

INTRODUCTORY CHEMISTRY I

CHM 101

INTRODUCTION

PROF. E. A. OLUYEMI

TOPIC: INTRODUCTION

- COURSE DISCRIPTION:
- Methods of Science:
- Measurement and Precision
- Significant figures
- Errors in quantitative measurements
- Nature of matter
- Elements and compounds
- Types of reactions

Introduction

- What is Chemistry?
- It is the study of Matter
- Chemistry is the science that deals with the characteristics properties of a substance that can be measured and the changes it undergoes.
- Chemistry is largely an experimental science that deals with things that can be measured.

Measurements and Precision

- What is measurement?
- Measurement is the comparison of a physical quantity with a unit (of measurement) or a standard.
- A complete measurement is made up of three parts namely: (1). Figure (2) Unit and (3). Uncertainty

Units

- For measurement in the laboratory, S.I. units are adopted and there are a number of common devices available for measurement.
- Note: No measurement is complete without a unit.

Examples of units

Basic Quantity	Device	Unit	Symbol
Length	Meter Rule	Metre	M
Mass	Chemical balance	Kilogram	kg
Weight	Spring Balance	Newton	N
Electric current	Ammeter	ampere	A
Time	Stop clock, watch	Second	s
Temperature	Thermometer	Kelvin Degree Celcius	K °C

Volume	Volumetric flask, Burette, Pipette, Measuring cylinder	Centimeter cube	Cm ³
Area	Square of length	squared metre	M ²
Concentration		Molar; Moles/Volume	M, mole/dm ³
Density		Mass/Volume	g/cm ³
Pressure		Force/unit area	kg/(m.s ²)

Multiplicity of base units

Prefix	Multiplicity	Symbol
Kilo	10^3	k
Mega	10^6	M
Giga	10^9	G
deci	10^{-1}	d
Centi-	10^{-2}	c
milli	10^{-3}	m
Micro	10^{-6}	μ
nano	10^{-9}	n
pico	10^{-12}	p

Figures

- Significant Figures: The number of digits reported for the value of a measurement or calculated.
- The numbers recorded in a measurement are called significant figures.
- Example: $1.86\text{kg} = 3 \text{ s.f.}$ $35.639 = 5 \text{ s.f.}$

Rules for counting significant figures:

- All non-zero integers are counted as significant figures: e.g. 1457, 9.12,
- All digits are significant except zeros at the beginning of the number.
- Zeros:
 - (a) **All leading zeros** i.e. zeros that precede all the non-zero digits are not significant, so they are not counted. 9.12; 0.912; 0.00192, all are 3 s.f.
 - (b) Captive Zeros: These are zeros that fall between non-zero digits.
They are always counted as significant figures. e.g. 1.008 has 4 s.f.
 - (c) Zeros at the right end of a number may or may not be significant.
They are significant if the number is written with a decimal point
- 100 = 1 s.f.; 9.00 = 3 s.f. 100. = 3 s.f.
- Exact numbers – Numbers obtained by counting. They are not obtained by measuring device. e.g. 10 experiments, 1 in = 2.54 cm. They are assumed to have unlimited number of significant figures

Use of Significant figures in calculation

- For Multiplication and Division
- The number of significant figures in the result must be the same as the number of significant figure in the measurement with the least number of significant figures:

$$\text{e.g. } 4.56 \times 1.4 = 6.384 \approx 6.4 - 2 \text{ s.f.}$$

$$= 0.0279027 \Rightarrow 0.0279 \text{ or } 2.79 \times 10^{-2}$$

- In addition and subtraction.

Use the number of decimal places in calculation.

The answer should contain the number of decimal places as the figure with the least number of decimal places.

$$\text{e.g. } 12.11 + 18.0 + 1.013 = 31.123 \Rightarrow 31.1 \text{ to 1 decimal place}$$

Uncertainties in Measurements

- If a particular measurement is repeated, you may not obtain precisely the same result because each measurement is subject to experimental error.
- If you perform a series of identical measurements of a quantity, the closeness of a set of values obtained is termed **Precision**. e.g. titre value: 25.05, 25.10, 25.00, 25.01, 24.95, 25.90.
- **Accuracy:** is the closeness of a single measurement to its true value.

Errors in Measurements

- Repetitions of a scientific measurement under controlled condition generally do not give identical results.
- Deviation from the correct value is termed errors in measurement.
- Measurements are accompanied by two kinds of errors:
- **Determinate errors** – also called Systematic errors: These vary from one measurement to another. They are due to biases in the measuring procedures
- They can be accounted for or minimized.
- **Indeterminate Errors** – also called Random Errors. These are caused by variability inherent in the process of making measurements.

Features of Determinate and Indeterminate errors

Determinate Errors	Indeterminate Errors
1. Sources of error can be traced or determined	Sources of error cannot be traced or determined
2. Errors can be avoided or compensated for	The error cannot be avoided
3. The error is either constant or systematic and therefore predictable	The errors are random (i.e. small difference) and are not predictable.

Minimisation of Determinate Error

1. Calibration of apparatus and application of corrections
2. Running of a blank determination
3. Running of a control determination
4. Use of independent method of analysis
5. Running parallel determinations
6. Use of standard addition techniques
7. Use of internal standard techniques
8. Isotopic dilution

MATTER

Definition and States of Matter

- Anything that has mass and can occupy a space.
- There are three (3) states of matter:
- **Solid:** Characterised by rigidity, relatively incompressible and has a fixed shape and volume.
e.g. Ice cube, iron bar, etc.
- **Liquid:** Relatively incompressible fluid. Has fixed volume but no fixed shape. e.g. water, gasoline etc.
- **Gas:** Easily compressible fluid. A gas will fill its container or almost any size and shape. e.g. air, oxygen, helium, etc.

Mixtures and Pure Substances.

- Virtually all the matter around us consists of mixtures of substances or Pure substances.
e.g. air, soil, etc.
- **Pure Substance:** Always have the same composition. They are either elements or compounds.

Elements, Compounds and Mixtures

- An **Element** is a substance that cannot be decomposed by any chemical reaction into simpler substances.
-
- A **Compound** is a substance composed of 2 or more elements chemically combined together.
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- **Mixtures:** A mixture is a material that can be separated by physical means into 2 or more substances.
- They are classified into 2 types:
- A Heterogeneous mixture and A Homogeneous mixture

A homogeneous mixture

- A **homogeneous mixture** (also called solution) is a mixture that is uniform in its properties throughout the given sample.
- Example: when a salt (solute) is dissolved in water and stir well. All parts of the resulting mixture have the same properties.
- Homogeneous mixtures are called solutions.
- When a solid substance dissolve in a liquid substance:
- The solid is called SOLUTE, e.g. NaCl
- The liquid is called SOLVENT e.g. H₂O.
- NaCl(s) + H₂O(l) -----? NaCl(aq)
- *Solute solvent* *solution*

Heterogeneous mixture

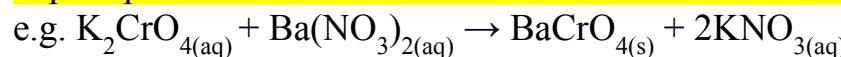
- **Heterogeneous mixture:** This contains regions that have different properties from those of other regions.
- Example: sand in water, concrete, etc.

Extensive and Intensive Properties

- All properties of matter are either extensive or intensive as well as physical and chemical properties.
- Intensive and extensive properties are types of physical properties of matter.
- **Extensive Properties:** These depend on the amount of matter being measured. e,g. Mass, volume, size, weight, length etc.
- **Intensive properties:** These do not depend on the amount f matter. e.g. density, colour, temperature, boiling point, hardness, refractive index, etc.
- The ratio between two extensive properties is an intensive property. Such as:
- Mass and volume.
- Density = $\frac{M}{V}$

Stoichiometry of Precipitation Reactions

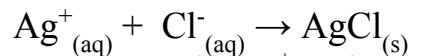
A precipitation reaction is one in which an insoluble substance is formed when two solutions are mixed.



Example

Calculate the mass of solid NaCl that must be added to 1.50 L of a 0.100 M AgNO_3 solution to precipitate all the Ag^+ ions in the form of AgCl [NaCl = 58.5]

Solution



Reaction ratio $\text{Ag}^+ : \text{Cl}^- = 1:1$

Thus, $n_{\text{AgNO}_3} = n_{\text{NaCl}} = 0.100 \times 1.50 = 0.150$ mole

But mass = number of moles x molar mass

i.e. mass = $0.150 \times 58.5 = 8.78$ g NaCl

Exercise

- When aqueous solutions of Na_2SO_4 and $\text{Pb}(\text{NO}_3)_2$ are mixed, PbSO_4 precipitates. Calculate the mass of PbSO_4 formed when 1.25 of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ and 2.00 L of 0.0250 M Na_2O_4 are mixed. [$\text{PbSO}_4 = 303.3$].
- 0.254 g of lead(II) ethanoate, on adding excess K_2CrO_4 solution, gave 0.130 g of lead(II) chromate precipitate. What is the percentage composition of Pb in the organic salt? [O = 16, Cr = 52, Pb = 207].
- 5.43 g sample of a pure salt, M_2SO_4 , was dissolved in water. The ion was precipitated by adding excess BaCl_2 solution when 4.67 g BaSO_4 was obtained. How many moles of were precipitated? Determine the molecular mass of M_2SO_4 , and hence, the atomic mass of M. [O = 16, S = 32, Ba = 137.3].
- A solution of ammonium Sulphate fertilizer was to be applied to the soil before planting some seeds. A given volume of water was put in a large container and 3.68 kg of fertilizer was dissolved in it. On analysis, 0.28 dm^3 of 0.35 mol dm^{-3} barium chloride was required to precipitate all the sulphate in 0.20 dm^3 of solution. What was the volume of the solution in the container? [H = 1, N = 14, O = 16, S = 32]

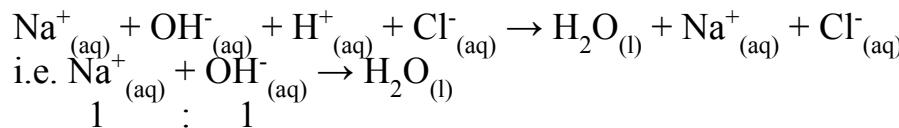
Acid-Base Stoichiometry

In acid-base stoichiometry, calculations involving neutralization reactions are dealt with.

Example

What volume of a 0.100 M HCl solution is needed to neutralize 25.0 mL of a 0.350 M NaOH solution?

Solution:



Now, n_{OH^-} in 25.0 mL of 0.350 M NaOH solution is:

$$25.0 \text{ mL} \times 1 \text{ L}/1000 \text{ mL} \times 0.350 \text{ mol OH}^-/\text{L NaOH} = 8.75 \times 10^{-3} \text{ mol OH}^-$$

Since the reaction occurs in a 1:1 ratio

$$n_{\text{OH}^-} = n_{\text{H}^+} = 8.75 \times 10^{-3} \text{ mol H}^+$$

The volume (V) of 0.100 M HCl required to furnish this amount of H⁺ ions is

$$V \times 0.100 \text{ mol H}^+/\text{L} = 8.75 \times 10^{-3} \text{ mol H}^+$$

$$\text{i.e. } V = 8.75 \times 10^{-3} \text{ mol H}^+ \times \text{L}/0.100 \text{ mol H}^+ = 8.75 \times 10^{-2} \text{ L} = 87.5 \text{ mL}$$

Note: The same result can be obtained from: $C_A V_A / C_B V_B = n_A / n_B$

Exercise:

1. In an experiment, 28.0 mL of 0.250 M HNO₃ and 53.0 mL of 0.320 M KOH are mixed. Calculate the amount of water formed in the resulting reaction. What is the concentration of H⁺ or OH⁻ ions in excess after the reaction goes to completion?
2. A student needed to standardize a solution of Ba(OH)₂. He prepared his standard solution with 0.200 g of potassium hydrogen phthalate acid, KHC₈H₄O₄. His titration indicated equivalence at 27.80 cm³ of Ba(OH)₂ solution. What is the molar concentration of the base? [KHC₈H₄O₄ = 204.2]
3. Aspirin tablet contains acetylsalicylic acid, C₉H₈O₄. Each tablet contains approximately 0.32 g of the acid. If 25.0 cm³ of Ca(OH)₂ is required for complete neutralization of the acid content in a tablet, what is the molar concentration of the base?
4. Backing soda, NaHCO₃, and milk of magnesia, Mg(OH)₂, are both used as antacids to neutralize excess HCl secreted in the stomach. Which of the antacids is more effective? [NaHCO₃ = 84.01; Mg(OH)₂ = 58.32]

Stoichiometry Involving Redox Reactions

A redox (Oxidation-Reduction) reaction involves transferring of electrons between reacting species or change of oxidation states of the atoms involved in the reaction. Customarily, the equation of the reaction has to be balanced before any meaningful calculations can be done.

Example

A 25.0 cm^{-3} portion of sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$, solution of concentration 0.30M is warmed and titrated against an acidified solution of KMnO_4 . If 45 cm^3 of KMnO_4 solution is required for the titration, determine the concentration of the KMnO_4 in (a) mol dm^{-3} ; (b) g dm^{-3} . [$\text{O} = 16$, $\text{K} = 39$, $\text{Mn} = 54.9$]



Solution

$$n_{\text{C}_2\text{O}_4^{2-}} = 25 \times 10^{-3} \times 0.3 = 7.5 \times 10^{-3} \text{ mol}$$



$$\text{From the balanced equation: } n_{\text{MnO}_4^-}/n_{\text{C}_2\text{O}_4^{2-}} = 2/5$$

$$\therefore n_{\text{MnO}_4^-} = 2/5 \times 7.5 \times 10^{-3} = 3.0 \times 10^{-3} \text{ mol}$$

(a) From: $n = CV$,

$$3.0 \times 10^{-3} = C \times 45 \times 10^{-3}$$

$$\text{Making C the subject of the formula gives } C = 3.0 \times 10^{-3} / 45 \times 10^{-3} = 0.067 \text{ mol dm}^{-3}$$

$$\begin{aligned}(\text{b}) \text{ g dm}^{-3} &= \text{mol dm}^{-3} \times \text{molar mass} \\&= 0.067 \times 157.9 = 10.58 \text{ g dm}^{-3}\end{aligned}$$

Exercise

What volume (mL) of 0.500 M KMnO_4 solution will react completely with 20.00 g of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ according to the ff equation? $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$.

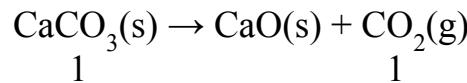
Gas Stoichiometry

In chemical reactions, gases are sometimes evolved. Very often, a Chemist can use information from the masses of substances reacting or those of the products some of which may be gaseous to solve chemical problems.

Example

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate (CaCO₃). Calculate the volume of CO₂ produced at s.t.p. from the decomposition of 152 g of CaCO₃ [CaCO₃ = 100.1; GMV a gas at s.t.p = 22.42 L]

Solution



$$n_{\text{CaCO}_3} = n_{\text{CO}_2}$$

$$\text{Now, } 152 \text{ g CaCO}_3 \times 1 \text{ mol CaCO}_3 / 100.1 \text{ g CaCO}_3 = 1.52 \text{ mol CaCO}_3$$

Thus, nCO₂ produced is also 1.52 mol.

At s.t.p., volume of 1.52 mol CO₂ is



$$1.52 \text{ mol CO}_2 \times 22.42 \text{ L/mol CO}_2 = 34.1 \text{ L CO}_2$$

Exercise

1. Consider the following chemical equation: $2\text{NO}_{2(\text{g})} \rightarrow \text{N}_2\text{O}_{4(\text{g})}$.

If 25.0 mL of NO₂ is completely converted to N₂O₄ gas under the same conditions, what volume will the N₂O₄ occupy?

2. How much CO is produced from the reaction of 1.0 kg of octane, C₈H₁₈, and 1.0 kg of oxygen? [H=1, C=12, O = 16].

Hint: $2\text{C}_8\text{H}_{18} + 17\text{O}_2 \rightarrow 16\text{CO} + 18\text{H}_2\text{O}$.

