2}$ is the time when $[A] = \frac{[A]_0}{2}$, so $\ln\frac{[A]_0}{2} = \ln[A]_0 - kt_{1/2}$
- So $\ln[A]_0 - \ln 2 = \ln[A]_0 - kt_{1/2}$, so $\ln 2 = kt_{1/2}$ and $t_{1/2} = \frac{\ln 2}{k}$

Therefore the half-life of a first order reaction does not depend on the concentration of reactant; it should therefore remain constant throughout the reaction

- If you use a concentration-time graph to deduce two successive half-lives for a reaction, and the values are the same or similar, the reaction is first order

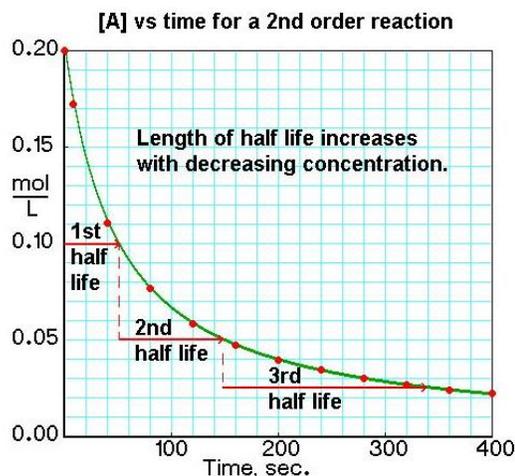


CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- Consider a second order reaction
 - rate = $k[A]^2$, so $-\frac{d[A]}{dt} = k[A]^2$, so $\frac{d[A]}{[A]^2} = -kdt$, so $\frac{1}{[A]} = kt + c$
 - c is the value of $\frac{1}{[A]}$ when $t = 0$; this can be written as $\frac{1}{[A]_0}$, so $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
 - The half-life $t_{1/2}$ is the time when $[A] = \frac{[A]_0}{2}$, so $\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$
 - So $[A]_0 kt_{1/2} = 1$ so $t_{1/2} = \frac{1}{[A]_0 k}$

Therefore the half-life of a second order reaction is inversely proportional to the concentration of reactant; as the concentration decreases, the half-life increases

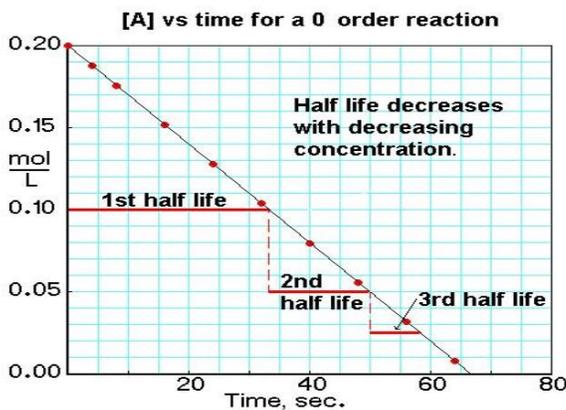
- If you use a concentration-time graph to deduce two successive half-lives for a reaction, and the second value is approximately double the first, the reaction is second order



- Consider a zero order reaction
 - rate = k , so $-\frac{d[A]}{dt} = k$, so $d[A] = -kdt$, so $[A] = -kt + c$
 - c is the value of $[A]$ when $t = 0$; this can be written as $[A]_0$, so $[A] = [A]_0 - kt$
 - The half-life $t_{1/2}$ is the time when $[A] = \frac{[A]_0}{2}$, so $\frac{[A]_0}{2} = [A]_0 - kt_{1/2}$
 - So $kt_{1/2} = \frac{[A]_0}{2}$ so $t_{1/2} = \frac{[A]_0}{2k}$

Therefore the half-life of a zero order reaction is directly proportional to the concentration of reactant; as the concentration decreases, the half-life decreases

- If you use a concentration-time graph to deduce two successive half-lives for a reaction, and the second value is approximately half of the first, the reaction is zero order



Lesson 6 – Explaining orders of reaction and the effect of temperature

(a) Explaining orders of reaction

- The orders of reaction for a chemical equation are not always the same as the reaction coefficients: Eg the reaction $\text{NO}_2 + \text{H}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$ has the following rate equation: $\text{rate} = k[\text{NO}_2]^2$
It is therefore not possible to predict the rate equation of a reaction simply by looking at the reaction coefficients
- Many reactions consist of a series of different steps, some of which are slow and some of which are very fast; it is the slowest step in a chemical reaction which determines how fast a reaction is; for this reason the slowest step in a chemical reaction is called the **rate-determining step**; changing the rate of this step will affect the overall rate of reaction; changing the rate of fast steps won't

Eg consider the reaction $\text{NO}_2 + \text{H}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$

This reaction happens in two steps:

Step 1: $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ this step is slow

Step 2: $\text{NO}_3 + \text{H}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O}$ this step is fast

The order of reaction with respect to NO_2 and H_2 can be predicted as follows:

- Step 1 is the slowest step and is therefore the rate-determining step
- This step involves two molecules of NO_2 , and so doubling the concentration of NO_2 will make collisions in this step four times more likely
- So the reaction is second order with respect to NO_2
- H_2 is not involved in this step; it is only involved in the second, fast step
- changing the concentration of H_2 therefore has no effect on the rate of reaction, and the reaction is zero order with respect to H_2

- The rate equation of a chemical reaction is determined by the number of each species involved in the rate-determining step of that reaction

(b) The effect of temperature on k

- In a typical rate equation $\text{rate} = k[\text{A}]^x[\text{B}]^y$, the effect of concentration and pressure on the rate of reaction are reflected in the changing values of $[\text{A}]$ and $[\text{B}]$; the effect of temperature, however, is reflected in different values of k at different temperatures; the value of the rate constant k increases with increasing temperature
- The value of k is affected by a number of factors but is most greatly affected by the fraction of successful collisions, $e^{-\frac{E_a}{RT}}$; the expression for the rate constant of a reaction can thus be written $k = Ae^{-\frac{E_a}{RT}}$, in which A is a pre-exponential constant called the Arrhenius constant
- The variation of k with T thus depends on the value of E_a and this can be used to calculate the activation energy of reaction graphically: $\ln(k) = \ln A - \frac{E_a}{RT}$, so a graph of $\ln(k)$ against $\frac{1}{T}$ will give a straight line of gradient $-\frac{E_a}{R}$; the gradient will be the same if a term proportional to k is used; the most convenient for most purposes is $\frac{1}{\text{time taken}}$

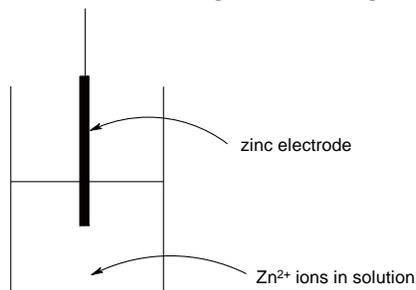
PART 3 - ELECTROCHEMISTRY

Lesson 1 – Electrode Potentials and EMF

(a) Electrochemical Cells

(i) Metal-Ion Electrode potentials

- Consider a zinc rod immersed in a solution containing Zn^{2+} ions (eg ZnSO_4):