Combustion Stoichiometry

Combustion is a chemical process in which substances combine with the oxygen in the air to produce heat and light. Substances undergoing combustion could be solids (e.g. coal) or liquids (e.g. petrol) or gases (e.g. butane). Sometimes, a combination of substances undergoes combustion simultaneously. With adequate data collected, it is possible to determine the various amounts of combustible materials participating in the combustion process.

Example

When 2.86 g of a mixture of 1-butene, C_4H_8 , and butane, C_4H_{10} , was burned in excess oxygen, 8.80 g of CO_2 and 4.14 g of H_2O were obtained. Calculate the percentage by mass of butane in the original mixture.

Solution:

$$n_{CO_2} = \frac{8.80}{44.0} = 0.200 \text{ mol } CO_2$$

$$n_{H_2O} = \frac{4.14}{18.0} = 0.230 \text{ mol } H_2O$$

Thus, we have 0.200 mol of C and 0.460 mol of H atoms.

Let x be the number of moles of C_4H_8 and y be the number of moles of C_4H_{10} .

Then, for C: $4x + 4y = 0.200$ ----- (1)

and for H: $8x + 10y = 0.460$ ----- (2)

Eq. (1) x 2: $8x + 8y = 0.400$ ----- (3)

Eq. (2) – Eq. (3): $2y = 0.060$

$\therefore y = 0.030 \text{ mol of } C_4H_{10}$

Substituting for y in Eq. (3) gives:

$$8x + 8(0.030) = 0.400$$

$$\text{i.e. } 8x + 0.240 = 0.400$$

$$\text{i.e. } 8x = 0.400 - 0.240 = 0.160$$

$$\therefore x = 0.020 \text{ mol } C_4H_8$$

Now, Mass _{C_4H_{10}} in the mixture = $0.030 \times 58 \text{ g} = 1.74 \text{ g } C_4H_{10}$

and Mass _{C_4H_8} in the mixture = $0.020 \times 56 \text{ g} = 1.12 \text{ g } C_4H_8$

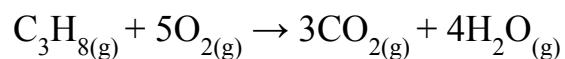
$$\text{Total} = 2.86 \text{ g}$$

$$\%C_4H_8 = \frac{1.12}{2.86} \times 100 = 39.2\%$$

$$\text{Hence, \% } C_4H_{10} = (100.0 - 39.2) = 60.8$$

2. What mass of oxygen is required to make 96.1 g of propane undergo complete combustion? [H = 1, C = 12, O = 16]

Solution:



$$\text{Now, } n_{\text{C}_3\text{H}_8} = 96.1/44 = 2.18 \text{ mol C}_3\text{H}_8$$

From the balanced equation, 5 moles of O₂ ≡ 1 mole of C₃H₈

$$\therefore \text{No. required} = 2.18 \text{ mol C}_3\text{H}_8 \times 5 \text{ mol O}_2 / 1 \text{ mol C}_3\text{H}_8 = 10.9 \text{ mol O}_2$$

$$\therefore \text{Mass of O}_2 \text{ required} = 10.9 \times 32 \text{ g} = 349 \text{ g O}_2$$

Percentage Yield

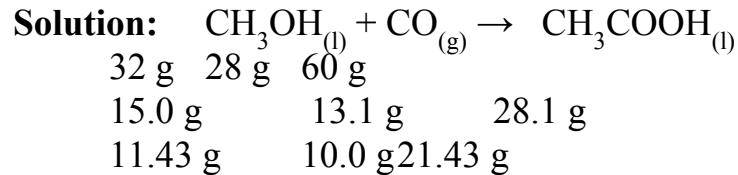
To determine the percentage yield of a reaction, the theoretical yield and the actual yield of the product must be established. The theoretical yield of a product is the maximum amount of the product that can be obtained by a reaction from given amounts of reactants; it is calculated from the stoichiometry of the reaction based on the limiting reagent. On the other hand, the actual yield of a product is the quantity of the product experimentally obtained.

Thus, percentage yield = (Actual yield/theoretical yield) × 100



Example:

In an experiment to produce acetic acid (CH₃COOH), 15.0 g of methanol (CH₃OH) and 10.0 g of carbon monoxide (CO) were placed in a reaction vessel in which case 19.1 g of acetic acid was obtained. (a) What is the theoretical yield of acetic acid? (b) What is the percentage yield of acetic acid? [H = 1, C = 12, O = 16]



Obviously from the computed table above, theoretically, 15.0 g CH₃OH requires 13.1 g CO, whereas only 10.0 g CO is available for the reaction. Hence, CO is the limiting reagent. Now, 10.0 g CO would require 11.43 g CH₃OH to give a theoretical yield of 21.43 g CH₃COOH.

$$\therefore \% \text{yield} = (\text{actual yield}/\text{theoretical yield}) \times 100 = (19.1/21.43) \times 100 = 89.1\%$$

P.T.O.

Exercise

1. Acetic acid can be produced by bubbling oxygen into acetaldehyde containing manganese(II) acetate under pressure at 60°C: $2\text{CH}_3\text{CHO}_{(\text{l})} + \text{O}_{2(\text{g})} \rightarrow 2\text{CH}_3\text{COOH}_{(\text{l})}$. If 20.0 g CH_3CHO and 10.0 g O_2 were put into a reaction vessel, how many grams of acetic acid will be produced? Assuming the actual yield of the acetic acid obtained in this experiment is 23.8 g, determine the percentage yield of acetic acid.
2. Boric acid, H_3BO_3 , can be produced by mixing water with diborane, B_2H_6 ; hydrogen is the other product. $[\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2]$. If 5.24 g of diborane reacts with 19.62 g of water, (a) which reagent is in excess and by how much? (b) what weight of boric acid is produced? (c) Assuming that the actual amount of boric acid produced is 20.93 g, what is the percentage yield? [H = 1.01, B = 10.81, O = 16.00]

Empirical Formula (EF) and Molecular Formula (MF)

The EF of a compound is the formula that shows the simplest ratio in which elements in 1 molecule of the compound combine. On the other hand, the MF expresses the actual number of atoms of each element present in 1 molecule of a compound. Thus, in terms of composition by mass:

$$(EF)_n = MF$$

i.e. $n = MF/EF$

Where $n = 1, 2, 3, \dots$

For example, in the table below, it can be seen that it is possible for two entirely different compounds to have the same percentage composition by wt e.g C₂H₂ and C₆H₆ both have 92.3%C and 7.7% H respectively.

Compound	EF	MF	n
Acetylene (Ethyne)	CH	C ₂ H ₂	2
Benzene	CH	C ₆ H ₆	6
Glucose	CH ₂ O	C ₆ H ₁₂ O ₆	6 
But-1-ene	CH ₂	C ₄ H ₈	4
Ethane-1,2-diol	CH ₃ O	C ₂ H ₆ O ₂	2

Example 1

1.587 g of a compound of nitrogen and oxygen is analyzed and found to contain 0.483 g N and 1.104g O. What is the EF of the compound? [N = 14; O = 16]

Solution

	N	O
Mass (g)	0.483	1.104
Moles	$0.483/14 = 0.0345$	$1.104/16 = 0.069$
Ratio	$0.0345/0.0345 = 1$	$0.069/0.0345 = 2$

$$\therefore \text{EF} = \text{NO}_2$$



Example 2

A compound on analysis was found to contain 17.5% Na, 39.7% Cr and 42.8% O. what is the empirical formula of this compound? [O = 16; Na = 23; Cr = 52]

Solution:

	Na	Cr	O
%Composition	17.5	39.7	42.8
No. of moles	$17.5/23=0.761$	$39.7/52=0.763$	$42.8/16=2.68$
Ratio	$0.761/0.761=1$	$0.763/0.763=1$	$2.68/0.763=3.5$
	= 1 = 2	= 1 = 2	= 7/2 = 7



Thus, the EF = $\text{Na}_2\text{Cr}_2\text{O}_7$.

Note: Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$, is ionic; so it has no molecular formula.

Exercise

(1) Benzoic acid is a white crystalline powder used as a food preservative. The compound contains 68.8% C, 5.0% H and 26.2% O by mass. What is its empirical formula?

(2) On analysis, an ammonium salt of an alkanoic acid gave 60.5% C and 6.5% H. If 0.309 g of the salt yield 0.0313 g of nitrogen, determine the empirical formula of the salt. [H = 1, C = 12, N = 14, O = 16]

Obtaining MF from EF

Example

An organic compound on analysis was found to contain only C, H and O. A 4.24-mg sample of it was completely subjected to combustion analysis and gave 6.21mg of CO_2 and 2.56 mg of H_2O . What is the mass percentage of each element in the compound? What is the molecular formula of this compound given that its molar mass is 60.00 amu? [H = 1, C = 12, O = 16]

Solution:

$$44 \text{ mg } \text{CO}_2 \equiv 2 \text{ mg C}$$

$$\therefore 6.21 \text{ mg } \text{CO}_2 = (12/44) \times 6.21 \text{ mg} = 1.69 \text{ mg C}$$

Also,

$$18 \text{ mg } \text{H}_2\text{O} \equiv 2 \text{ mg H}$$

$$\therefore 2.56 \text{ mg } \text{H}_2\text{O} = (2/18) \times 2.56 \text{ mg} = 0.284 \text{ mg H}$$

$$\text{So, \%H} = (0.284/4.24) \times 100 = 6.7\% \text{ H.}$$

$$\begin{aligned}\text{Hence, mass \% O} &= 100 - (39.9 + 6.7) \\ &= 100.0 - 46.6 = 53.4\%\end{aligned}$$



Now,

	C	H	O
%Composition	39.9	6.7	53.4
Amount	$39.9/12 = 3.33$	$6.7/1 = 6.70$	$53.4/16 = 3.34$
Hence, $\text{MF} = \text{C}_n\text{H}_{2n}\text{O}_2$	$3.33/3.33 = 1$	$6.7/3.33 = 2$	$3.34/3.33 = 1$

But $(\text{EF}_2)_n = \text{MF}$

i.e. $(\text{CH}_2\text{O})_n = 60$

i.e. $(30)n = 60$

$\therefore n = 2$.

Hence, $\text{MF} = (\text{CH}_2\text{O})_2 = \text{C}_2\text{H}_4\text{O}_2$

1) Exercise

- 1) Menthol. The substance that gives odour to mentholated cough syrups, is composed of C, H, and O. A 0.1005-g sample of it is subjected to combustion analysis upon which 0.2829 g of CO₂ and 0.1159 g H₂O are produced. If the molar mass of menthol is 156 g, what are its EF and MF? [H = 1, C = 12, O = 16]
- 2) 10.0 g of hydrated calcium sulphate, CaSO₄.xH₂O, weighs 7.90 g after being heated to a constant mass. Calculate the value of water of crystallization in the hydrated salt. [H = 1, O = 16, S = 32, Ca = 40]
- 3) 0.07g of a given hydrocarbon occupies 56.0 cm³at s.t.p. when vaporized. What is the formula of the hydrocarbon given that it contains 14.29%H by mass? [H = 1, C = 12]

Further Exercise on Empirical and Molecular Formulae (19/02/2021)

4. A metallic element X with a relative atomic mass x forms two oxides P and Q. Oxide P contains 70.0% of X while Q contains 72.4% of X. If the first oxide has the formula X_2O_3 , what is the formula of the second oxide? [O = 16].

5. A non-metallic element R with relative atomic mass r forms two oxides C and D. Oxide C contains 50.0% of R, while oxide D contains 40.0%. If the formula for C is RO_2 , what is the formula for D? [O = 16].

6. What is the formula of an industrial raw material whose composition is 28.1% Fe, 35.7% Cl and 36.2% water of crystallization? [H = 1, O = 16, Cl = 35.5, Fe = 56]

7. A 4.30 g hydrated sodium Sulphate, $Na_2SO_4 \cdot nH_2O$, was heated until only its anhydrous form, Na_2SO_4 , which weighed 2.12 g was remaining. Calculate the value of n in $Na_2SO_4 \cdot nH_2O$

Oxidation and Reduction (Redox) Reactions

Generally, a redox reaction is one in which electrons are transferred between species or in which atoms change oxidation states. More specifically and depending on what happens exactly during the reaction, oxidation and reduction can be defined in a number of ways as seen in the table below:

	Oxidation	Reduction
1.	Addition of oxygen	Removal of oxygen
2.	Removal of hydrogen	Addition of hydrogen
3.	Addition of electronegative elements	Removal of electronegative elements
4.	Removal of electrons	 Addition of electrons
5.	Increase in oxidation number	Decrease in oxidation number

Oxidation Numbers

The oxidation number (o.n.) or oxidation state (o.s.) of an atom in a substance is the actual charge of the atom if it exists as a monatomic ion; it is the hypothetical charge assigned to an atom in a substance taking into account the relative electronegativities of other atoms in the substance.

Rules for Assigning Oxidation Numbers

1. The oxidation state (o.s.) of an atom of an element in an uncombined state is zero e.g. atoms in S, K, Na, Cl₂, O₂ etc have zero oxidation states.
2. The o.s. of an ion equals the charge on the ion e.g. Na⁺ = +1; Cl⁻ = -1; Al³⁺ = +3, SO₄²⁻ = -2; NH₄⁺ = +1.
3. The o.s. of some elements in their compounds are the same e.g. elements in Group I (Li, Na, K, ...) have o.s. of +1, while those in Group II (Be, Mg, Ca, ...) have o.s. of +2.
4. The o.s. of oxygen is -2 in most of its compounds; an exception is O in peroxides where the o.o. is -1 and in combination with F to form OF₂ where it has o.s. of +2. The super oxides (LiO₂, NaO₂, RbO₂) are unusual where oxygen has a fractional o.s. of -½.
5. The o.s. of hydrogen is +1 in most of its compounds except in binary compounds (metal hydrides) e.g. CaH₂ where it has -1 o.s.
6. The o.s. of F is -1 in all of its compound; each of the other halogens (Cl, Br, I) has o.s. of -1 in binary compounds, except when the other element is another halogen above it in the Periodic Table or the other element is oxygen.
7. The algebraic sum of o.s. of all atoms in a neutral molecule (e.g. KMnO₄, Na₂CO₃, Na₂Cr₂O₇, etc) is zero.
8. In a complex ion, the algebraic sum of o.s. of all the atoms is equal to the charge on the ion e.g. Cr₂O₇²⁻ = -2



NOTE:

1. Some elements have the capacities of exhibiting several o.s. For example, S in H₂S, S, SCl₂, H₂SO₃ and H₂SO₄ has o.s. of -2, 0, +2, +4 and +6 respectively, while Cl has o.s. of -2, +1, +4, +5 and +7 respectively in HCl, Cl₂O₇, ClO₂, KClO₃ and KClO₄.
2. The same element in a compound can have different o.s. For example, N in NH₄NO₃ has -3 and +5 o.s., while Fe in Fe₃O₄ (i.e. Fe^{II}Fe₂^{III}O₄).
3. Oxidation numbers (other than zero) are always written as directed numbers.

Example:

Calculate the oxidation number of (a) Mn in KMnO_4 and (b) Cr in $\text{Cr}_2\text{O}_7^{2-}$ [K = +1, O = -2]

Solution

$$(a) \text{KMnO}_4 = 0$$

$$\text{i.e. K} + \text{Mn} + 4(\text{O}) = 0$$

$$\text{i.e. } +1 + \text{Mn} + 4(-2) = 0$$

$$\therefore \text{Mn} = +7$$

$$(b) \text{Cr}_2\text{O}_7^{2-} = -2$$

$$\text{i.e. } 2\text{Cr} + 7(\text{O}) = -2$$



$$\text{i.e. } 2\text{Cr} + 7(-2) = -2$$

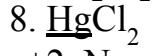
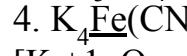
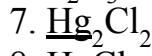
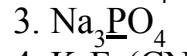
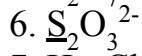
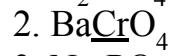
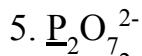
$$\text{i.e. } 2\text{Cr} - 14 = -2$$

$$\Rightarrow 2\text{Cr} = +12$$

$$\therefore \text{Cr} = +6$$

Exercise

Determine the oxidation number(s) of the underlined elements in the following compounds or ions:



[K = +1, O = -2, Ba = +2, Na = +1, CN^- = -1, Cl = -1]

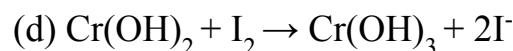
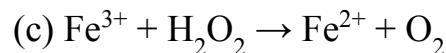
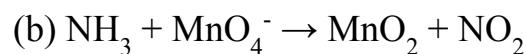
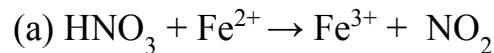
Balancing Simple Oxidation–Reduction (Redox) Equations

Redox reactions do not deviate from the law of conservation of matter. Just as atoms are neither created nor destroyed in a chemical reaction, so also, charges are conserved in a redox reaction.

Sometimes, the medium (acid solution or basic solution) in which the redox reaction is taking place is not explicitly stated. If an acid or base is one of the reactants or products, the solution or medium is the same. If ammonia is present, it is acidic. If metals which would form insoluble hydroxides are shown in their ionic form, the solution is acidic.

Example

State whether each of the following equations should be balanced in acid or basic solution:



Methods used in Balancing Redox Equations

There are many ways to balance redox equations systematically but the two most commonly used are:

(A) Half-cell Reaction (Ion-Electron) Method

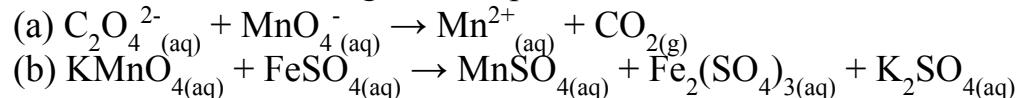
(B) Oxidation-State Method

(A) Balancing Redox Equations Using Half-Cell Reaction Method

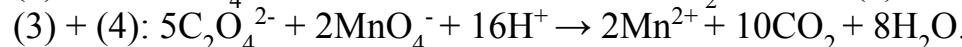
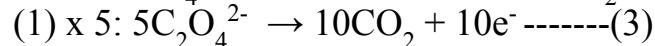
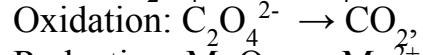
1. Write down the half-equations to show the species reduced or oxidized and the products formed.
2. Balance all atoms (except oxygen) on the LHS and RHS of the half-equations.
3. For reactions taking place in an acidic medium, determine the difference in the number of oxygen atom present on the left and right hand sides of the half-equations; represent the difference in oxygen with H_2O on the side with minimum oxygen atom and balance up with H^+ on the other side.
4. For reactions taking place in an alkaline medium, represent the difference in oxygen atoms with H_2O on the side with the maximum oxygen atom and balance up with OH^- on the other side.
5. Balance with respect to charges by adding an appropriate number of electrons.
6. Balance the half-equations such that the number of electrons lost equals the number of electrons gained.
7. Add the half-equations together cancelling out species that appear unchanged on both sides of the equation.

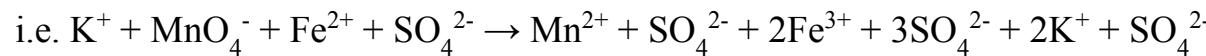
Example I

1. Balance the following redox equations/reactions in acidic solution:

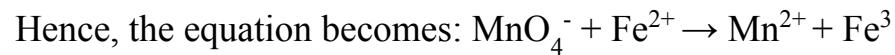


Solution:

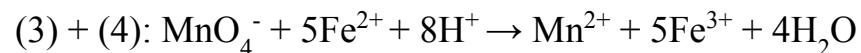
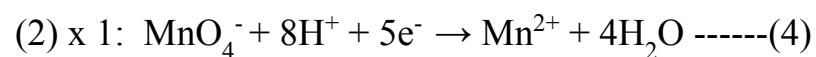
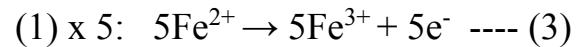
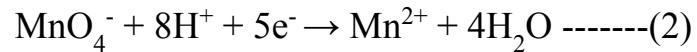
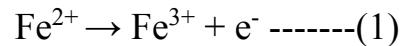




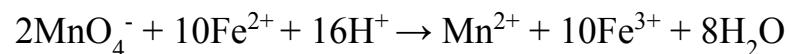
Thus, K^+ and SO_4^{2-} are spectator ions.



Now,

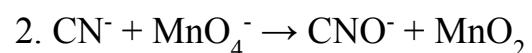
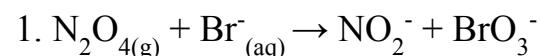


Written in terms of the original equation, we have:

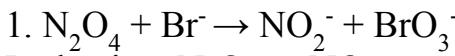


Example II

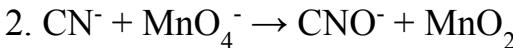
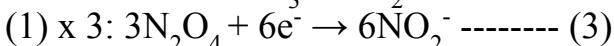
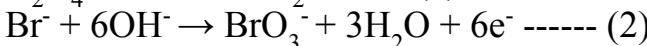
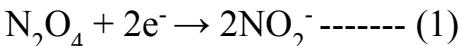
Balance the following redox reactions in a basic medium



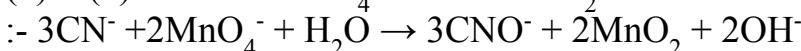
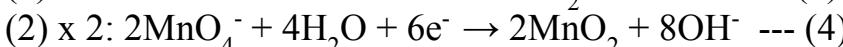
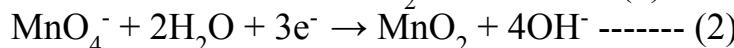
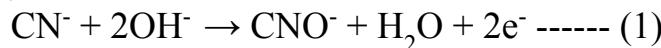
Solution



Now,

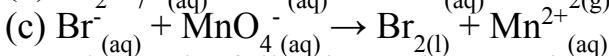
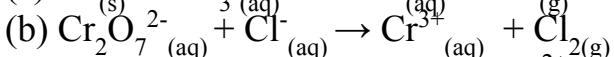
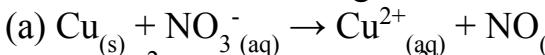


Now,

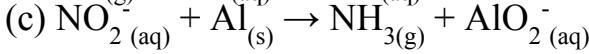
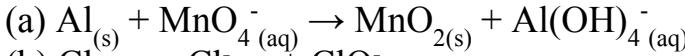


Exercise

1. Balance the following redox reactions in acidic medium using the half-reaction method



2. Balance the following redox reactions in basic solution using the half-reaction method

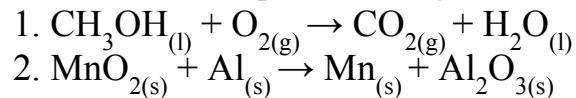


(B) Balancing Redox Equations Using Oxidation-state Method

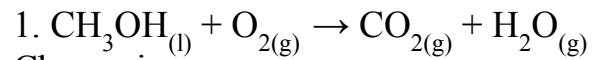
1. Assign the oxidation state of all atoms.
2. Decide which element is oxidized and determine the increase in oxidation state.
3. Decide which element is reduced and determine the decrease in oxidation state.
4. Choose coefficients for the species containing the atom oxidized and the atom reduced such that the total increase in oxidation state equals the total decrease in oxidation state.
5. Balance the remainder of the equation by inspection.

Example

Balance the ff equation using oxidation state method



Solution:



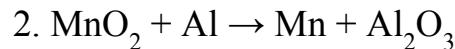
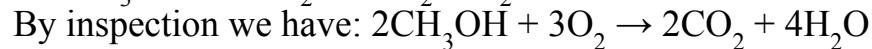
Change in o.s.

C = +4 - 2 = +6; increase in o.s. = oxidation

O = -2 - 0 = -2; decrease in o.s. = reduction

6:2 = 3:1

So 3 oxygen atoms are needed to balance the increase in O. S. of 1 carbon atom.



Change in o.s.

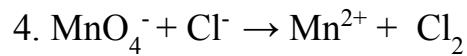
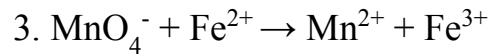
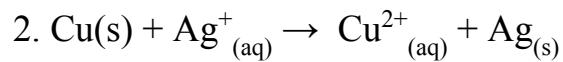
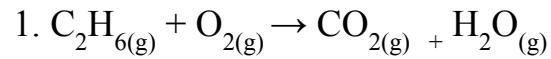
Mn: 0 - +4 = -4; decrease in o.s. = reduction

Al: +3 - 0 = +3; increase in o.s. = oxidation



Exercise

Balance the following redox reactions using o.s. method



ATOMIC THEORY AND NATURE OF ATOMS

Suggested Text Books

- Advanced Chemistry by Philip Mathew. Cambridge University Press
- Chemistry by Steven S. Zumdahl and Susan A. Zumdahl 7th Edition Houghton Mifflin Company, Boston NY

DEFINITIONS

Atomic Theory: Is the conception that elements are made up of atoms. It is a **theory** that states that **matter** is composed of particles called **atoms**

Atoms: Are the building blocks of which all the matter in the universe is made up of.

Matter: Matter is defined as anything that has weight and occupies space. Matter: is made up of atoms. There are three states of matter, they are solids, liquids and gases.

A scientific theory: is an idea suggested by a scientist in scientific book or journal and is generally accepted by other scientists after due considerations, verifications and explanations.

Historical Development of atoms

The ideas about atoms dated back to the period of ancient Greek philosophers in the 5th Century BC. For years, philosophers debated the question of whether matter is continuous or discontinuous and are therefore made up of particles. Democritus and Leucippus Greek philosophers speculated that matter is made up of discrete indivisible particles of called atoms.

In about 1808, John Dalton tried to give some explanations about the atoms by putting forward some ideas which were called Dalton Atomic Theory. The central feature of Dalton Atomic Theory was that an atom is indivisible particle.

Later on twelve (12) other scientists such as: Faraday, Davy, William Crookes, JJ Thompson, Robert Millikan, Ernest Rutherford, James Chadwick, Henry Moseley, Niels Bohr, de-Broglie, Heisenberg and Erwin Schrodinger provided scientific experimental evidences

and information that fitted into a model of atomic structure. Their findings brought about other discoveries about the atom which will be considered one after the other.

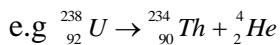
I. Dalton Atomic Theory: John Dalton was the first scientist to propose the first modern atomic theory. He made five proposals as follows:

- i. All matter are made up of small tiny particles called atoms that are indivisible and indestructible (particulate nature of matter)
- ii. All atoms of the same element are identical having the same mass, volume, chemical properties etc.
- iii. Atoms of different elements have different weights, volume, chemical properties etc.
- iv. Chemical combination takes place between atoms of different elements in simple whole numbers to form compounds.
- v. Atoms cannot be created.

MODIFICATION TO DALTON'S ATOMIC THEORY IN THE LIGHT OF MODERN CHEMISTRY

- a. **Atoms are indivisible;** This is no longer true because atoms are now divisible into sub-atomic particles called electrons, protons and neutrons.
- b. **Atoms are indestructible and cannot be created:** This is no longer true in the light of nuclear reaction where atoms are destroyed and new ones created. New atoms

$^{234}_{90} Th$, $^4_2 He$ are formed from radioactive decay of $^{238}_{92} U$ in the nuclear reaction below:



- c. **The atoms of a particular element are all exactly alike/identical:** This is no longer true in the light of Isotopy where atoms of a particular element can have different atomic masses
 $^{35} Cl$ and $^{37} Cl$ have different atomic masses 35 and 37 respectively.

- d. **Chemical combination takes place between small whole numbers of atoms:** This is no longer valid in the light of organic chemistry where molecules are more complex.

INVESTIGATION INTO THE STRUCTURE OF THE ATOM

Generally, Dalton regarded the atom as homogenous sphere having no electrons, protons and neutrons. His idea was proved wrong by various experiments carried out by different Scientists.

It has been proved that there are many sub-atomic particles and new ones are being discovered and/or predicted: The three main basic sub-atomic particles of great importance are Protons, Neutrons and Electrons as presented in the table below. A positron (with symbol ${}_{+1}^0 e$) has also been discovered as a positively charged electron which shows up in the course of some nuclear reactions.

Table: Values of the symbol, charge and mass of electrons, protons and neutron

Sub-atomic particles	Discovery	Symbol	Mass (kg)	Charge(c)	Ratio of masses
Electrons	Crooke J.J. Thompson (1897)	${}_{-1}^0 e$	9.11×10^{-31}	(-1.602×10^{-19}) -ve	1/1838
Protons	Goldstein (1886)	${}_{1}^1 P$	1.67×10^{-27}	(1.602×10^{-19}) +ve	1
cNeutrons	James Chadwick (1932)	${}_{0}^1 n$	1.67×10^{-27}	Nil	1

i. **Michael Faraday and Davy's experiments:** In their experiments on electrolysis in (1833) have reported that **atoms are electrical in nature** and may possibly consist of sub-atomic particles .

ii. **Crooke's Experiment (Discovery of electrons):**

In Crook's experiment a glass tube sealed at both ends were used. In the glass tube he fixed metal plates at each end, one end was connected to the positive end while the other is connected to the negative terminal of a high voltage battery. An outlet through which the tube is connected to a vacuum pump was introduced and the experiment was conducted in the dark. The pressure inside the tube was reduced to a low value **He then noticed some rays travelling from the cathode towards the anode and called them cathode rays.** The deflection of the rays in applied electric and magnetic fields showed them to be negatively charged particles.

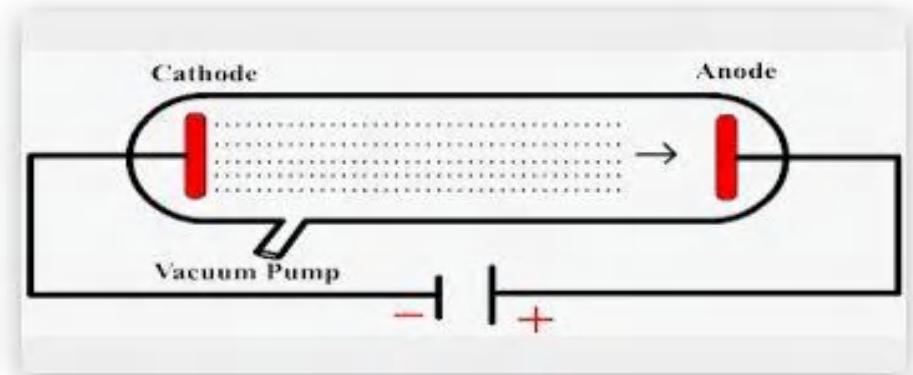


Fig. Cathode ray tube Experiments

Source:

https://www.google.com/search?q=Crooke%27s+experiment&tbo=isch&ved=2ahUKEwiHtLvg1P3uAhUV_hoKHd2jDIQQ2-cCegQIABAA&oq=Crooke%27s+experiment&gs_lcp=CgNpbWcQAzoECAAQQzoCCAA6BggAEAcQHjoGCAAQBRAeOgYIABAIEB46BAgAEB5Q7tMDWPm8BGCY1gRoAHAeACAAZsKiAG9V5IBDTAuMy40LTMuMS41LjSYAQCgAQGgA

[Qtnd3Mtd2l6LWltZ8ABAQ&sclient=img&ei=NbozYMfFDpX8a93HsqAI&bih=496&biw=1024&client=firefox-b-d](https://www.google.com/search?q=Qtnd3Mtd2l6LWltZ8ABAQ&sclient=img&ei=NbozYMfFDpX8a93HsqAI&bih=496&biw=1024&client=firefox-b-d)

iii. **J.J. Thompson experiment (1897):** Investigated into the properties of cathode rays and led to the discovery of electron (cathode ray) as a subatomic particle. J.J. Thompson **determined the charge to mass ratio (e/m) from the magnetic and electric fields and measured the extent of deflection of cathode rays.** He found out that the value of e/m ratio of cathode rays (electrons) remained the same whatever the nature of gas used to fill the discharge tube. **Hence he concluded that all atoms contained electrons and reported that the charge to mass ratio (e/m) =**