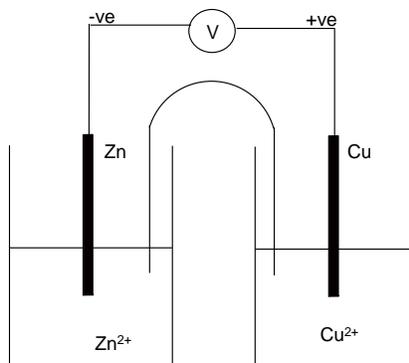
- the Zn atoms on the rod can deposit two electrons on the rod and move into solution as Zn^{2+} ions: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$; this process would result in an accumulation of negative charge on the zinc rod
- alternatively, the Zn^{2+} ions in solution could accept two electrons from the rod and move onto the rod to become Zn atoms: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}$; this process would result in an accumulation of positive charge on the zinc rod
- in both cases, a potential difference is set up between the rod and the solution; this is known as an **electrode potential**
- A similar electrode potential is set up if a copper rod is immersed in a solution containing copper ions (eg CuSO_4), due to the following processes:
 - $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$: reduction (rod becomes positive)
 - $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$: oxidation (rod becomes negative)
- No chemical reaction is taking place - there is simply a potential difference between the rod and the solution; the potential difference will depend on the nature of the ions in solution, the concentration of the ions in solution, the type of electrode used and the temperature

(ii) Creating an emf

- If two different electrodes are connected, the potential difference between the two electrodes will cause a current to flow between them; thus an **electromotive force (emf)** is established and the system can generate electrical energy
- The circuit must be completed by allowing ions to flow from one solution to the other; this is achieved by means of a **salt bridge** - often a piece of filter paper saturated with a solution of an inert electrolyte such as $\text{KNO}_3(\text{aq})$
- The e.m.f can be measured using a **voltmeter**; voltmeters have a high resistance so that they do not divert much current from the main circuit

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- The combination of two electrodes in this way is known as an **electrochemical cell**, and can be used to generate electricity; the two components which make up the cell are known as half-cells
- A typical electrochemical cell can be made by combining a zinc electrode in a solution of zinc sulphate with a copper electrode in a solution of copper sulphate:



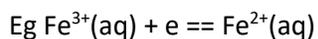
- electrons flow from the zinc electrode to the copper electrode
 - reduction thus takes place at the copper electrode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Cu}(\text{s})$
 - oxidation thus takes place at the zinc electrode: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}$
 - the overall cell reaction is as follows: $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
 - the copper electrode is positive; the zinc electrode is negative
 - the sulphate ions flow through the salt bridge from the $\text{Cu}^{2+}(\text{aq})$ solution to the $\text{Zn}^{2+}(\text{aq})$ solution, to complete the circuit and compensate for the reduced Cu^{2+} concentration and increased Zn^{2+} concentration
 - the cell reaction including spectator ions can thus be written as follows: $\text{CuSO}_4(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{ZnSO}_4(\text{aq})$
- The positive electrode is the electrode at which reduction is taking place; the negative electrode is the electrode at which oxidation is taking place
 - The external connection must be made of a metallic wire in order to allow electrons to flow; the salt bridge must be made of an aqueous electrolyte to allow ions to flow
 - By allowing two chemical reagents to be connected electrically, but not chemically, a reaction can only take place if the electrons flow externally; thus chemical energy is converted into electrical energy

(iii) Other half-cells

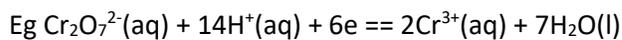
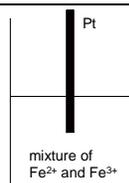
- Half-cells do not necessarily have to consist of a metal immersed in a solution of its ions; any half-reaction can be used to create a half-cell
- If the half-reaction does not contain a metal in its elemental state, an inert electrode must be used; platinum is generally used in this case, as it is an extremely inert metal
- If a gas is involved, it must be bubbled through the solution in such a way that it is in contact with the electrode

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

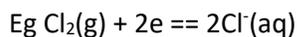
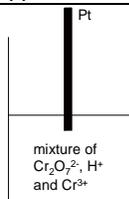
- A few examples are shown below:



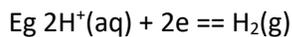
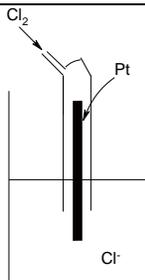
A platinum electrode is used, immersed in a solution containing both Fe^{2+} and Fe^{3+} ions:



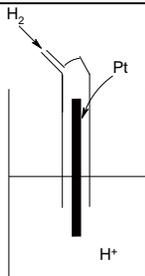
A platinum electrode is used, immersed in a solution containing $\text{Cr}_2\text{O}_7^{2-}$, H^+ and Cr^{3+} ions:



A platinum electrode is used, immersed in a solution containing Cl^- ions. Chlorine gas is bubbled through the solution, in contact with the electrode:



A platinum electrode is used, immersed in a solution containing H^+ ions. Hydrogen gas is bubbled through the solution, in contact with the electrode:



Lesson 2 – conventional representation and measurement

(iv) Conventional representation of cells

- As it is cumbersome and time-consuming to draw out every electrochemical cell in full, a system of notation is used which describes the cell in full, but does not require it to be drawn
- Half-cells are written as follows:
 - the electrode is placed on one side of a vertical line
 - the species in solution, whether solid, liquid, aqueous or gaseous, are placed together on the other side of the vertical line
 - if there is more than one species in solution, and the species are on different sides of the half-equation, the different species are separated by a comma

Eg $\text{Zn}^{2+}(\text{aq}) + 2\text{e} \rightleftharpoons \text{Zn}(\text{s})$ is represented $\text{Zn} \mid \text{Zn}^{2+}$

Eg $\text{Fe}^{3+}(\text{aq}) + \text{e} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ is represented $\text{Pt} \mid \text{Fe}^{2+}, \text{Fe}^{3+}$

Eg $\text{Cl}_2(\text{g}) + 2\text{e} \rightleftharpoons 2\text{Cl}^{-}(\text{aq})$ is represented $\text{Pt} \mid \text{Cl}_2, \text{Cl}^{-}$

- When two half-cells are connected to form a full electrochemical cell, the cell is written as follows:
 - the two half-cells are placed on either side of two vertical broken lines (which represent the salt bridge)
 - the electrodes are placed on the far left and far right, and the other species are placed adjacent to the vertical broken lines in the centre
 - on the left, the the lower oxidation state species is written first, and the higher oxidation state species is written second
 - on the right, the higher oxidation state species is written first, and the lower oxidation state species is written second
 - if the direction of the cell reaction is known, the oxidation reaction is placed on the left and the reduction on the right:

Eg Cell reaction = $\text{Zn}(\text{s}) + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{H}^{+}, \text{H}_2 \mid \text{Pt}$

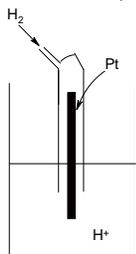
Eg Cell Reaction = $\text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^{+}(\text{aq})$ $\text{Pt} \mid \text{H}_2, \text{H}^{+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

Eg Cell reaction = $\text{Ag}^{+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Ag}(\text{s}) + \text{Fe}^{3+}(\text{aq})$ $\text{Pt} \mid \text{Fe}^{2+}, \text{Fe}^{3+} \parallel \text{Ag}^{+} \mid \text{Ag}$