$1.759 \times 10^{11} \text{ C kg}^{-1}$. Below is a diagram of Thompson's cathode rays tube that he used for his experiment:

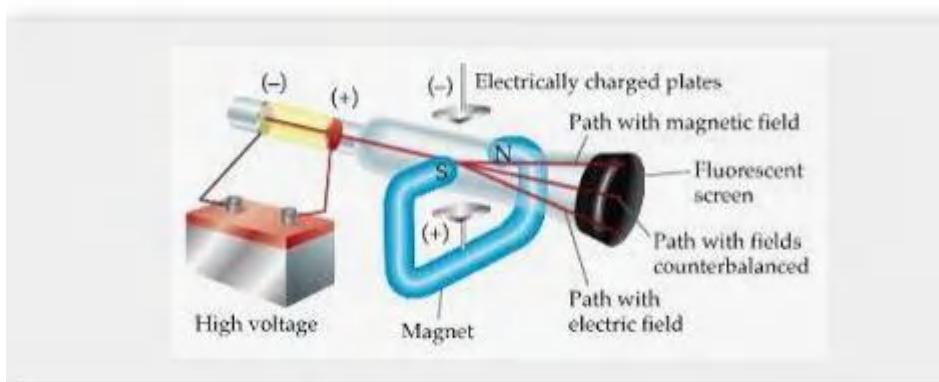


Fig: JJ Thompson Cathode Ray Tube Experiment demonstrating electric and magnetic field deflections of a cathode ray

From J.J. Thompson experiment can further explained using the diagram above. The following deductions were made:

- i. The cathode rays cause fluorescent screen (Inner wall of the screen is made of Zinc Sulfide) to glow with a green light when high voltage current was turned on
- ii. The rays are bent towards the positive electrode (anode) when an electric field was placed on their path. This shows that the rays are negatively charged. A magnetic field has a similar effect on cathode rays. Cathode rays are bent towards the N-pole of the magnet when strong magnetic field was placed on their path. When no field is applied the cathode rays (electrons) move in a straight line and forms spot at point where we have path with field counterbalanced on the screen in the figure.
- iii An object placed behind a perforated anode casts a shadow on the screen. This shows that the cathode rays travel in straight lines.
- iv. The rays can impact mechanical motion on a tiny paddle wheel. This shows that the rays possess momentum (K.E) and hence, mass
- v. The rays penetrate sheet of metals such as 1mm thick aluminum, without casting a shadow. Even the very small hydrogen atom cannot pass through a metal. The outcome of the experiment is that the particles in cathode rays are smaller than atoms.
- vi. No matter what metal was used as the cathode and no matter what the residual gas was in the tube, the mass/charge ratio of the particle making up the rays remain constant.

The protons (Goldstein Experiment 1886)

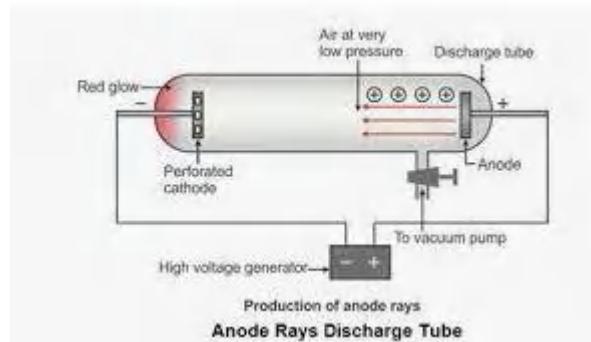


Fig: Positive rays (Canal Rays) travelling from anode to cathode (Goldstein's expt. 1886)

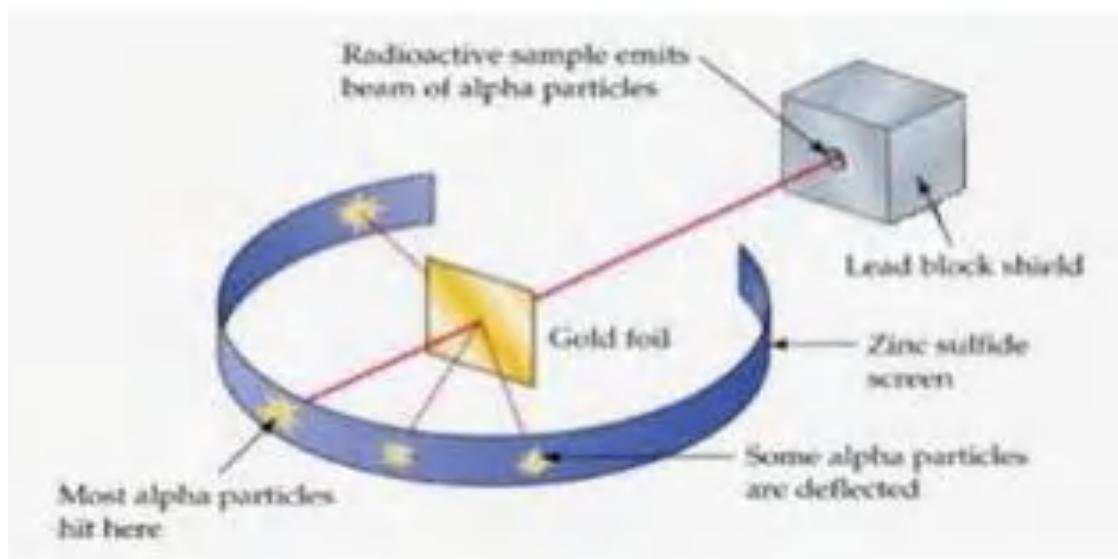
Goldstein in his experiment observed that when the cathode of a cathode ray tube was perforated as shown in the diagram above, positively charged rays (**which he called canal rays**) passed through the holes in the cathode to hit the glass walls end near the cathode. **The particles were bent towards the cathode of an electric field and towards the south-pole of a magnet.** He found out that the particle has an equal but opposite charge to the cathode ray particles and has a mass equal to that of a hydrogen atom.

v. **The Neutron (James Chadwick experiment 1932):** Early chemists found it difficult to correlate the mass of an atom with the number of protons present in the nucleus. In 1920, Rutherford suggested that an uncharged particle of almost the same mass as the proton may be present in atoms subsequently. **In 1932 Chardwick bombarded Beryllium with α -rays (4_2He) just for it to emit particles that were different in properties from those of electrons and protons. He showed that the particles were not deflected by electric or magnetic field and therefore possessed no charge. The particles were named neutrons.**

vi. Ernest Rutherford Nuclear atom (Alpha scattering experiment 1911)

In his experiment Rutherford bombarded a thin gold foil with alpha particles generated from a radioactive source. He found out that most of the alpha particles passed

through the foil while a few of them (1 out of 8,000) were deflected back.



Rutherford's Atomic Model: Experiment ...

Fig: Rutherford's Alpha scattering experiment

The above observation was explained by Rutherford in which he suggested (nuclear model) in which **an atom has a small positively charged centre (Nucleus) where nearly all the mass is concentrated**. Clearly his experiment showed that an atom consist of a dense centre of positive charge called nucleus with electrons moving around the nucleus at a distance that is large relative to the nuclear radius. Furthermore, his experiment showed that the heavy nucleus was made up of still smaller particles called protons.

Atomic Theory and Nature of Atoms- Lecture II

Instructor: Professor A.O. Ogunfowokan

vii. **Henry Moseley's (1913) experiment and Atomic no:** Suggested that the number of protons in the nucleus (atomic no) is a fundamental characteristics of an atom. This was explained by bombarding a number of elements with cathode rays otherwise called electrons. The energy provided by the cathode rays caused elements to emit X-rays. He further investigated the relationship between the frequency of the X-rays and the nature of the elements emitting the X-rays. Moseley showed that for any particular line in X-ray spectra, the frequency, ν is defined as : $V^{1/2} = a(Z-k)$ where Z is the atomic number, a and k are constants. The regularity of this frequency from element to element in the periodic table was consistent with the atomic no (Z) and not with mass no (A). Thus Z was used to denote the number of protons in the nucleus for a neutral atom. **The experiment shows that the atomic number, which is the number of protons in the nucleus of an atom, determined the order of elements in the periodic table. Therefore successive elements in the periodic table arose by a stepwise addition of one proton to the nucleus of the preceding one. In conclusion, he showed that the position of an element in the periodic table depended on its atomic number and not mass number.**

viii. **Robert Millikan's Experiment:** Carried out the oil drop experiment in 1909. He was able to determine the charge on an electron to be 1.602×10^{-19} C. **Details of this Experiment can be found in Advance Chemistry by Philip Mathews pages 6-7.** By his result and considering the value of e/m ratio earlier reported by J.J. Thompson which was 1.76×10^{11} Ckg⁻¹ it was possible to calculate the mass of an electron (**m**).

$$\text{Given that } e/m = 1.76 \times 10^{11} \text{ Ckg}^{-1} \text{ and } e = 1.602 \times 10^{-19}$$

If $e/m = 1.76 \times 10^{11} \text{ C kg}^{-1}$ making m the subject of the formula and substituting for the value of e in the new equation we have:

$$m = \frac{1.602 \times 10^{-19} C}{1.76 \times 10^{11} \text{ C kg}^{-1}} = 9.11 \times 10^{-31} \text{ kg}$$

Therefore, mass (m) of an $e^- = 9.11 \times 10^{-31} \text{ kg}$

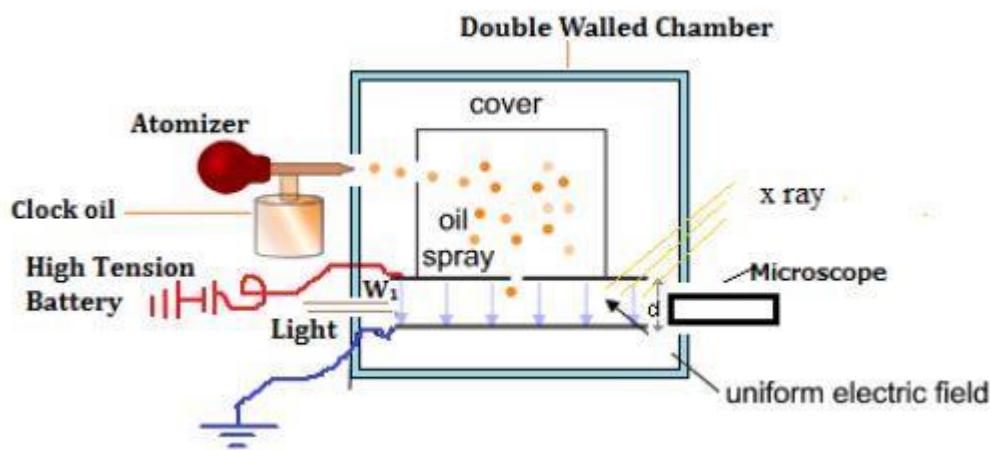


Fig. Diagram of Millikan's Oil drop experiment

ix. Niels Bohr (1913): Put forward a model of the atom based on the quantum mechanics originally developed by Planck. According to the Hypothesis of Plank (1900) radiant energy is emitted or absorbed in bundles other than a continuous flow. Each bundle, called a photon or a quantum contains an amount of energy which depends on the frequency of the radiation. The value of the quantum is related to the frequency of radiation by the equation:

$$E=H\nu \text{ where } h = \text{Planck's constant. } \nu = \text{frequency of radiation}$$

Bohr proposed that electrons move round the nuclei of atoms in orbital or shells at various distances from the nuclei with electrons prevented from falling into the nuclei by centrifugal

force. The orbits/shells/energy levels are designated by letters, K, L, M,N,Q as shown in the diagram below:

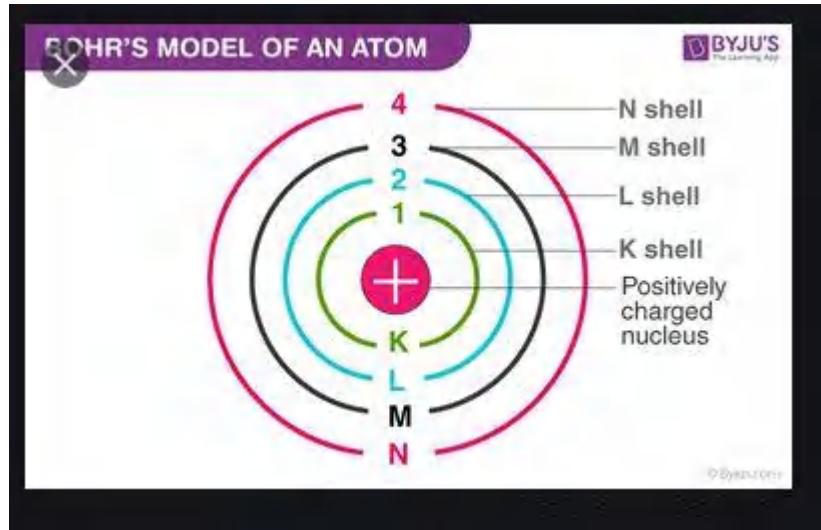


Fig: Bohr's Model of an Atom

Source: https://www.google.com/search?q=Atomic+orbits/shells&client=firefox-b-d&sxsrf=ALeKk031KNCLiZjzkeEnnZzGE_zDUsEl-g:1614527649743&source=lnms&tbo=isch&sa=X&ved=2ahUKEwi3xauY-IzvAhXnVBUIHQfbADIQ_AUoAXoECCIQAw&biw=1024&bih=496 (Retrieved 28th

February, 2021)

The max no of e^{-s} that can be accommodated by an energy level is $2n^2$ where n is the value of the principal energy level /shell/ orbit. As one moves outwards from nucleus starting from K to Q shell the energy increases.

Table: maximum number of Electrons and Energy levels

No principal level	Energy	Designation	Maximum number of electrons ($2n^2$)
1	K		2
2	L		8
3	M		18
4	N		32
5	O		50
6	P		72
7	Q		98

Bohr's model also explained the discrete lines in the atomic spectrum of hydrogen. This is based on the concept that the electron can move round the nucleus in certain permissible orbits (Energy levels). The ground state ($n = 1$ or K-shell) is the lowest energy state available to the e^- and it is usually the most stable state. The excited state ($n = 2, 3 \dots 7$ or K, L, M...Q shells) is any level higher than the ground state. Any electron in a particular energy level has a definite amount of energy associated with it at that level. Transition or movement of e^- from one energy level to another is possible. When electron therefore changes its state it either absorbs or emit the exact amount of energy (ΔE) which will bring it from the initial state to the final state according to the following equation:

$$\Delta E_{\text{electron}} = E_{\text{final}} - E_{\text{initial}}$$

When electron is excited it moves from the ground state (lower energy level) to the excited state (higher energy level) and hence absorb energy. On returning to the exited state to the ground state (lower energy level) it emits energy giving rise to a line in the spectrum. The

lines in the spectrum are referred to as Lyman Series, Balmer Series, Paschen Series, Brachett Series, Pfund series. This is the basis for the hydrogen atomic spectrum.

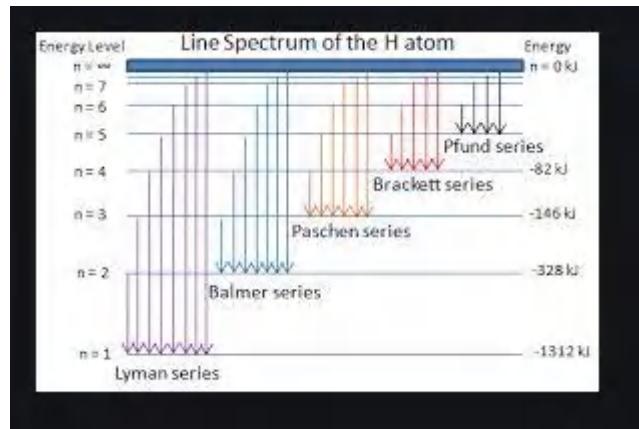


Fig: Line Spectrum of H atom

Limitation of Bohr's Theory

In the Bohr's theory of spectra, only one quantum number was postulated to describe an electron orbit of hydrogen. Experimental observations on fine structure and the splitting of lines in a magnetic field revealed that four quantum numbers are required for a complete description of the state of an electron in an atom.