- This method of representing electrochemical cells is known as the conventional representation of a cell, and it is widely used
- One advantage of this notation is that it is easy to see the reduction and oxidation processes taking place:
 - On the LHS (oxidation): electrode \rightarrow reduced species \rightarrow oxidised species
 - On the RHS (reduction): oxidised species \rightarrow reduced species \rightarrow electrode

(v) Measuring Electrode Potentials

- The emf of electrochemical cells is easy to measure, but the individual electrode potentials themselves cannot actually be measured at all; it is only possible to measure the potential difference between two electrodes
- It is therefore only possible to assign a value to a half-cell if one half-cell is arbitrarily allocated a value and all other electrodes are measured relative to it; an electrode used for this purpose is known as a reference electrode; the electrode conventionally used for this purpose is the standard hydrogen electrode:



- the gas pressure is fixed at 1 atm, the temperature is 25°C and the H⁺ ions have a concentration of 1.0 mol dm⁻³
- this electrode is arbitrarily assigned a value of 0.00V
- using this electrode, it is possible to assign an electrode potential to all other half-cells
- Voltmeters measure potential on the right-hand side of the cell and subtract it from the potential on the left-hand side of the cell: **Emf = E_{RHS} - E_{LHS}**; if the standard hydrogen electrode is placed on the left-hand side of the voltmeter, therefore, the E_{LHS} will be zero and the emf of the cell will be the electrode potential on the right-hand electrode:
 - Example: if a Zn²⁺(aq) + 2e == Zn(s) electrode is connected to the standard hydrogen electrode and the standard hydrogen electrode is placed on the left, the emf of the cell is found to be -0.76V; the Zn²⁺(aq) + 2e == Zn(s) half-cell thus has a standard electrode potential of -0.76V
 - Example: if a Cu²⁺(aq) + 2e == Cu(s) electrode is connected to the standard hydrogen electrode and the standard hydrogen electrode is placed on the left, the emf of the cell is +0.34V; the Cu²⁺(aq) + 2e == Cu(s) half-cell thus has an electrode potential of +0.34V
- The standard electrode potential of a half-reaction can be defined as is “the emf of a cell where the left-hand electrode is the standard hydrogen electrode and the right-hand electrode is the standard electrode in question”
- The electrode potential depends on the conditions used, including temperature, pressure and concentration of reactants; it is therefore necessary to specify the conditions used when measuring electrode potentials; these conditions are normally set at a temperature of 298 K, a pressure of 1 atm and with all species in solution having a concentration of 1.0 mol dm⁻³; these are known as **standard conditions**; electrode potentials measured under these conditions are known as **standard electrode potentials**; they are denoted by the symbol E^o

Lesson 3 – Using electrode potentials and non-standard conditions

(vi) Using standard electrode potentials

- The equation $\text{emf} = E_{\text{RHS}} - E_{\text{LHS}}$ can be applied to electrochemical cells in two ways:
 - to predict the emf of a cell if the electrode potentials are known:
eg: if a standard copper electrode ($\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$: +0.34 V) and a standard zinc electrode ($\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$: -0.76 V) are connected, with the copper electrode placed on the left, the emf of the cell will be
 $-0.76 \text{ V} - 0.34 \text{ V} = -1.1 \text{ V}$
 - to determine the electrode potential of one half-cell if the other is known and the emf is measured:
Eg If the standard copper electrode (+0.34V) is placed on the left, and the standard silver electrode is placed on the right, the emf of the cell is found to be +0.46V; therefore the electrode potential at the silver electrode will be $E_{\text{RHS}} - \text{emf} + E_{\text{LHS}} = 0.46 + 0.34 = +0.80 \text{ V}$
- In fact, the hydrogen electrode is rarely used in practice for a number of reasons:
 - the electrode reaction is slow
 - the electrodes are not easily portable
 - it is difficult to maintain a constant pressure

Once one standard electrode potential has been measured relative to the standard hydrogen electrode, it is not necessary to use the standard hydrogen electrode again; any electrode whose electrode potential is known could be used to measure standard electrode potentials

(vii) Non-standard conditions

- The relationship between the electrode potential E and the conditions is given by the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \quad (Q = \text{reaction quotient for the reduction half-reaction})$$

- For the half-equation $\text{Cu}^{2+}(\text{aq}) + 2\text{e} \rightleftharpoons \text{Cu}(\text{s})$, $Q = \frac{1}{[\text{Cu}^{2+}]}$ so $E = E^{\circ} + \frac{RT}{nF} \ln [\text{Cu}^{2+}]$
Example: E° for $\text{Cu}^{2+}(\text{aq}) + 2\text{e} \rightleftharpoons \text{Cu}(\text{s})$ is +0.34 V, so calculate E if $[\text{Cu}^{2+}] = 0.1 \text{ mol dm}^{-3}$
Answer: $E = 0.34 + (8.31 \times 298 / 2 \times 96500) \times \ln 0.1 = +0.31 \text{ V}$
- For the half-equation $\text{Fe}^{3+}(\text{aq}) + \text{e} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$, $Q = \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ so $E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$
Example: E° for $\text{Fe}^{3+}(\text{aq}) + \text{e} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ is +0.77 V, so calculate E if $[\text{Fe}^{2+}] = 0.1 \text{ mol dm}^{-3}$ and $[\text{Fe}^{3+}] = 0.5 \text{ mol dm}^{-3}$
Answer: $E = 0.77 - (8.31 \times 298 / 2 \times 96500) \times \ln 0.1/0.5 = +0.81 \text{ V}$

- It is possible to predict how the electrode potential will vary if non-standard conditions are used by using Le Chatelier's Principle:
 - if the oxidizing agent has a concentration greater than 1.0 mol dm^{-3} , it is more likely to favour reduction and the electrode potential will be more positive than the standard electrode potential
 - if the oxidising agent has a concentration of less than 1.0 mol dm^{-3} , it is more likely to favour oxidation and the electrode potential will be more negative than the standard electrode potential
 - for reducing agents, the reverse is true.

Eg: $\text{Fe}^{2+}(\text{aq}) + 2\text{e} \rightleftharpoons \text{Fe}(\text{s})$ Standard electrode potential = -0.44 V
If $[\text{Fe}^{2+}] = 0.1 \text{ mol dm}^{-3}$ the electrode potential = -0.50 V

- The concentration is lower than standard so reduction is less likely to take place, and hence the electrode potential is more negative than expected
- If the temperature is higher than 298 K, then the system will move in the endothermic direction and the electrode potential will change accordingly; if the pressure is greater than 1 atm, then the system will move to decrease the pressure and the electrode potential will change accordingly

Lesson 4 – The Electrochemical Series

(b) Predicting the Feasibility of Redox Reactions**(i) The Electrochemical Series**

- If all of the standard electrode potentials are arranged in order, usually starting with the most negative, a series is set up which clearly shows the relative tendency of all the half-reactions to undergo oxidation and reduction. This series is known as the electrochemical series, and a reduced form of this series is shown as follows:

HALF-EQUATION			E°/V
$\text{Li}^+(\text{aq}) + \text{e}$	==	$\text{Li}(\text{s})$	-3.03
$\text{K}^+(\text{aq}) + \text{e}$	==	$\text{K}(\text{s})$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}$	==	$\text{Ca}(\text{s})$	-2.87
$\text{Na}^+(\text{aq}) + \text{e}$	==	$\text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}$	==	$\text{Mg}(\text{s})$	-2.37
$\text{Be}^{2+}(\text{aq}) + 2\text{e}$	==	$\text{Be}(\text{s})$	-1.85
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}$	==	$\text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}$	==	$\text{Fe}(\text{s})$	-0.44
$\text{V}^{3+}(\text{aq}) + \text{e}$	==	$\text{V}^{2+}(\text{aq})$	-0.26
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}$	==	$\text{Pb}(\text{s})$	-0.13
$2\text{H}^+(\text{aq}) + 2\text{e}$	==	$\text{H}_2(\text{g})$	0.00
$\text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{e}$	==	$2\text{S}_2\text{O}_3^{2-}(\text{aq})$	+0.09
$\text{Cu}^{2+}(\text{aq}) + \text{e}$	==	$\text{Cu}^+(\text{aq})$	+0.15
$4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}$	==	$\text{H}_2\text{SO}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+0.17
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}$	==	$\text{Cu}(\text{s})$	+0.34
$\text{Cu}^+(\text{aq}) + \text{e}$	==	$\text{Cu}(\text{s})$	+0.52
$\text{I}_2(\text{aq}) + 2\text{e}$	==	$2\text{I}^-(\text{aq})$	+0.54
$2\text{H}^+(\text{aq}) + \text{O}_2(\text{g}) + 2\text{e}$	==	$\text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{Fe}^{3+}(\text{aq}) + \text{e}$	==	$\text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Ag}^+(\text{aq}) + \text{e}$	==	$\text{Ag}(\text{s})$	+0.80
$2\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{e}$	==	$\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+0.81
$\text{Br}_2(\text{aq}) + 2\text{e}$	==	$2\text{Br}^-(\text{aq})$	+1.09
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}$	==	$2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}$	==	$2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{Cl}_2(\text{g}) + 2\text{e}$	==	$2\text{Cl}^-(\text{aq})$	+1.36
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}$	==	$\text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{MnO}_4^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}$	==	$\text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.70
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}$	==	$2\text{H}_2\text{O}(\text{l})$	+1.77
$\text{Ag}^+(\text{aq}) + \text{e}$	==	$\text{Ag}(\text{s})$	+1.98
$\text{F}_2(\text{g}) + 2\text{e}$	==	$2\text{F}^-(\text{aq})$	+2.87

- Note that all half-equations are written as reduction processes; this is in accordance with the IUPAC convention for writing half-equations for electrode reactions

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- The electrochemical series has a number of useful features:
 - all the species on the left-hand side of the series can accept electrons and be reduced to a lower oxidation state; they are therefore all oxidising agents; all the species on the right-hand side of the series can give up electrons and be oxidised to a higher oxidation state, and are thus reducing agents
 - the higher a half-equation is located in the electrochemical series, the more negative the standard electrode potential and the greater the tendency to undergo oxidation; the reducing agents at the top of the series are thus very strong, and the oxidising agents very weak; the lower down a half-equation is located in the electrochemical series, the more positive the standard electrode potential and the greater the tendency to undergo reduction; the oxidising agents at the bottom of the series are thus very strong, and the reducing agents very weak
 - If two half-cells are connected, the half-cell higher up the electrochemical series (ie more negative) will undergo oxidation and the half-cell lower down the electrochemical series (ie more positive) will undergo reduction
 - It is possible to use the electrochemical series to predict whether or not any given redox reaction will occur

(ii) Cell Potential

- The **cell potential** (E_{cell}) for a reaction is given as $E_{\text{red}} - E_{\text{ox}}$, where E_{red} is the electrode potential of the reduction half-equation and E_{ox} is the electrode potential of the oxidation half-equation
 - If (E_{cell}) is positive, the reaction is feasible and is expected to take place
 - If (E_{cell}) is negative, the reaction is not feasible and is expected to take place
- Eg consider the reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$; this reaction can be broken down into its two half equations: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$ (ox) and $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu(s)}$ (red); E_{cell} is therefore $+0.34 - (-0.76) = +1.10 \text{ V}$ and the reaction is feasible
- Eg consider the reaction: $\text{Zn}^{2+}(\text{aq}) + \text{Cu(s)} \rightarrow \text{Zn(s)} + \text{Cu}^{2+}(\text{aq})$; this reaction can be broken down into its two half equations: $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-}$ (ox) and $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn(s)}$ (red); E_{cell} is therefore $-0.76 - (-0.34) = -1.10 \text{ V}$ and the reaction is not feasible
- Since the more positive electrodes are at the bottom of the electrochemical series, the oxidising agents in these systems will oxidise any reducing agent which lies above it in the electrochemical series
 - Eg $\text{H}^{+}(\text{aq})$ will oxidise Pb(s) to $\text{Pb}^{2+}(\text{aq})$, and any other metal above it, but will not oxidise Cu(s) to $\text{Cu}^{2+}(\text{aq})$ or any metal below it: $\text{Pb(s)} + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 - Acids such as nitric acid, however, which contains the more powerful oxidising agent $\text{NO}_3^{-}(\text{aq})$, will oxidise any reducing agent with a standard electrode potential more negative than $+0.81 \text{ V}$, eg Cu(s) : $\text{Cu(s)} + 4\text{H}^{+}(\text{aq}) + 2\text{NO}_3^{-}(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O(l)}$
- Reducing agents will reduce any oxidising agent which lies below it in the electrochemical series:
 - Eg Fe^{2+} ($+0.77$) will reduce any oxidising agent below it in the electrochemical series; it will therefore reduce Ag^{+} to Ag ($+0.80 \text{ V}$) but not I_2 to I^{-} ($+0.54 \text{ V}$)
- Cell potentials are a good way to predict whether or not a given reaction will take place; however it does only apply if the reacting species are under the same conditions, including concentration, as those of the electrode potential; many reactions which are not expected to occur do in fact take place if the solutions are hot or concentrated, and many reactions which are expected to occur do not take place if the solutions are too dilute

(iii) Kinetic Stability

- Cell potentials can be used effectively to predict whether or not a given reaction will take place, but they give no indication as to how **fast** a reaction will proceed; in many cases E_{CELL} is positive but no apparent reaction occurs; this is because many reactants are kinetically stable; the reaction has a high activation energy so is very slow at room temperature; there are many examples of this in inorganic chemistry:



$$E = -0.42\text{V}, E = -2.38\text{V} \text{ so } E_{\text{CELL}} = E_r - E_o = +1.96\text{V}$$

So a reaction is expected but no reaction takes place.