Wave-mechanical model

X. de-Broglie (Dual nature of an electron): Suggested a wave-particle duality nature for an electron. In other words he suggested that an electron can behave as a wave or as a particle. He further generated an equation in which he connected the particle-like property of momentum, mv , with the wave-like property of wavelength, λ as shown below:

(i) As a wave electron conforms to the Planck's quantum mechanical equation thus:

$$E = h\nu = hc / \lambda \text{ where } \nu = \frac{c}{\lambda} \dots *$$

(ii) As a particle, electron conforms to the Einstein's equation thus:

$$E = mc^2 \dots **$$

Where E = Energy emitted by a quantum of radiation; h = Planck's constant $= (6.626 \times 10^{-34} \text{ Js})$;

ν = frequency s^{-1} or hertz; c = velocity; λ = de Broglie's wavelength (m); m = mass of electron (kg)

Combining equation * and ** we have de-Broglie equation :

$$E = hc / \lambda = mc^2$$

By cross multiplication we have:

$$\lambda = \frac{hc}{mc^2} = \frac{h}{mc}$$

Therefore, de-Broglie equation is given as:

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

λ = de Broglie's wavelength

Atomic Theory and Nature of Atoms Lecture III

Instructor: Professor A.O. Ogunfowokan

Werner Heisenberg uncertainty principle: Was a scientist who proposed the uncertainty principle with suggested that it was **impossible to know the momentum and the location of any electron with certainty. It is therefore impossible to measure with complete accuracy both the position and momentum of an electron.**

If the uncertainty in position is ΔX and uncertainty in momentum is ΔP .

The Heisenberg's equation is given thus:

$$\Delta P \cdot \Delta X \geq h / 2\pi$$

i.e.:

The more accurately you know the position (i.e., the smaller Δx is), the less accurately you know the momentum (i.e., the larger Δp is); and vice versa.

Erwin Schrodinger: Schrodinger wave equation is a mathematical expression describing the energy and position of the electron in space and time, taking into account the matter wave nature of the electron inside an atom

Time-independent Schrödinger equation in compressed form can be expressed as:

$$\hat{H} \Psi = E \Psi$$

↓ ↓
Hamiltonian Energy
Operator eigenvalue
(Energy operator)

Ψ = wave function or region of finding an electron (eigen-function)

E = Energy of an electron (eigen-value)

Solving the Schrödinger equation gives us Ψ and Ψ^2 . With these we get the quantum numbers and the shapes and orientations of orbitals that characterize electrons in an atom or molecule. The summation of the square of wave function (Ψ^2) with respect to the volume of the element (ΔV) gives the probability of space where an electron is located in an energy level. This region of maximum probability of where an electron is located is referred to as orbital or electron orbit according to the equation:

$$\int \Psi^2 dv \approx \ell$$

Each orbital of an atom and the electrons accommodated are described completely by a set of **four quantum numbers** and three of these numbers are derived from the Schrodinger wave equation.

The four quantum numbers are:

1. The principal quantum number (n): described the size/ Energy level in which the orbital is located. It takes values from $n = 1, 2, 3, \dots, 7$ i.e. K, L, M, N... Q shells
2. Angular/Azimuthal/subsidiary quantum number (ℓ): Describes the shape of the orbital and can have values $\ell = 0, 1, 2, \dots, (n-1)$.

The table below shows the values of Subsidiary/Angular/Azimuthal quantum numbers and shapes of the orbitals:

ℓ	0	1	2	3	4
Orbital type	s	p	d	f	g

3. The magnetic quantum number (m) describes the orientation of orbital in space.

Magnetic quantum number gives the number of orbitals of each type. It has values from m . $m = -\ell, -\ell+1, \dots, 0, \dots, +\ell$

For: $\ell = 0, m = 0$

$\ell = 1, m = -1, 0, +1$

$\ell = 2, m = -2, -1, 0, 1, 2$

$\ell = 3, m = -3, -2, -1, 0, 1, 2, 3$

4. Spin quantum number (m_s): describes the spin of electrons either clock wisely or anti clock wisely.

Spin quantum number m_s describes the magnetic properties of an electron. It has values of $+\frac{1}{2}$ or $-\frac{1}{2}$. The $m_s = +\frac{1}{2}$ for electron with the spin up \uparrow and $m_s = -\frac{1}{2}$ for electron that spin down \downarrow .

Number	Symbol	Possible Values
Principal Quantum Number	n	1, 2, 3, 4, ...
Angular Momentum Quantum Number	ℓ	0, 1, 2, 3, ..., $(n - 1)$
Magnetic Quantum Number	m_l	$-\ell, \dots, -1, 0, 1, \dots, \ell$
Spin Quantum Number	m_s	+1/2, -1/2

Quantum numbers These four quantum numbers are used to describe the probable location of an electron in an atom.

Source: <https://courses.lumenlearning.com/introchem/chapter/quantum-numbers/>

Shapes and degeneracy of orbitals

S/No	Type of orbitals	Orbital Shape	Degeneracy (No of orbitals in Subshell)	Maximum number of electrons
1	S orbital	Spherical 	Non-Degenerate	2
2.	p- orbital	Dumbbell Shape The three p orbitals are aligned along perpendicular axes	Three degenerate	6 electrons
3.	d-Orbital	Double Dumbbell Shape 	Five degenerate	10 electrons
4.	f-Orbital	Complicated	Seven degenerate	14 electrons

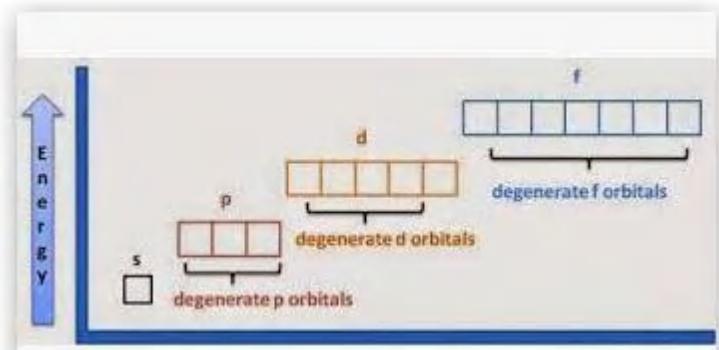


Fig. Degenerate Orbitals showing increase in Energy

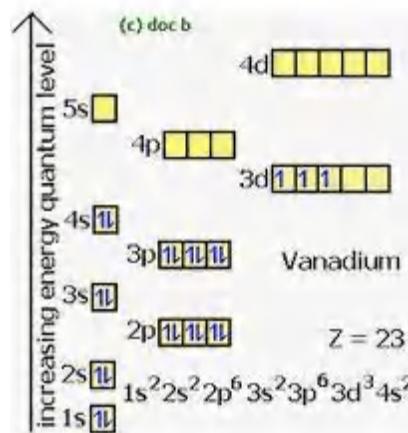


Fig. Orbitals fed with electrons for Vanadium and Increasing Energy Level

Possible allowed combination and quantum numbers and atomic orbital's

Principal quantum no. (n)	Angular quantum no. (ℓ) $\ell = 0, 1, 2 \dots (n-1)$	Magnetic quantum, no (m) $m = 1 \dots 0+l$	Spin quantum no. (s) $\pm \frac{1}{2}$	Max no of e ^{-s} in sub-shell	Total no. e ^{-s} (2n ²)	Type of orbital
n = 1 (K-shell)	$\ell = 0$	m = 0	$\pm \frac{1}{2}$	2 e ^{-s}	2e ^{-s}	1s
n = 2 (L-shell)	$\ell = 0$	m = 0	$\pm \frac{1}{2}$	2 e ^{-s}		2s
	$\ell = 1$	m = -1	$\pm \frac{1}{2}$			
		m = 0	$\pm \frac{1}{2}$		8e ^{-s}	
		m = +1	$\pm \frac{1}{2}$			2p
n = 3 (M-shell)	$\ell = 0$	m = 0	$\pm \frac{1}{2}$	2e ^{-s}		3s
	$\ell = 1$	m = -1	$\pm \frac{1}{2}$			
		m = 0	$\pm \frac{1}{2}$	6e ^{-s}		3p
		m = +1	$\pm \frac{1}{2}$			
	$\ell = 2$	m = 2	$\pm \frac{1}{2}$		18e ^{-s}	
		m = -1	$\pm \frac{1}{2}$	10e ^{-s}		3d
		m = 0	$\pm \frac{1}{2}$			
		m = +1	$\pm \frac{1}{2}$			
		m = +2	$\pm \frac{1}{2}$			

Q. What orbital's are occupied by electron describe by the quantum numbers: (i) $n = 4$, $\ell = 0$ (ii) $n = 3$, $\ell = 1$? What values of m and s could each electron have?

Solution: (i) $n = 4$, $\ell = 0$

$\ell = 0 \rightarrow$ s-orbital

$n = 4$ implies the forth quantum shell

The orbital is therefore a 4s orbital; meaning an s orbital in the forth quantum shell.

$m = 0$; $s = \pm \frac{1}{2}$

ii. $n = 3$, $\ell = 1$

$\ell = 1 \Rightarrow$ p-orbital

i.e. the orbital is 3p

$m = -1, 0, +1$

$S = \pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}$

Modern ideas of atomic structure

Recall that:

An atom consist of three sub-atom particles called electrons (e^-), protons (p) and neutrons (n)

- p, is positively charge while neutrons n, is neutral
- They (p & n) both occupy the central region of an atom
- The central region of atom is called nucleus
- Electron is negatively charged

- In a neutral atom number of protons (n_p) = atomic no = number of e^- represented by letter **Z**
- Mass number represents the number of p + number of neutrons in a neutral atom represented by letter **A**.
- In any given neutral atom of an element ${}^A Y_Z$
- A = mass number and Z = atomic number
- Number of neutrons in a neutral atom = A-Z

e.g ${}_{17}^{37} Cl$ number of e^- = 17

number of p = 17

number of n = 20 i.e. $(A-Z) = 37 - 17 = 20$

For the anion:

e.g ${}_{16}^{32} S^{2-}$ number of e^- = 16 + 2 = 18 e^{-s}

Number of protons (n_p) = 16 Number of neutrons (n_n) = 32 - 16 = 16

For a positive ion/Cation:

${}_{20}^{40} Ca^{2+}$

Number of protons (n_p) = 20

Number of electrons (e^-) = 20 - 2 = 18 e^{-s}

Number of neutrons (n_n) = 40 - 20 = 20

Atomic Theory and Nature of Atoms Lecture IV

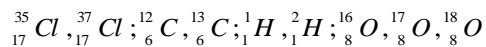
Instructor: Professor A.O. Ogunfowokan

Relative atomic mass: of the element is the weighted mean of the mass of the isotopes of the atoms of the element e.g. see blow

$$\text{R.A.M} = \frac{(\text{Wt. of isotope A} \times \text{Abundance of A}) + (\text{Wt. of Isotope B} \times \text{Abundance of B}) + \dots + (\text{Wt. of Isotope n} \times \text{abundance of n})}{100}$$

Relative molecular Mass: of an element or compound is the mass of one molecule of the element or compound compared with the mass of an atom of $^{12}_6 C$ which is arbitrarily assigned as 12.00

Isotopes: are atoms of an element with the same atomic no of Z (same no of protons and electrons) but different relative atomic masses because of the different no of neutrons e.g.



Note that atomic number determines the position of the element in the periodic table, and also the chemical reactivity of the atom. Isotopes of an element therefore have the same chemical properties but different physical properties.

Example 1: There are 2 isotopes of chlorine with mass no 35 and 37 respectively. If the isotopes exist in the ratio of 3:1, the lighter isotope being more abundant, what is the relative atomic mass of chlorine?

Solution:

Contribution by Isotope 35 with abundance 3 = $35 \times 3 = 105$

Contribution by isotope 37 with abundance 1 = $37 \times 1 = 37$

Total contribution by the two isotopes = $105 + 37 = 142$

The above contribution is made up of atoms 3 + 1 = 4 atoms

i.e. The weighted mean = $\frac{142}{4} = 35.5$

Therefore R.A.M = 35.5

Example2: Given that the abundance of the lighter bromine isotope is 50.54% , calculate the natural atomic weight of bromine, if the element has only two naturally occurring isotopes weighing 78.9184 and 80.9163 respectively. Express your answer to 3 significant figure.

Natural Atomic weight =

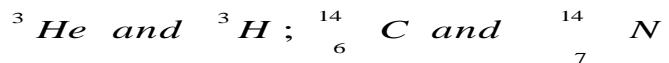
$$\frac{\text{Mass of isotope A} \times \text{abundance isotope A} + \text{Mass of Isotope B} \times \text{abundance of isotope B}}{100}$$

% abundance of isotope A = 50.54 and since the element has only two naturally occurring Isotopes, the % abundance of Isotope B therefore = $100 - 50.54 = 49.46$

$$\begin{aligned}\text{Atomic weight} &= \frac{(50.54 \times 78.9184) + (49.46 \times 80.9163)}{100} = 79.907 \\ &= 79.9 \text{ to 3 sig. fig.}\end{aligned}$$

Exercise: Given that the mean relative atomic mass of chlorine prepared in the laboratory is 35.5 and assuming that chlorine contains two isotopes of mass no 35 and 37, what is the % age composition of the isotope of mass no of 37?

Isobar: These are nuclides with the same atomic mass e.g. $^{14}_6 C$ and $^{14}_7 N$



Isotope: Are nuclides with the same number of neutrons e.g. $^3_2 He$ and $^2_1 H$ have one neutron each while each of $^{30}_{14} Si$, $^{31}_{15} P$, and $^{32}_{16} S$ have sixteen neutrons

A nuclide: is a specific nuclear species. It is a nucleus with a given number of neutrons and protons (nucleons). It is not the same as element. It is in fact possible to have different nuclides of the same element e.g. $^2_1 H$ is deuterium, $^3_1 H$ tritium, they are of the same element, hydrogen but different nuclides.

Exercise: Five isotopes of Zn occur in nature $^{64}_{30} Zn$ (48.6%) of atomic mass of 63.9291 amu,

$^{66}_{30} Zn$ (27.9%) with atomic mass of 65.9260 amu; $^{67}_{30} Zn$ (4.1%) with atomic mass 66.9721 amu;

$^{68}_{30} Zn$ (18.8%) with atomic mass 67.9249 amu and $^{70}_{30} Zn$ (0.6%) with atomic mass of 69.9253 amu.

Calculate the atomic weight of Zn

Avogadro theory- states that under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.

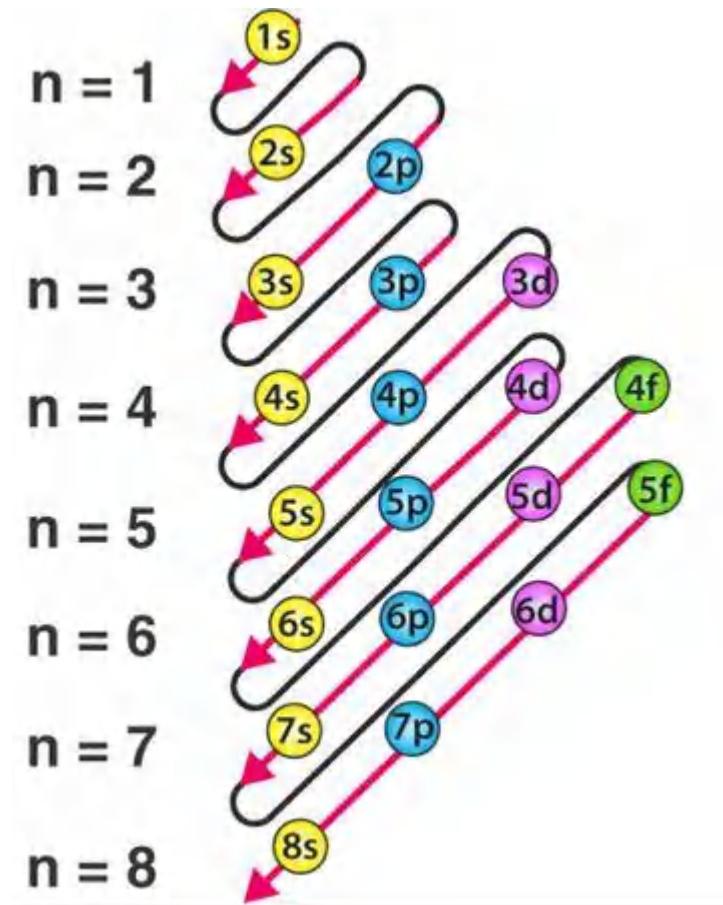
A mole: a standard scientific unit for measuring large quantities of very small entities such as atoms, molecules, or other specified particles. A mole can further be defined as the mass or volume of a substance that contains Avogadro's number of particles (6.02×10^{23})

A mole therefore contains 6.02×10^{23} particles. The number 6.02×10^{23} is referred to as Avogadro's constant or **Avogadro's number which is designated with a symbol N_A .** The particles here are usually atoms, molecules, electrons, ions, neutrons, protons etc

Electron configuration

This is the arrangement of electrons of an element into atomic orbitals. The ground state electronic configuration of an element is governed by 3 rules:

1. Aufbau principle: states that electrons in their ground state are added to an atom one at a time starting with the lowest energy level i.e. the sublevels with lower energies are filled up before those with higher energies according to the diagram below:



In filling electrons into orbitals the following scheme is usually followed using the Aufbau principle above:

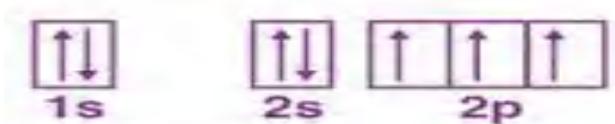
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s etc

Table: Ground state electronic configuration for the 1st 30 elements

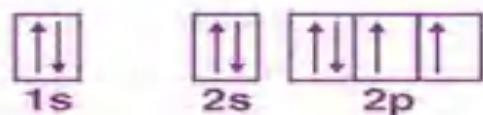
Atomic no	Symbol	Electronic configuration	Shorthand form
1	H	1s ¹	1s ¹
2	He	1s ²	1s ² = [He]
3	Li	1s ² 2s ¹	[He] 2s ¹
4	Be	1s ² 2s ²	[He]2s ²
5	B	1s ² 2s ² 2p ¹	[He]2s ² 2p ¹
9	F	1s ² 2s ² 2p ⁵	[He]2s ² 2p ⁵
10	Ne	Ne ² 2s ² 2p ⁶	[Ne]
17	Cl	1s ² 2s ² 2p ⁶ 3s ² 3p ⁵	[Ne]3s ² 3p ⁵
18	Ar	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶	[Ar] or [Ne]3s ² 3p ⁶
19	K	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹	[Ar]4s ¹
28	Ni	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁸	[Ar]4s ² 3d ⁸
29	Cu	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹ 3d ¹⁰	[Ar] 4s ¹ 3d ¹⁰
30	Zn	1s ₂ 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰	[Ar]4s ² 3d ¹⁰

2. **Pauli exclusion principle:** States that no two electrons in the same atom can have the same value for all the four quantum numbers (n, l, m and s)
3. **Hund's rule of maximum multiplicity:** State that in filling of a particular orbitals, p, d, f, each of the degenerate orbitals in a sub shell must be filled/occupied by one electron i.e. singly before paring begins. According to this rule electron pairing in p, d and f orbitals cannot occur until each orbital of a given subshell contains one electron each or is singly occupied.

e.g₁ for ₇N = 1s² 2s² 2p³



e.g₂ for ₈O = 1s² 2s² 2p⁴



e.g₃ Carbon atom ₆C = 1s² 2s² 2p²

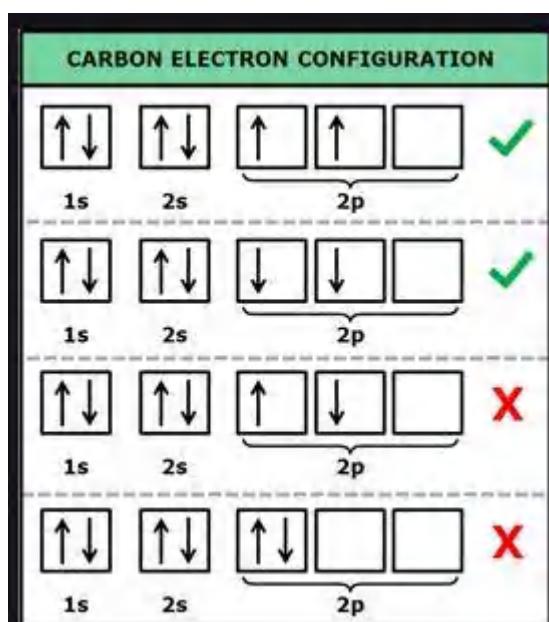


Table Representation of arrangements of electrons

Atomic Number	Element	1s	2s	2p _x	2p _y	2p _z	Number of unpaired electrons
1	H	↑					1
2	He	↑↓					0
3	Li	↑↓	↑				1
4	Be	↑↓	↑↓				0
5	B	↑↓	↑↓	↑	↑		1
6	C	↑↓	↑↓	↑	↑		2
7	N	↑↓	↑↓	↑	↑	↑	3
8	O	↑↓	↑↓	↑↓	↑	↑	2
9	F	↑↓	↑↓	↑↓	↑↓	↑	1
10	Ne	↑↓	↑↓	↑↓	↑↓	↑↓	0

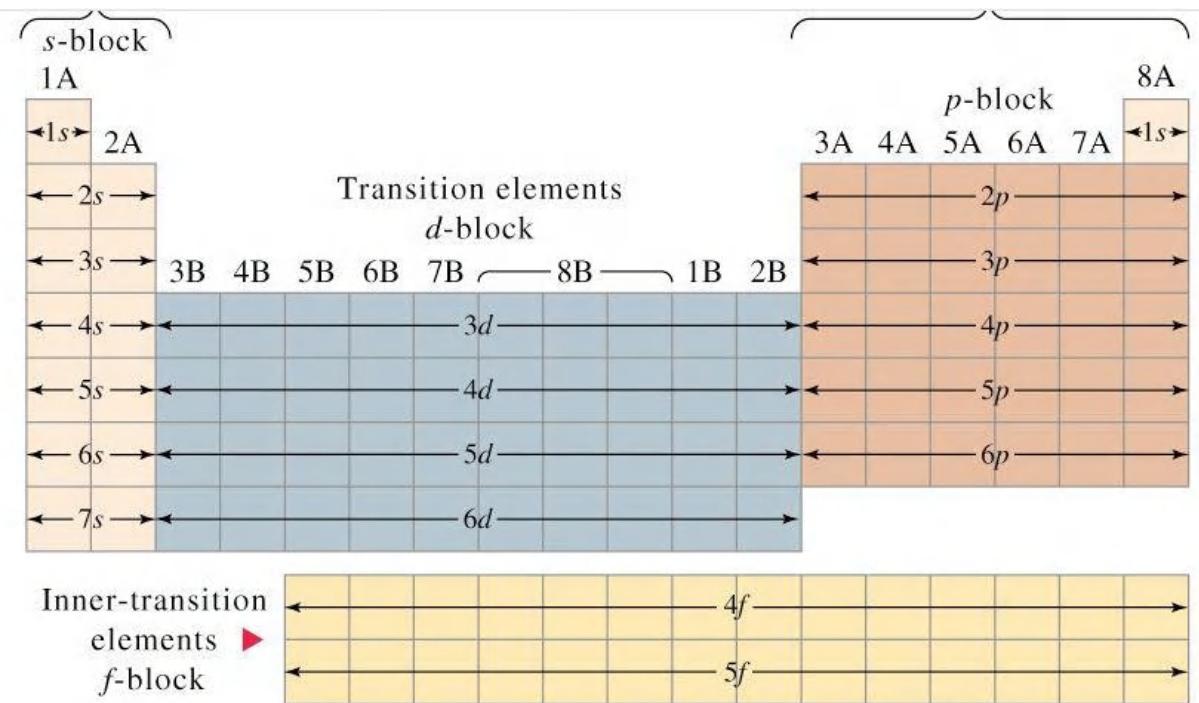
Fig: Arrangements of electrons in the first 10 elements in the periodic table using Hund's rule

The periodic law

In the Periodic Table (PT), the elements are arranged in order of increasing atomic number (Recall Henry Mosely Experiment) or in order of increase nuclear charge with their symbols.

The periodic table arranges the elements into several horizontal rows called periods. Elements H and He belong to the 1st row/period. Elements with the same chemical properties are placed in the same vertical columns called groups. There are eighteen groups and seven periods in the periodic table.

The P.T. can also be divided into 4 main regions according to whether s, p or d or f orbitals are being filled.



Atomic Theory and Nature of Atoms Lecture 5 of 5

Instructor: Professor A.O. Ogunfowokan

The P.T. can also be divided into 4 main regions/blocks according to whether s, p, d or f orbitals are being filled. This classification was based on the type of sublevel accommodating the very last electron when feeding the available electrons of atoms into the sublevels Fig. X below. **Groups 1A-8A** are the main/Tall groups while **1B, 2B,8B** are the short groups or subgroups. **Group 8 or 0** are called noble gas group. Hydrogen does not belong to any group. Elements in **group 1**, Li, Na, K etc are called alkali metals. Elements in **group 2**, Be, Mg, Ca etc. are called alkaline earth metals. The elements in **group 7**, F, Cl, Br, etc. are called halogens. Metals at the bottom of Group 1 are the most powerful reducing agents, while non-metals to the top of Group 7 are the most powerful oxidising agents. Elements in **d-block and f-block** are called transition and inner transition elements respectively Fig X below.

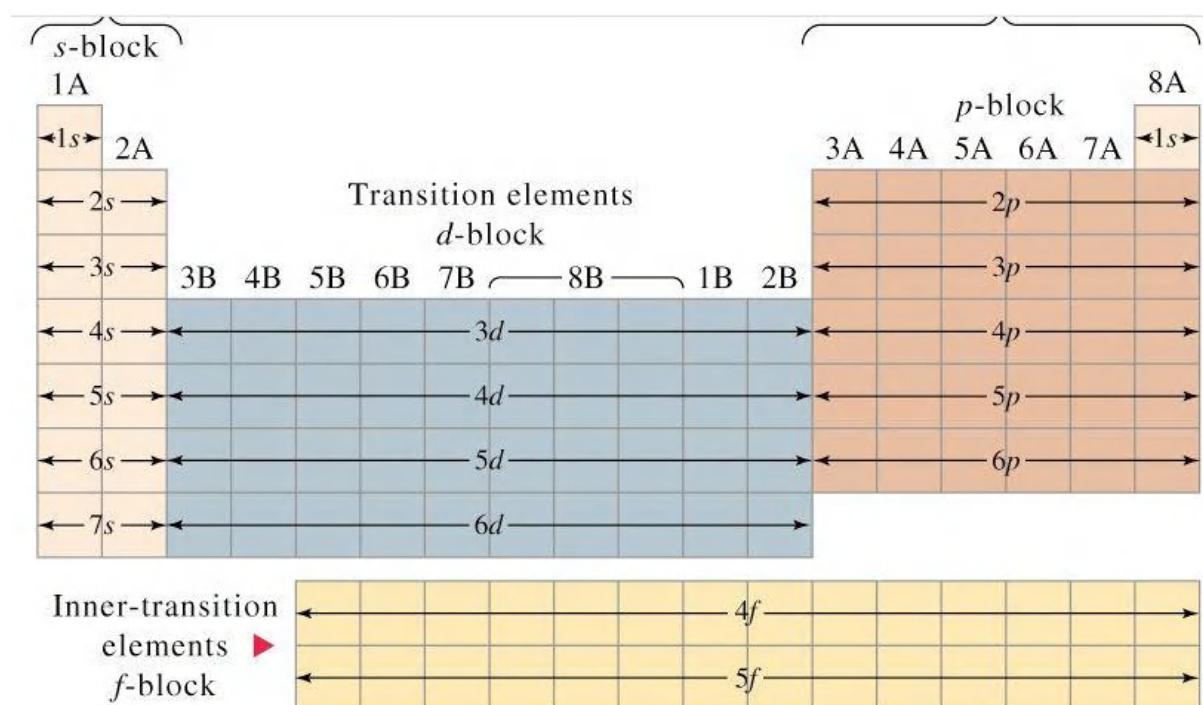


Fig X- The Periodic Table of elements showing blocks s, p, d and f of elements

The periodic law states that the properties of the elements vary in relation to their atomic numbers. The chemical properties of elements therefore are periodic function of their atomic numbers. The majority of elements in the periodic table are metals only **about twenty are non-metals. Metals are found to the left of zig-zag line in the figure Y below and non-metals to the right. Many elements close to the zig-zag line, exhibit both metallic and non-metallic properties and are called metalloids. The following elements-Boron (B), Silicon (Si), Germanium (Ge), Arsenic (Arsenic) and tellurium (Te) in the periodic table are called metalloids.**

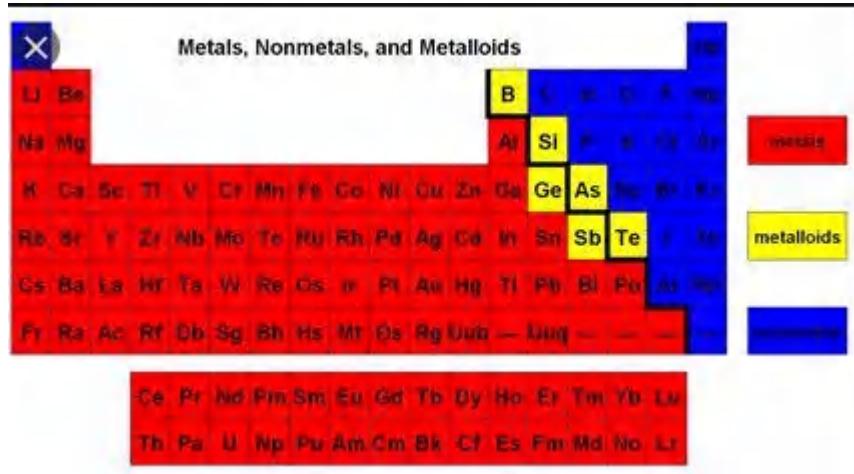


Fig. Y- Periodic Table showing Metals, Non-metals and Metalloids

DIVISION OF ELEMENTS INTO s, p AND d-BLOCKS –further explanation

The division into s, p and d-blocks depends on the orbital that is last fed with electrons in the atom. In groups 1 and 2 elements, the last orbital that is fed with electrons is “s”. Hence, the two groups belong to s-block. By the same explanation, elements in groups 3-8 belong to p-block. In case of the transition elements the last electrons go into d-orbitals. Hence these elements belong to d-block as shown in Fig Z below:

1s ¹																1s ²		
2s ¹	2s ²															2p ¹ 2p ² 2p ³ 2p ⁴ 2p ⁵ 2p ⁶		
3s ¹	3s ²															3p ¹ 3p ² 3p ³ 3p ⁴ 3p ⁵ 3p ⁶		
4s ¹	4s ²	3d ¹	3d ²	3d ³	3d ⁵	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ¹⁰	3d ¹⁰	4p ¹	4p ²	4p ³	4p ⁴	4p ⁵	4p ⁶	
5s ¹	5s ²	4d ¹	4d ²	4d ⁴	4d ⁵	4d ⁵	4d ⁷	4d ⁸	4d ¹⁰	4d ¹⁰	4d ¹⁰	5p ¹	5p ²	5p ³	5p ⁴	5p ⁵	5p ⁶	
6s ¹	6s ²			5d ²	5d ³	5d ⁴	5d ⁵	5d ⁶	5d ⁷	5d ⁹	5d ¹⁰	5d ¹⁰	6p ¹	6p ²	6p ³	6p ⁴	6p ⁵	6p ⁶
7s ¹	7s ²			6d ²	6d ³	6d ⁴	6d ⁵	6d ⁶	6d ⁷	6d ⁸	6d ¹⁰	6d ¹⁰	7p ¹	7p ²	7p ³	7p ⁴	7p ⁵	7p ⁶
		5d ¹	4f ¹	4f ³	4f ⁴	4f ⁵	4f ⁶	4f ⁷	4f ⁷	4f ⁹	4f ¹⁰	4f ¹¹	4f ¹²	4f ¹³	4f ¹⁴	4f ¹⁴		
		6d ¹	6d ²	5f ²	5f ³	5f ⁴	5f ⁶	5f ⁷	5f ⁷	5f ⁹	5f ¹⁰	5f ¹¹	5f ¹²	5f ¹³	5f ¹⁴	5f ¹⁴		

Fig Z: Showing filling of electrons into the last orbital for each element

SOME IMPORTANT CHARACTERISTICS OF THE ELEMENTS IN THE PERIODIC TABLE

I. PERIODICITY OF ATOMIC RADIUS:

The atomic radius is the distance from the nucleus to the outermost electron in the atom.