This is because the activation energy is too high (magnesium will react with steam and slowly with hot water)

(iv) Cell potential, equilibrium constant and free energy change

- A reaction is feasible if ΔG is negative; a reaction is feasible if E_{cell} is positive; free energy and cell potential are linked by the expression $\Delta G = -nFE_{\text{cell}}$ (n = number of electrons in redox reaction, F = Faraday)
- ΔG is also linked to the equilibrium constant of a reaction K_c by the expression $\Delta G = -RT \ln K_c$; if $K_c > 1$, $\Delta G = -ve$ and if $K_c < 1$, $\Delta G = +ve$
- It follows that $E_{\text{cell}} = \frac{RT}{nF} \ln K_c$

Example: the reaction $\text{Fe}^{2+} + \text{Ag}^+ \rightarrow \text{Fe}^{3+} + \text{Ag}$ has an E_{cell}^o of +0.03 V; calculate ΔG and K_c for the reaction

$$- \Delta G = -nFE_{\text{cell}} = -1 \times 96500 \times 0.03 = -2895 \text{ Jmol}^{-1} = -2.9 \text{ kJmol}^{-1}$$

$$- K_c = \exp\left(\frac{nFE_{\text{cell}}}{RT}\right) = 3.22$$

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

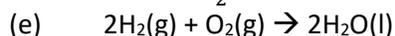
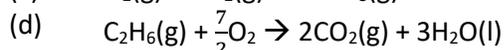
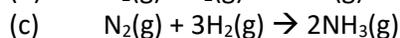
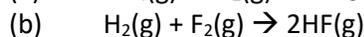
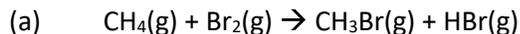
Questions

- 1.1** The combustion of methane is an exothermic reaction: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ $\Delta H = -890 \text{ kJmol}^{-1}$
- What will be the enthalpy change for the following reaction? $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$
 - Calculate the heat energy released when 100 g of methane is burned
 - Calculate the heat energy released when 500 cm³ of methane is burned at 298 K and 300 kPa
 - Calculate the mass of methane required to produce 50,000 kJ of heat energy
- 1.2** Photosynthesis is an endothermic reaction: $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ $\Delta H = +2802 \text{ kJmol}^{-1}$
- What will be the enthalpy change for the following reaction? $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$
 - Calculate the amount of light energy required to make 1000 g of glucose
 - Calculate the amount of light energy required to absorb 500 cm³ of carbon dioxide is at 298 K and 100 kPa
 - Calculate the mass of glucose which can be made when a tree absorbs 10,000 kJ of light energy
- 1.3** When 5.73 g of sodium chloride (NaCl) dissolves in 100 cm³ of water, the temperature of the water fell from 22.4 °C to 19.8 °C. Calculate the molar enthalpy of solution of NaCl.
- 1.4** When 2.3 g of magnesium chloride (MgCl₂) dissolves in 200 cm³ of water, the temperature rose by 3.4 °C. Calculate the molar enthalpy of solution of MgCl₂.
- 1.5** If 50 cm³ of 0.1 mol dm⁻³ HCl and 50 cm³ of 0.1 mol dm⁻³ NaOH are mixed, the temperature of the solution rises by 0.68 °C. Calculate the molar enthalpy of neutralisation of HCl by NaOH.
- 1.6** If 50 cm³ of 1.0 mol dm⁻³ NaOH is added to 25 cm³ of 2.0 mol dm⁻³ CH₃COOH, the temperature rose by 8.3 °C. Calculate the molar enthalpy of neutralisation of CH₃COOH by NaOH.
- 1.7** A spirit burner containing ethanol (C₂H₅OH) was used to heat 100 cm³ of water in a copper can by 30 °C. As a result, the mass of the spirit burner decreased by 0.62 g. Calculate the molar enthalpy of combustion of ethanol.
- 1.8** A spirit burner containing butan-1-ol (C₄H₉OH) was used to heat 200 cm³ of water in a copper can by 20 °C. As a result, the mass of the spirit burner decreased by 0.81 g. Calculate the molar enthalpy of combustion of butan-1-ol.
- 1.9** Write equations for the reactions represented by the following enthalpy changes:
- The enthalpy of formation of propane
 - The enthalpy of formation of calcium oxide
 - The enthalpy of combustion of propane
 - The enthalpy of combustion of hydrogen
 - The enthalpy of neutralisation of sulphuric acid by potassium hydroxide
 - The enthalpy of solution of anhydrous calcium chloride

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

1.10 Use the following data to estimate the enthalpy changes for the reactions below:

bond	$\Delta H_b/\text{kJmol}^{-1}$	bond	$\Delta H_b/\text{kJmol}^{-1}$	bond	$\Delta H_b/\text{kJmol}^{-1}$
C-H	+413	H-F	+565	C=C	+611
C-Br	+280	N≡N	+945	H-H	+435
H-Br	+366	F-F	+158	N-H	+391
Br-Br	+193	C=O	+805	O=O	+498
C-C	+347	O-H	+464	I-I	+151



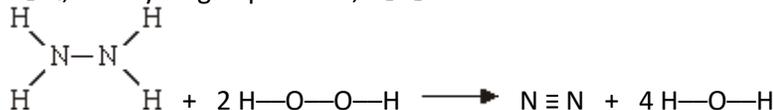
1.11 The enthalpy change for the following reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is -9 kJmol^{-1}

Use this information and the values in the above table to calculate the bond dissociation energy for the H-I bond

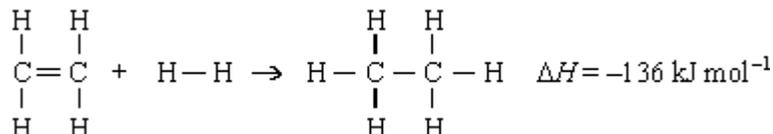
1.12 Some mean bond enthalpies are given below:

Bond	N-H	N-N	N≡N	H-O	O-O
Mean bond enthalpy/ kJ mol^{-1}	388	163	944	463	146

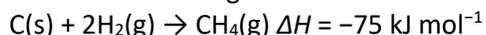
Use these data to calculate the enthalpy change for the following gas-phase reaction between hydrazine, N_2H_4 , and hydrogen peroxide, H_2O_2



1.13 Use the following equation and data from the table above to calculate a value for the C-H bond enthalpy in ethane:

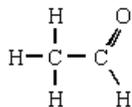


1.14 Given the following data:



What is the enthalpy change, in kJ mol^{-1} , of this reaction? $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{s}) + 4\text{H}(\text{g})$

1.15



Ethanal has the structure:



Use the mean bond enthalpy data above to calculate the enthalpy change for this reaction.

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- 1.16 (a) Write an equation to show the complete combustion of ethene (C₂H₄)
 (b) Use the following data to calculate the enthalpy of combustion of ethene:

Substance	H ₂ O(l)	CO ₂ (g)	Ethene C ₂ H ₄ (g)
ΔH _f /kJmol ⁻¹	-286	-393	+52

- 1.17 Given the following data: ΔH_f(CH₄) = -74.8 kJmol⁻¹, ΔH_f(CH₃Cl) = -134.5 kJmol⁻¹, ΔH_f(HCl) = -92.3 kJmol⁻¹; calculate ΔH for the reaction CH₄(g) + Cl₂(g) → CH₃Cl(g) + HCl(g)

- 1.18 Given the data:

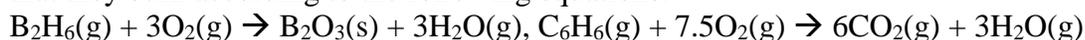
Substance	H ₂ O(l)	NH ₃ (g)
ΔH _f /kJmol ⁻¹	-286	-46

Calculate the enthalpy change of the following reaction: 4NH₃(g) + 3O₂(g) → 2N₂(g) + 6H₂O(l)

- 1.19 Given the following data:

Substance	B ₂ H ₆ (g)	B ₂ O ₃ (s)	C ₆ H ₆ (g)	CO ₂ (g)	H ₂ O(g)
ΔH _f /kJmol ⁻¹	+31.4	-1270	+83.9	-393	-242

Calculate the enthalpy of combustion of gaseous diborane (B₂H₆) and gaseous benzene (C₆H₆) given that they burn according to the following equations:



- 1.20 The enthalpy of combustion of ethanol is -1380 kJmol⁻¹. Calculate the enthalpy of formation of ethanol, given that the enthalpies of formation of carbon dioxide and water are -393.7 and -285.9 kJmol⁻¹ respectively.
- 1.21 Calculate the enthalpy of formation of butane (C₄H₁₀) from the following data:
 Enthalpy of combustion of carbon = -393.6 kJmol⁻¹
 Enthalpy of combustion of hydrogen = -285.9 kJmol⁻¹
 Enthalpy of combustion of butane = -2877.1 kJmol⁻¹

- 1.22 Given the following data:

Substance	CH ₃ CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH=CH ₂	H ₂
ΔH _f /kJmol ⁻¹	-2877	-2717	-286

Calculate ΔH for the following reaction: CH₃CH₂CH=CH₂ + H₂ → CH₃CH₂CH₂CH₃

- 1.23 Given the following data:

CH ₄ (g) + 2O ₂ (g) → CO ₂ (g) + 2H ₂ O(l)	ΔH = -890 kJmol ⁻¹
CO(g) + 1/2O ₂ (g) → CO ₂ (g)	ΔH = -284 kJmol ⁻¹
C(s) + O ₂ (g) → CO ₂ (g)	ΔH = -393 kJmol ⁻¹
H ₂ (g) + 1/2O ₂ (g) → H ₂ O(l)	ΔH = -286 kJmol ⁻¹

Calculate

- (a) The enthalpy of formation of methane
 (b) The enthalpy of formation of carbon monoxide
 (c) The enthalpy change when methane is burned in limited oxygen to form carbon monoxide and water

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

1.24 Use the data below to calculate the lattice enthalpy of potassium chloride:

Process	Enthalpy change/kJmol ⁻¹
Standard enthalpy of atomisation of potassium	+90
First ionisation enthalpy of potassium	+420
Bond dissociation enthalpy of chlorine	+244
First electron affinity of chlorine	-360
Standard enthalpy of formation of potassium chloride	-436

1.25 (a) Calculate the first electron affinity of chlorine from the following data:

Process	Enthalpy change/kJmol ⁻¹
Ca(s) → Ca(g)	+190
Ca(g) → Ca ⁺ (g) + e	+590
Ca ⁺ (g) → Ca ²⁺ (g) + e	+1140
1/2Cl ₂ (g) → Cl(g)	+121
Ca ²⁺ (g) + 2Cl ⁻ (g) → CaCl ₂ (s)	-2184
Ca(s) + Cl ₂ (g) → CaCl ₂ (s)	-795

(b) The lattice formation enthalpy of CaCl₂(s) is -760 kJmol⁻¹. Use this information and that in the table above to calculate the enthalpy of formation of CaCl, and hence explain why CaCl₂ is formed and not CaCl.

1.26 Draw a Born-Baber cycle to show the formation of CaS from its elements. Hence calculate the lattice formation enthalpy of CaS given the following information:

Enthalpy of formation of CaS(s) = -482 kJmol⁻¹

Enthalpy of atomisation of Ca(s) = +178 kJmol⁻¹

Enthalpy of atomisation of S(s) = +279 kJmol⁻¹

First ionisation enthalpy of Ca = +590 kJmol⁻¹

Second ionisation enthalpy of Ca = +1145 kJmol⁻¹

First electron affinity of S = -200 kJmol⁻¹

Second electron affinity of S = +539 kJmol⁻¹

1.27 Calculate the enthalpy of solution of silver chloride given the following data:

Lattice enthalpy of silver chloride: -905 kJmol⁻¹

Enthalpy of hydration of Ag⁺: -464 kJmol⁻¹

Enthalpy of hydration of Cl⁻: -364 kJmol⁻¹

1.28 Calculate the enthalpy of solution of the hydroxides of barium, calcium and magnesium given the following data (all in kJmol⁻¹):

lattice enthalpy of Ba(OH)₂: -2235

lattice enthalpy of Ca(OH)₂: -2650

lattice enthalpy of Mg(OH)₂: -2995

hydration energies: Ba²⁺: -1360, Ca²⁺: -1650, Mg²⁺: -1920, OH⁻: -460

Use your answers to explain the trend in solubility of the group (II) hydroxides.

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- 1.29** (a) Use the following enthalpies of formation to calculate the enthalpy change for the reaction:
 $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
 $\Delta H_f(\text{kJ mol}^{-1})$: $\text{NaHCO}_3(\text{s}) -951$, $\text{Na}_2\text{CO}_3(\text{s}) -1131$, $\text{CO}_2(\text{g}) -394$, $\text{H}_2\text{O}(\text{g}) -242$
- (b) Use the following entropies to calculate the entropy change for the same reaction:
 $S(\text{J mol}^{-1}\text{K}^{-1})$: $\text{NaHCO}_3(\text{s}) 102$, $\text{Na}_2\text{CO}_3(\text{s}) 135$, $\text{CO}_2(\text{g}) 214$, $\text{H}_2\text{O}(\text{g}) 189$
- (c) Predict the temperature range for which this reaction will be feasible.
- 1.30** (a) Use the following data to calculate the entropy change when one mole of ammonia is formed from its elements: $S(\text{J K}^{-1}\text{mol}^{-1})$: $\text{N}_2(\text{g}) = 191.6$, $\text{H}_2(\text{g}) = 130.6$, $\text{NH}_3(\text{g}) = 192.3$
- (b) Given that the enthalpy of formation of ammonia is -46 kJ mol^{-1} , determine the range of temperatures for which this reaction is feasible.
- (c) Why is the reaction often carried out at temperatures lower than this?
- 1.31** (a) Use the following data to explain why NaCl is soluble in water at 298 K:
 $\text{NaCl}(\text{s}) \rightarrow \text{Na}(\text{aq}) + \text{Cl}(\text{aq})$, $\Delta H = +31 \text{ kJ mol}^{-1}$; $S(\text{Na}^+(\text{aq})) = 320.9 \text{ J K}^{-1}\text{mol}^{-1}$, $S(\text{Cl}^-(\text{aq})) = 56.5 \text{ J K}^{-1}\text{mol}^{-1}$,
 $S(\text{NaCl}(\text{s})) = 72.1 \text{ J K}^{-1}\text{mol}^{-1}$
- (b) Are there any temperatures at which you would not expect NaCl to dissolve in water?
- 1.32** The enthalpy of solution of AgF is -20 kJ mol^{-1}
- (a) Explain why the entropy change for the dissolving of AgF in water is positive.
- (b) Explain why AgF is soluble in water at all temperatures.

- 1.33** Consider the following data:

	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	0	0	+90.4
$S^\circ/\text{J K}^{-1} \text{mol}^{-1}$	192.2	205.3	211.1

- (a) Write an equation to show the formation of nitrogen monoxide from its elements.
- (b) Calculate the minimum temperature at which this reaction is feasible.
- (c) Suggest why this reaction does not proceed significantly in car engines, even though the temperature is higher than the critical temperature.
- (d) Calculate K_c for this reaction at 300 K.
- 1.34** Consider the following data:

	$\text{C}(\text{graphite})$	$\text{C}(\text{diamond})$
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	0	+1.9
$S^\circ/\text{J K}^{-1} \text{mol}^{-1}$	5.7	2.4

Explain why the conversion of graphite to diamond is not feasible at any temperature.