There are three factors that determine the radius of an atom.

These are:

- The attractive force between the nucleus and the outermost electrons;
- The shielding (screening) of the outermost electrons by the inner electrons; and
- The number of shells occupied by electrons.

For elements in the same group, the added shells make the atomic radius to increase down the group. For elements in the same period, the number of occupied shells is the same. Since nuclear charge (i.e. charge in the nucleus which is brought about by number of protons) increases as we move from left to right, it follows that the atomic radius decreases.

II. PERIODICITY OF IONIZATION ENERGY/POTENTIAL

Ionization energy is the amount of energy required for the removal of an electron. The energy required to remove one mole of an electron completely from one mole of isolated gaseous atoms of an element is known as the first ionization energy.



IE = Ionization Energy/ Ionization potential

2nd I.E. is the needed energy to remove completely the 2nd electron from a singly charged ion.

The unit of ionization energy is kJ mol^{-1} . Ionization energy increases from left to right along a particular period in the periodic table. This is so for two reasons.

- Atomic radius decreases from left to right across the period. This increases the grip which the nuclear charge has for the outer-shell electrons.
- Also, nuclear charge increases from left to right. Hence the grip which the nucleus has on the outermost electrons is increased.

Ionization energy decreases down the group of the periodic table. This is because of the added shells whose effect off-sets the effect of the increase in nuclear charge.

III. PERIODICITY OF ELECTRON AFFINITY

Electron affinity is a measure of the ease of gain of electron. It is the energy released when a gaseous atom accepts an electron to form a gaseous negative ion.



EA = Electron affinity

Electron affinity is the energy involved in the process. The non-metals are usually the elements that gain/ capture electrons. They are said to have high affinity for electrons.

Thus, electron affinity increases from left to right along the period while it decreases down the group in the periodic table.

IV. PERIODICITY OF ELECTRONEGATIVITY (χ)

Electronegativity is defined as the relative ability of an atom in a molecule to attract electrons. It follows the same trend as electron affinity. Thus, electronegativity increases, from left to right and decreases down the group of the periodic table. Electronegativity has been defined by Mulliken as half the sum of ionization energy (IE) and electron affinity (EA) values of atoms of an element according to the equation below:

$$\text{Electronegativity } (\chi) = \text{IE} + \text{EA}/2$$

METALLIC AND NON-METALLIC CHARACTER

The metallic character is the ability of an element to behave as a metal.

Along the period in the periodic table, metallic character decreases while non-metallic character increases. Down a particular group of the periodic table metallic character increases while non-metallic character decreases.

CHEMICAL EQUILIBRIA



OWOYOMI Olanrewaju PhD

What is Chemical Equilibrium?

- During our classes on STOICHIOMETRY, we assume that reactions proceed to completion. However, we need to know that:
 1. When all the reactants in a reaction are used up the reaction is said to have **gone to completion**. However, in some reactions not all the reactants are used.
 2. Reactions that go to completion are *irreversible*. However, in some reactions the reactants form products (in a forward reaction), and the products can change back into reactants (in a reverse reaction).
 3. In all reactions, as the amount of reactant in a reaction decreases the product is formed more slowly. In a reversible reaction, as the amount of product increases the reactant is formed more quickly. Eventually the rate of the forward reaction (reactants →products) equals the rate of the reverse reaction (products → reactants).
- At this point there are still reactants present but there does not *appear* to be any further change taking place. The reaction is said to be in chemical equilibrium.
- For illustration you can check the link below for a simulation of equilibrium:
- <http://www.youtube.com/embed/C5jDmG4nVV8>

Definitions of Chemical Equilibrium

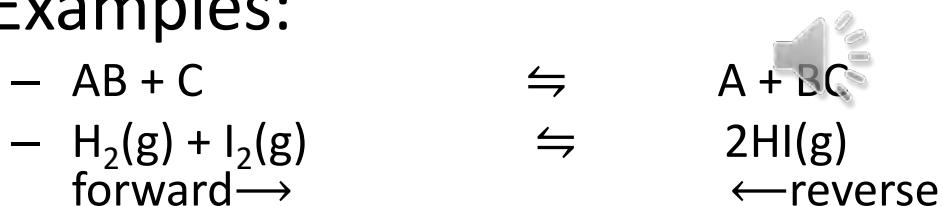
- Chemical equilibrium is the state of a reversible reaction where the rate of the forward reaction equals the rate of the reverse reaction.
 - While a reaction is in equilibrium the concentration of the reactants and products are constant.

Examples of Chemical Equilibrium

- **A bottle of cold Coca –cola or Sprite drink**
 - Carbon (IV) oxide dissolved in the bottled liquid
 - There is also carbon (IV) oxide in the space between the liquid and the cap
 - There is a constant movement of CO₂ from the liquid to the gas phase, and from the gas phase into the liquid. However, a cursory look at the bottle  there does not appear to be any change. The system is in equilibrium.
 - $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$
- **Equilibrium within your body**
 - Oxygen transport by haemoglobin in your body without which you can not survive
 - The haemoglobin takes up oxygen, but releases it and this is done through changes in the chemical equilibrium of this reaction in different places in our bodies.
 - $\text{haemoglobin}(\text{aq}) + 4\text{O}_2(\text{g}) \rightleftharpoons \text{haemoglobin}(\text{O}_2)_4$

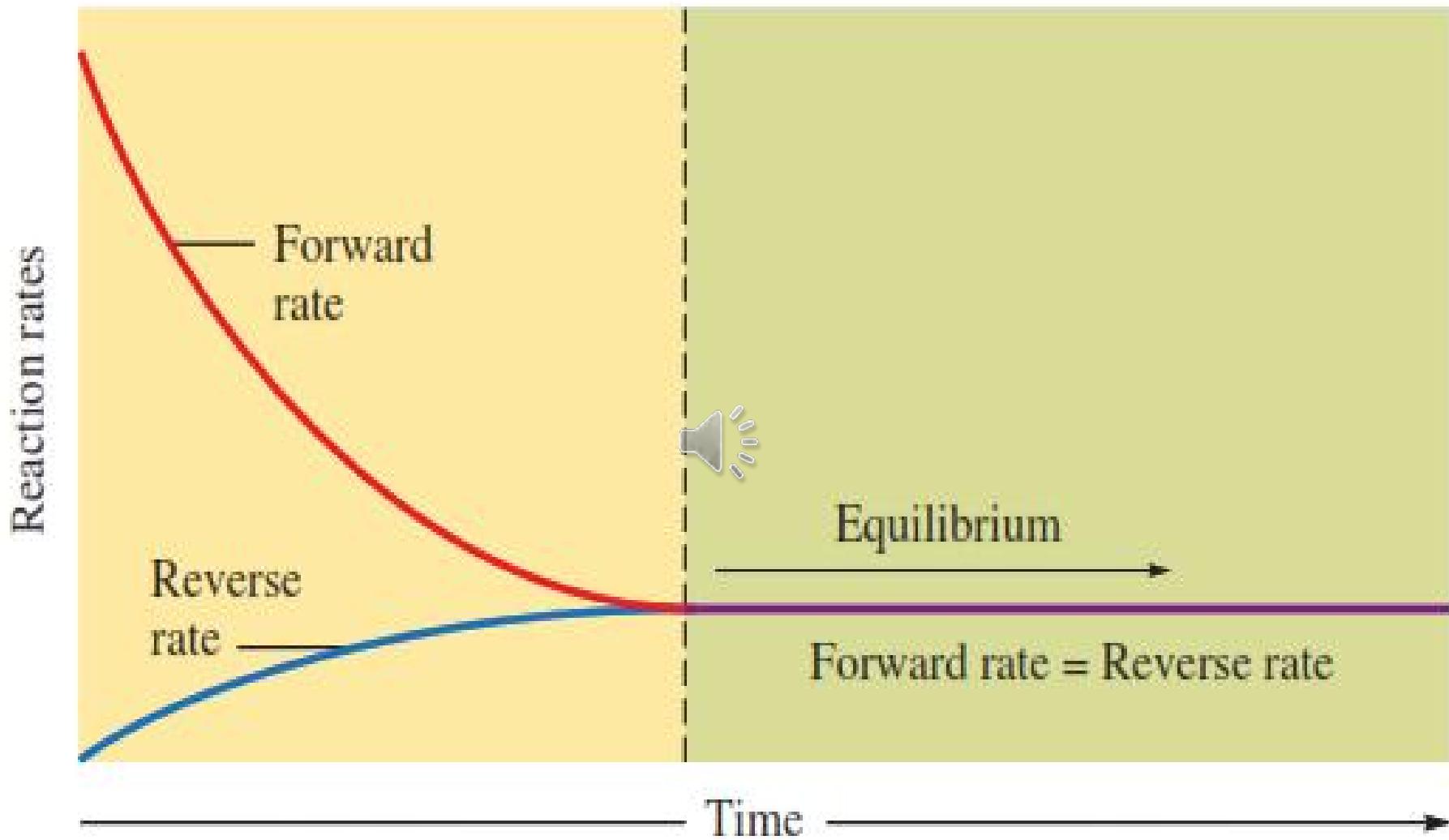
REVERSIBLE PROCESSES

- A reversible reaction is a chemical reaction that can proceed in both the forward and reverse directions. In other words, the reactants and products of the reaction may reverse roles.
- A special double-headed arrow (\rightleftharpoons) is used to show this type of reversible reaction:
- Examples:



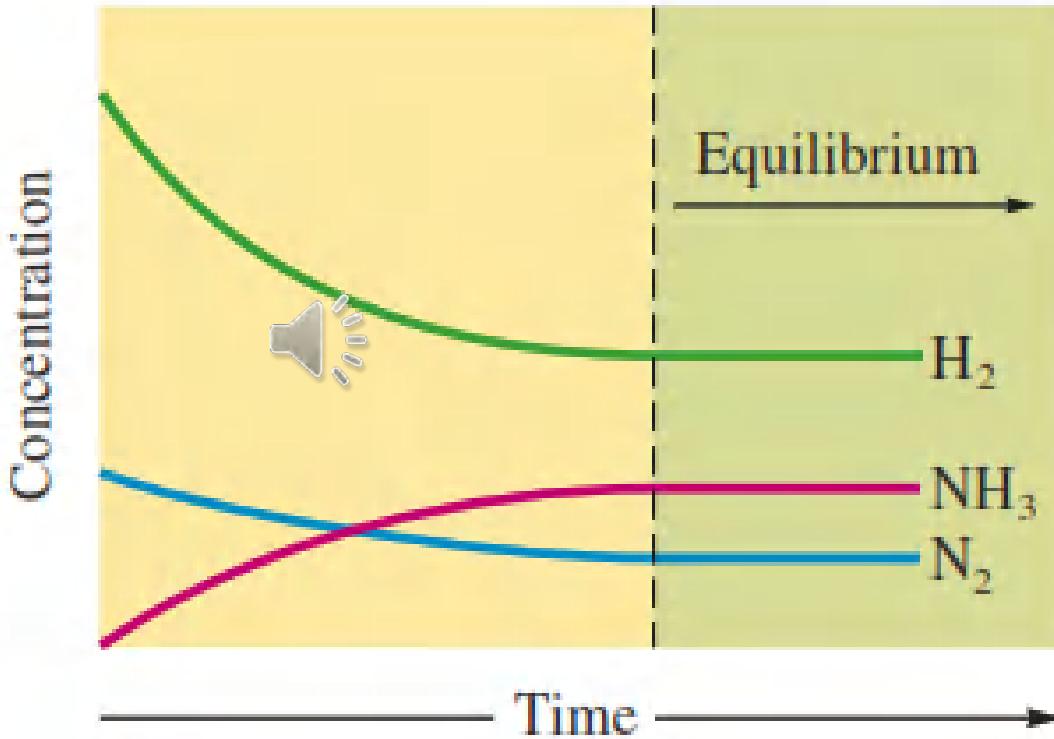
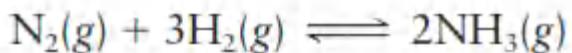
- The forward reaction is: $\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$
- The reverse reaction is: $2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$
- The two examples above illustrate the concept of DYNAMIC EQUILIBRIUM

A graphical illustration can be seen on the next slide



Equilibrium and Stoichiometry

- The relationship between STOICHIOMETRY and EQUILIBRIUM will be illustrated using the reaction for the synthesis of ammonia (NH_3) from elemental nitrogen (N_2) and hydrogen (H_2)



- Because of the **stoichiometry** of the reaction:
 - H₂ disappears three times as fast as N₂ does, and NH₃ forms twice as fast as N₂ disappears.

EQUILIBRIUM CONSTANT



The Law of Mass Action

- At constant temperature the product of active masses on one side of a chemical equation, when divided by the product of active masses on the other side of the chemical equation, is a constant, regardless of the amounts of each substance present at the beginning of the action.
 - At constant temperature the rate of reaction is proportional to the concentration of each kind of substance taking part in the reaction
- The above law is based on experimental observations – fundamentally empirical
- For the hypothetical reversible reaction: $A + B \rightleftharpoons C + D$
 - Rate of forward reaction: $r_f = k_f C_A C_B$
 - Rate of reverse reaction: $r_r = k_r C_C C_D$
- At equilibrium: rate of forward reaction = rate of reverse reaction and

$$k_f C_A C_B = k_r C_C C_D$$

- The ratio

$$\frac{k_f}{k_r} = K_C = \frac{C_C C_D}{C_A C_B}$$

- Is known as the equilibrium constant K_C .
- Generally, for: $aA + bB \rightleftharpoons cC + dD$

- ALT.

$$K_C = \frac{C_C^c C_D^d}{C_A^a C_B^b}$$


$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The square bracket stands for the concentration of the species at *equilibrium*. However, for concentrations of species not at equilibrium, the ratio is known as REACTION QUOTIENT, Q

Determination of equilibrium concentrations of reactants and products

- Before we can know the equilibrium constant, we need to first know the equilibrium concentrations of the reactants and products
- Example:
 - At 35 °C, 3.00 mol of pure nitrosyl chloride gas, NOCl(g), is contained in a sealed 3.00 L flask. The nitrosyl chloride gas decomposes to nitric oxide gas, NO(g), and chlorine gas, Cl₂(g) until equilibrium is reached. At equilibrium, the concentration of nitric oxide gas is 0.043 mol/L. Determine the equilibrium concentrations of nitrosyl chloride gas and chlorine gas under the conditions used



Solution

- $[NOCl]_o = \frac{3.00 \text{ mol}}{3.00 \text{ dm}^3} = 1.00 \text{ mol dm}^{-3}$

Concentration	$2NOCl_g$	\rightleftharpoons	$2NO_g$	+	Cl_2g
Initial	1.0		0		0
Change	-2x		+2x		+x
Equilibrium	$1.0 - 2x$		2x		x



- Given that $[NO]_{eq} = 0.043 \text{ mol dm}^{-3} = 2x$
 $\therefore x = \frac{0.043 \text{ mol dm}^{-3}}{2} = 0.0215 \text{ mol dm}^{-3}$

$\Rightarrow [Cl_2]_{eq} = x = 0.0215 \text{ mol dm}^{-3}$, and

$$\begin{aligned}
 [NOCl]_{eq} &= (1.00 - 2(0.0215)) \text{ mol dm}^{-3} \\
 &= (1.00 - 0.043) = 0.957 \text{ mol dm}^{-3}
 \end{aligned}$$

- Example 2:
- Phosphorus pentachloride gas, $\text{PCl}_5(\text{g})$, will decompose to phosphorous trichloride, $\text{PCl}_3(\text{g})$, and chlorine, $\text{Cl}_2(\text{g})$, at 160°C . In a sealed vessel, the reaction will proceed to equilibrium:



- A chemist places 3.00 mol of phosphorous pentachloride gas into a sealed 1.50 L flask at 160°C . At equilibrium, he observes there is 0.300 mol of phosphorous trichloride gas and some chlorine gas. Calculate the equilibrium concentrations of gaseous phosphorous pentachloride and chlorine.