- 1.35** Use the data provided to calculate the entropy change and the free energy change for the following reaction at 298 K: $\text{CH}_3\text{COCl}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{HCl}(\text{g})$ $\Delta H^\ominus = -21.6 \text{ kJ mol}^{-1}$

	$\text{CH}_3\text{COCl}(\text{l})$	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$	$\text{HCl}(\text{g})$
$S^\ominus/\text{J K}^{-1}\text{mol}^{-1}$	201	161	259	187

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

2.1 In the following reaction: $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
In a total reaction volume of 100 cm^3 , the concentration of MnO_4^- was monitored and at the start of the reaction it was found to be decreasing at $1.2 \times 10^{-5}\text{ mol dm}^{-3}\text{ s}^{-1}$. Calculate:

- The rate at which $[\text{H}^+]$ is decreasing
- The volume of CO_2 being produced per second
- The rate of reaction

2.2 (a) Explain what is meant by the terms collision frequency, collision energy and activation energy
(b) Explain why not all collisions between reactants lead to a chemical reaction
(c) Complete the table below to show the effect of concentration, temperature and catalysts on collision frequency, collision energy and activation energy

	Increase in concentration (or pressure)	Increase in temperature	Addition of catalyst
Collision Frequency			
Collision Energy			
Activation Energy			

2.3 (a) On the same axes, sketch the Maxwell-Boltzmann distribution of molecular energies for a low temperature T_1 and a higher temperature T_2 .
(b) If the temperature is increased from T_1 to T_2 , explain what happens to:
(i) the mean kinetic energy of the particles
(ii) the area under the graph
(iii) the number of particles having the most common amount of energy
(c) Hence explain why a small increase in temperature can cause a large increase in the rate of reaction.

2.4 (a) Explain the meaning of the term catalyst
(b) Explain how a catalyst lowers the activation energy for a reaction
(c) Use the Maxwell-Boltzmann distribution of molecular energies to explain how this leads to an increase in reaction rate

2.5 Use the expression $e^{-\frac{E_a}{RT}}$ to calculate:
(a) How many times faster a reaction with an activation energy of 50 kJ mol^{-1} will take place at 310 K than at 300 K
(b) How many times faster a reaction with an activation energy of 100 kJ mol^{-1} will take place at 310 K than at 300 K
(c) How many times faster a reaction with an activation energy of 50 kJ mol^{-1} at 300 K will take place compared to a reaction with an activation energy of 100 kJ mol^{-1} at 300 K

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- 2.6** The initial rates of the reaction $2A + B \rightarrow 2C + D$ at various concentrations of A and B are given below:

[A] moldm ⁻³	[B] moldm ⁻³	Initial rate /moldm ⁻³ s ⁻¹
0.01	0.20	0.10
0.02	0.20	0.20
0.01	0.40	0.40

- (a) What is the order of reaction with respect to A and B?
 (b) What is the overall order of reaction?
 (c) What is the rate constant?
 (d) What will be the rate of the reaction if the concentrations of A and B are both 0.01 moldm⁻³?

- 2.7** For the reaction $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$, the following rate data were collected:

Initial [NO]/M	Initial [H ₂]/M	Initial rate/Ms ⁻¹
0.60	0.37	3.0 x 10 ⁻³
1.20	0.37	1.2 x 10 ⁻²
1.20	0.74	1.2 x 10 ⁻²

Deduce the rate equation and calculate the value of the rate constant.

- 2.8** For the reaction $PCl_3 + Cl_2 \rightarrow PCl_5$, the following data were obtained:

Experiment No.	[PCl ₃]/moldm ⁻³	[Cl ₂]/ moldm ⁻³	Rate / moldm ⁻³ s ⁻¹
1	0.36	1.26	6.0 x 10 ⁻⁴
2	0.36	0.63	1.5 x 10 ⁻⁴
3	0.72	2.52	4.8 x 10 ⁻³

Deduce the rate equation and the value of the rate constant.

- 2.9** The data in the table below relates to the reaction between hydrogen and nitrogen monoxide at 673K. $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

Experiment number	Initial concentration of H ₂ /moldm ⁻³	Initial concentration of NO /moldm ⁻³	Initial rate of production of N ₂ / moldm ⁻³ s ⁻¹
1	2.0 x 10 ⁻³	6.0 x 10 ⁻³	6.0 x 10 ⁻³
2	3.0 x 10 ⁻³	6.0 x 10 ⁻³	9.0 x 10 ⁻³
3	6.0 x 10 ⁻³	1.0 x 10 ⁻³	0.5 x 10 ⁻³

Deduce the rate equation and calculate the rate constant.

- 2.10** The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature:

Experiment	Initial concentration of A/mol dm ⁻³	Initial concentration of B/mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.15	0.24	0.45 x 10 ⁻⁵
2	0.30	0.24	0.90 x 10 ⁻⁵
3	0.60	0.48	7.20 x 10 ⁻⁵

Deduce the rate equation and calculate the value of the rate constant.

- 2.11** The following data were obtained in a second series of experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature:

Experiment	Initial concentration of A/mol dm ⁻³	Initial concentration of B/mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	0.75	1.50	9.30 x 10 ⁻⁵
5	0.20	0.10	To be calculated

The rate equation for this reaction is rate = $k[C]^2[D]$

Calculate the value of the rate constant and deduce the initial rate of reaction in Experiment 5.

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

2.12 Acidified hydrogen peroxide reacts with iodide ions to form iodine according to the following equation:



The **initial rate** of this reaction is investigated by measuring the time taken to produce sufficient iodine to give a blue colour with starch solution.

A series of experiments was carried out, in which the concentration of iodide ions was varied, while keeping the concentrations of all of the other reagents the same. In each experiment the time taken (t) for the reaction mixture to turn blue was recorded.

The initial rate of the reaction can be represented as $\frac{1}{t}$, and the initial concentration of iodide ions can be represented by the volume of potassium iodide solution used.

A graph of $\log_{10} \left(\frac{1}{t} \right)$ on the y-axis against $\log_{10} (\text{volume of KI(aq)})$ is a straight line. The gradient of this straight line is equal to the order of the reaction with respect to iodide ions.

The results obtained are given in the table below. The time taken for each mixture to turn blue was recorded on a stopclock graduated in seconds.

Expt.	Volume of KI(aq) / cm ³	log ₁₀ (volume of KI(aq))	Time / s	log ₁₀ $\frac{1}{t}$
1	5	0.70	71	-1.85
2	8	0.90	46	-1.66
3	10	1.00	37	-1.57
4	15	1.18	25	-1.40
5	20	1.30	19	-1.28
6	25	1.40	14	-1.15

- (a) Use the results given in the table to plot a graph of $\log_{10} \left(\frac{1}{t} \right)$ on the y-axis against $\log_{10} (\text{volume of KI(aq)})$. Draw a straight line of best fit on the graph, ignoring any anomalous points.
- (b) Determine the gradient of the line you have drawn. Give your answer to two decimal places. Hence deduce the order of reaction with respect to iodide ions.

2.13 Sulphur dichloride dioxide, SO₂Cl₂, decomposes according to the equation: SO₂Cl₂(g) → SO₂(g) + Cl₂(g)

In an experiment, the concentration of the reactant SO₂Cl₂ was measured over a period of time. The results are shown below:

Time/s	0	500	1000	2000	3000	4000
[SO ₂ Cl ₂]/moldm ⁻³	0.50	0.43	0.37	0.27	0.20	0.15

- (a) Plot a graph to show the variation of concentration with time
- (b) Calculate the rate of reaction initially
- (c) Calculate the rate of reaction when [SO₂Cl₂] = 0.5 moldm⁻³ and hence deduce the order of reaction
- (d) Calculate the first and second half-lives of the reaction and hence deduce the order of reaction

2.14 Hydrogen peroxide, H₂O₂, decomposes according to the equation: 2H₂O₂(g) → 2H₂O(g) + O₂(g)

In an experiment, the concentration of the reactant H₂O₂ was measured over a period of time. The results are shown below:

Time/s	0	15	30	60	100	180
[H ₂ O ₂]/moldm ⁻³	0.40	0.28	0.19	0.07	0.03	0.01

- (a) Plot a graph to show the variation of concentration with time
- (b) Calculate the rate of reaction initially
- (c) Calculate the rate of reaction when [SO₂Cl₂] = 0.2 moldm⁻³ and hence deduce the order of reaction
- (d) Calculate the first and second half-lives of the reaction and hence deduce the order of reaction

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

- 2.15** Consider the reaction: $\text{BrO}_3^- + 6\text{H}^+ + 6\text{Br}^- \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$
The rate equation for this reaction is: $\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$
Give two reasons why you can tell that this reaction involves more than one step.
- 2.16** Consider the following reaction: $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$
The rate equation for the reaction is: $\text{rate} = k[\text{NO}_2]^2$
(a) Suggest a likely rate determining step for the reaction.
(b) Hence suggest a two-step mechanism for this reaction.
- 2.17** The reaction $\text{X} + \text{Y} \rightarrow \text{W}$ proceeds according to the following mechanism:
Step 1: $2\text{X} \rightarrow \text{Z}$ (slow)
Step 2: $\text{Z} + \text{Y} \rightarrow \text{W} + \text{X}$ (fast)
Show that these two steps are consistent with the overall equation and suggest a rate equation for this reaction.
- 2.18** The reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ has the following rate equation: $\text{rate} = k[\text{NO}]^2$.
Suggest a two-step mechanism for the reaction
- 2.19** It takes approximately 3 minutes to boil an egg at sea level, where the boiling point of water is 100 °C. At an altitude of 5000 m, water boils at 95 °C and it takes 30 minutes to boil an egg. What is the activation energy of the egg boiling process?
- 2.20** A reaction with an activation energy of 100 kJmol^{-1} takes 10 minutes to complete at 25 °C
(a) How long will the reaction take at 35 °C?
(b) How long will the reaction take at 25 °C if a catalyst is added which reduces the activation energy to 95 kJmol^{-1} ?

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

3.1 Draw the conventional representation of the electrochemical cells to show how you would use the following feasible reactions to make electricity:

- (a) $\text{Fe(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Cu(s)}$
 (b) $\text{Fe}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$
 (c) $\text{Zn(s)} + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(l)}$

3.2 Use the following data to deduce the chemical reaction taking place in the cells below, and calculate the emf of each cell:

Half-reaction	E/V
$\text{Zn}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Zn(s)}$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Fe(s)}$	-0.44
$\text{Fe}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Ag}^{+}(\text{aq}) + \text{e} \rightarrow \text{Ag(s)}$	+0.80
$\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^{-}(\text{aq})$	+1.36

- (a) $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt}$
 (b) $\text{Fe} \mid \text{Fe}^{2+} \parallel \text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt}$
 (c) $\text{Ag} \mid \text{Ag}^{+} \parallel \text{Cl}_2, \text{Cl}^{-} \mid \text{Pt}$

3.3 Draw a labelled diagram to show how you would measure the standard electrode potential of the $\text{Fe}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Fe}^{2+}(\text{aq})$ half-reaction.

3.4 Use the Nernst equation to deduce the electrode potentials of the following half-cells:

- (a) $\text{Zn}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Zn(s)}$ when $[\text{Zn}^{2+}] = 0.05 \text{ mol dm}^{-3}$
 (b) $\text{Ag}^{+}(\text{aq}) + \text{e} \rightarrow \text{Ag(s)}$ when $[\text{Ag}^{+}] = 0.01 \text{ mol dm}^{-3}$
 (c) $\text{Fe}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Fe}^{2+}(\text{aq})$ when $[\text{Fe}^{3+}] = 1.5 \text{ mol dm}^{-3}$ and $[\text{Fe}^{2+}] = 0.1 \text{ mol dm}^{-3}$

3.5 Predict how the electrode potentials of the $\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^{-}(\text{aq})$ ($E^{\circ} = +1.36 \text{ V}$) and $2\text{H}^{+}(\text{aq}) + 2\text{e} \rightarrow \text{H}_2(\text{g})$ ($E^{\circ} = +0.00 \text{ V}$) when the gas pressures are increased in each half-cell.

CHEM 121 – INTRODUCTION TO KINETICS AND THERMODYNAMICS

3.6 Consider the following electrochemical data:

Half-equation	E°/V
$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	-0.14
$2H^+(aq) + 2e \rightarrow H_2(g)$	0.00
$Cu^{2+}(aq) + e \rightarrow Cu^+(aq)$	+0.15
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	+0.34
$Cu^+(aq) + e \rightarrow Cu(s)$	+0.52
$I_2(aq) + 2e \rightarrow 2I^-(aq)$	+0.54
$2H^+(aq) + O_2(g) + 2e \rightarrow H_2O_2(aq)$	+0.68
$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e \rightarrow Ag(s)$	+0.80
$NO_3^-(aq) + 2H^+(aq) + e \rightarrow NO_2(g) + H_2O(l)$	+0.81
$Br_2(aq) + 2e \rightarrow 2Br^-(aq)$	+1.09
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$H_2O_2(aq) + 2H^+(aq) + 2e \rightarrow 2H_2O(l)$	+1.77
$Ag^+(aq) + e \rightarrow Ag(s)$	+1.98

- (a) Use the data above to determine whether the following reactions will proceed under standard conditions:
- $Ag^+(aq) + Fe^{2+}(aq) \rightarrow Ag(s) + Fe^{3+}(aq)$
 - $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$
 - $Cu(s) + Pb^{2+}(aq) \rightarrow Cu^{2+}(aq) + Pb(s)$
 - $2Fe^{3+}(aq) + 2Br^-(aq) \rightarrow 2Fe^{2+}(aq) + Br_2(aq)$
 - $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$
- (b) Use the data above to suggest a possible reaction which might take place between the reactants below, and determine whether the reaction will be feasible under standard conditions:
- Pb with hydrochloric acid
 - Cu with hydrochloric acid
 - Cu with nitric acid
 - $CrCl_3(aq)$ with $CuSO_4(aq)$
 - $Fe_2(SO_4)_3(aq)$ with $KI(aq)$
 - $AgNO_3(aq)$ with itself
 - $H_2O_2(aq)$ with itself
- (c) Suggest why there is no apparent reaction when lead and nitric acid are mixed under standard conditions.
- (d) Calculate the free energy change for the reaction in (a) (iii)
- (e) Write an expression for the equilibrium constant K_c in (a) (iii) and calculate its value under standard conditions.