- Given that $[PCl_5]_o = \frac{3.00 \text{ mol}}{1.5 \text{ dm}^3} = 2.00 \text{ mol dm}^{-3}$

Concentration	PCl_5g	\rightleftharpoons	PCl_3g	+	Cl_2g
Initial	2.00		0		0
Change	-x		+x		+x
Equilibrium	$2.00 - x$		x		x

- $[PCl_3]_{eq} = \frac{0.30 \text{ mol}}{1.5 \text{ dm}^3} = 0.2 \text{ mol dm}^{-3} = x$
 - $\Rightarrow [Cl_2]_{eq} = x = 0.2 \text{ mol dm}^{-3}$
 - $\therefore [PCl_5]_{eq} = 2.00 - x = 1.8 \text{ mol dm}^{-3}$
- With the examples above, we can then solve for the equilibrium constant

- Using example 1 above, the expression for the equilibrium constant is

$$\begin{aligned} K_c &= \frac{[NO]^2_{eq}[Cl_2]_{eq}}{[NOCl]_{eq}} = \frac{0.043^2 \times 0.0215}{0.957} \\ &= 4.15 \times 10^{-5} \end{aligned}$$

From example 2:



$$\begin{aligned} K_c &= \frac{[PCl_3]_{eq}[Cl_2]_{eq}}{[PCl_5]_{eq}} = \frac{0.20 \times 0.20}{1.80} \\ &= 2.22 \times 10^{-2} \end{aligned}$$

EQUILIBRIUM CONSTANT

PART 2

Characteristics of the Equilibrium Constant

- The magnitude of K and the position of equilibrium
 - $K \gg 1 \Rightarrow$ equilibrium favours product formation, equilibrium is therefore shifted to the right.
 - $K \ll 1 \Rightarrow$ equilibrium favours formation of reactants, equilibrium is therefore, shifted to the left
 - $K = 1 \Rightarrow$ equilibrium concentrations of the products are the same as those of the reactants
- Variation of K with stoichiometry of reaction
 - Consider the formation of ammonia (NH_3) from nitrogen (N_2) and hydrogen (H_2) at a given temperature, K is 0.013 for the reaction
$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$
 - Calculate K for the following reactions at this temperature

- a. $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$
- b. $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$
- c. $\text{NH}_3(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g)$
- d. $2\text{N}_2(g) + 6\text{H}_2(g) \rightleftharpoons 4\text{NH}_3(g)$

- SOLUTIONS:
- For the given reaction, the equilibrium constant expression is

$$K = \frac{[\text{NH}_3]}{[\text{N}_2][\text{H}_2]^3}$$

- a. The equilibrium expression for (a) is

$$K^a = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}} = \left(\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right)^{1/2} = K^{1/2}$$

- a. The equilibrium expression for (b) is

$$K^b = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \left(\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right)^{-1} = K^{-1} = \frac{1}{K}$$

- SOLUTIONS CONT'D

- c. The equilibrium constant expression for (c) is

$$K^c = \frac{[N_2]^{1/2} [H_2]^{3/2}}{[NH_3]} = \left(\frac{[N_2][H_2]^3}{[NH_3]^2} \right)^{1/2} = \left(\frac{1}{K} \right)^{1/2}$$

- d. The equilibrium expression for (d) is

$$K^d = \frac{[NH_3]^4}{[N_2]^2 [H_2]^6} = \left(\frac{[NH_3]^2}{[N_2][H_2]^3} \right)^2 = K^2$$

- The above results can be summarized as follows:

- i. The equilibrium expression for a reaction written in reverse is the reciprocal of that for the original reaction. That is $K_{reverse} = \frac{1}{K_{original}}$
 - ii. When the balanced equation for a reaction is multiplied by a factor n, the equilibrium expression for the new reaction is the original expression raised to the nth power. That is $K_{new} = (K_{original})^n$

SOLVING EQUILIBRIUM PROBLEMS



- For the gas phase reaction above, the concentrations found at 490°C in a certain experiment are, in mole litre⁻¹

$$[H_2] = 8.62 \times 10^{-4}, [I_2] = 2.63 \times 10^{-3}, [HI] = 1.02 \times 10^{-2}$$

- Calculate the equilibrium constant K_c for the equilibrium as written
- What would be the value of for the reverse reaction



SOLUTION:

a.

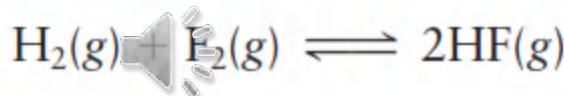
$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.02 \times 10^{-2})^2}{(8.62 \times 10^{-4})(2.36 \times 10^{-3})} = 45.9$$

- b. For the reaction written in the reverse direction, $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

$$K'_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{K_c} = \frac{1}{45.9} = 2.18 \times 10^{-2}$$

- Suppose that for a synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 moles of H_2 and 6.000 moles of F_2 are mixed in a 3.000-L flask. The equilibrium constant for the synthesis reaction at this temperature is 1.15×10^{-2} . Calculate the equilibrium concentration of each component
- SOLUTION:

We begin as usual by writing the balanced equation for the re



The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$$

The initial concentrations are

$$[\text{H}_2]_0 = \frac{3.000 \text{ mol}}{3.000 \text{ L}} = 1.000 \text{ M}$$

$$[\text{F}_2]_0 = \frac{6.000 \text{ mol}}{3.000 \text{ L}} = 2.000 \text{ M}$$

$$[\text{HF}]_0 = 0$$

Concentration	$H_2(g)$	+	$F_2(g)$	\rightleftharpoons	$2HF(g)$
Initial	1.00		2.00		0
Change	-x		-x		2x
Equilibrium	$1.00 - x$		$2.00 - x$		$2x$

Substituting the equilibrium concentrations into the equilibrium expression gives

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)}$$

To solve for x , we perform the indicated multiplication,

$$(1.000 - x)(2.000 - x)(1.15 \times 10^2) = (2x)^2$$

to give

$$(1.15 \times 10^2)x^2 - 3.000(1.15 \times 10^2)x + 2.000(1.15 \times 10^2) = 4x^2$$

and collect terms,

$$(1.11 \times 10^2)x^2 - (3.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

This expression is a quadratic equation of the general form

$$ax^2 + bx + c = 0$$

where the roots can be obtained from the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this example $a = 1.11 \times 10^2$, $b = -3.45 \times 10^2$, and $c = 2.30 \times 10^2$. Substituting these values into the quadratic formula gives two values for x :

$$x = 2.14 \text{ mol/L} \quad \text{and} \quad x = 0.968 \text{ mol/L}$$

- Since x cannot be greater than the initial concentrations of any of the components, $x = 2.14 \frac{\text{mol}}{\text{L}}$ is not valid. Hence, $x = 0.968 \frac{\text{mol}}{\text{L}}$. And the equilibrium concentrations are as follows:

$$[\text{H}_2] = 1.000 \text{ M} - 0.968 \text{ M} = 3.2 \times 10^{-2} \text{ M}$$

$$[\text{F}_2] = 2.000 \text{ M} - 0.968 \text{ M} = 1.032 \text{ M}$$

$$[\text{HF}] = 2(0.968 \text{ M}) = 1.936 \text{ M}$$

- For confirmation, substitute these values back into the equilibrium expression $\frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(1.936)^2}{(3.2 \times 10^{-2})(1.032)} = 1.13 \times 10^2$

This value is in close agreement with the given value for $K (1.15 \times 10^2)$, so the calculated equilibrium concentrations are correct.

Equilibrium Constant in terms of Partial Pressure



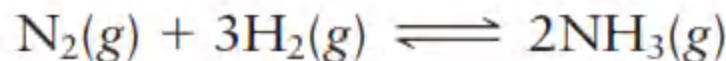
- For gas phase equilibria, it is easy to measure the pressure of gases than the molar concentration.
- The equilibrium constant can therefore be expressed in terms of the partial pressure of the gaseous components provided the gases behave nearly ideally during the experiment. Consequently, from the ideal gas equation:

$$PV = nRT$$

- Which can also be written as 

$$P = \left(\frac{n}{V}\right)RT = CRT$$

- where C is the molar concentration.
- Thus, at constant T , pressure is directly proportional to molar concentration. For example, in the synthesis of ammonia from hydrogen and nitrogen



- The equilibrium constant expression is

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{C_{\text{NH}_3}^2}{(C_{\text{N}_2})(C_{\text{H}_2}^3)}$$

- Substituting for C in terms of the partial pressure as obtained in the previous slide i.e. $C = \frac{P}{RT}$ to obtain

$$= \frac{\left(\frac{P_{\text{NH}_3}}{RT}\right)^2}{\left(\frac{P_{\text{N}_2}}{RT}\right)\left(\frac{P_{\text{H}_2}}{RT}\right)^3} = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4}$$

$$= \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} \times (RT)^{4-2} = K_p (RT)^2$$

– Where $K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$

- Consider also the synthesis of hydrogen iodide from fluorine and iodine molecules: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K_c = \frac{C_{HI}^2}{C_{H_2} C_{I_2}} = \frac{\left(\frac{P_{HI}}{RT}\right)^2}{\frac{P_{H_2}}{RT} \frac{P_{I_2}}{RT}} = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} \times (RT)^{2-2} = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} \times (RT)^0$$

$$\Rightarrow K_c = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} = K_p$$

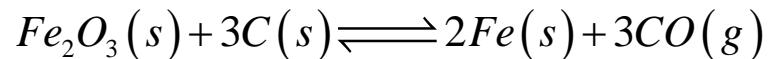


- A careful look at the two examples above will show that, for a general hypothetical reaction: $aA + bB \rightleftharpoons cC + dD$
- The relationship between K_c and K_p is
- $$K_c = K_p (RT)^{-\Delta n} \quad \text{OR} \quad K_p = K (RT)^{\Delta n}$$

$\Delta n = \text{sum of the coefficients of gaseous products} - \text{sum of the coefficients of gaseous reactants}$
i.e. $\Delta n = (c + d) - (a + b)$

TYPES OF EQUILIBRIA

- Reversible reactions involving species in the same phase such as the various examples given above – homogeneous equilibria
- Reversible processes involving species existing in more than one phase – heterogeneous equilibria. For example: $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$



- These reactions contain pure solids (CaCO_3 , CaO , Fe_2O_3 , C, Fe and Fe_3O_4) and pure liquids (H_2O and PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K_1 = [\text{CO}_2], K_{p,1} = P_{\text{CO}_2}$$

$$K_2 = [\text{CO}]^3, K_{p,2} = P_{\text{CO}}^3$$

$$K_3 = \frac{1}{[\text{H}_2]^4}, K_{p,3} = \frac{1}{P_{\text{H}_2}^4}$$

$$K_4 = \frac{1}{[\text{Cl}_2]}, K_{p,4} = \frac{1}{P_{\text{Cl}_2}}$$

PROBLEMS ON EQUILIBRIUM INVOLVING PARTIAL PRESSURES



- Lexan is a plastic used to make compact discs, eyeglass lenses, and bullet-proof glass. One of the compounds used to make Lexan is phosgene (COCl_2), a poisonous gas. Phosgene is produced by the reaction: $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$
for which $K_c = 4.5 \times 10^9$ at 100.8°C . Calculate K_p at 100.8°C .

- SOLUTION

Recall that $K_p = K_c (RT)^{\Delta n}$ where $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$$\begin{aligned}\Rightarrow K_p &= 4.5 \times 10^9 \times (0.0821 \times (100.8 + 273))^{(1-2)} \\ &= \frac{4.5 \times 10^9}{(0.0821 \times 373.8)} = 1.47 \times 10^8\end{aligned}$$


- In a study of the equilibrium $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$
A sample of 0.6365 g of pure SO_3 is placed in a 1.00 litre container and heated to a temperature of 827°C . The equilibrium total pressure at this temperature is 1.00 atm. Calculate the percent dissociation of SO_3 under these conditions and the values of K_c and K_p

- SOLUTION

$$\text{Mole of } \text{SO}_3 = 0.6365/80 = 0.00795 \text{ mole}$$

$$\text{Total mole of gases at equilibrium, } n_{Total} = \frac{PV}{RT} = \frac{1.00 \times 1.00}{0.0821 \times 1100} = 1.107 \times 10^{-2} \text{ mole}$$

Concentration	$2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$		
Initial	0.00795	0	0
Change	-2x	+2x	+x
Equilibrium	0.00795 - 2x	2x	x

At equilibrium:

$$n_{Total} = 0.00795 - 2x + 2x + x = 0.00795 + x$$

$$\text{i.e. } n_{Total} = 0.00795 + x = 0.01107$$

$$\Rightarrow x = 0.01107 - 0.00795 = 0.00312 \text{ mole}$$

$$\Rightarrow [\text{SO}_3] = 0.00795 - 2x = 0.00172 \text{ mol L}^{-1}$$

$$[\text{SO}_2] = 2x = 0.00623 \text{ mol L}^{-1}$$

$$[\text{O}_2] = x = 0.00312 \text{ mol L}^{-1}$$

$$K_c = \frac{[SO_2]^2 [O_2]}{[SO_3]^2} = \frac{0.00623^2 \times 0.00312}{0.00172^2} = 0.0409$$

$$K_p = K_c (RT)^{\Delta n}$$

$$\Rightarrow K_p = (0.0821 \times 1100)^{(2+1)-(2)}$$

$$= 0.0409 \times 0.0821 \times 1100$$

$$= 3.70$$

$$\begin{aligned}\% \text{ dissociation of } SO_3 &= \frac{2x}{0.00795} \times 100 \\ &= \frac{0.00623}{0.00795} \times 100 = 78.3\%\end{aligned}$$

- At a particular temperature, $K_n = 0.25$ for the reaction



- A flask containing only N_2O_4 at an initial pressure of 4.5 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.
- A flask containing only NO_2 at an initial pressure of 9.0 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.
- From your answers to parts a and b, does it matter from which direction an equilibrium position is reached?

The reaction must proceed to products to reach equilibrium because no product is present initially. Summarizing the problem in a table where x atm of N_2O_4 reacts to reach equilibrium:



Initial	4.5 atm	0
Change	$-x$	$+2x$
Equil.	$4.5 - x$	$2x$



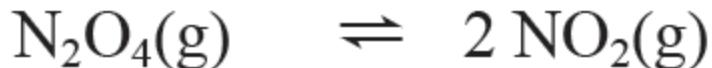
$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(2x)^2}{4.5 - x} = 0.25, \quad 4x^2 = 1.125 - (0.25)x, \quad 4x^2 + (0.25)x - 1.125 = 0$$

$$x = \frac{-0.25 \pm [(0.25)^2 - 4(4)(-1.125)]^{1/2}}{2(4)} = \frac{-0.25 \pm 4.25}{8}, \quad x = 0.50$$

- The other value ($x = -0.5625$) being negative and unreasonable

$$P_{\text{NO}_2} = 2x = 1.0 \text{ atm}; \quad P_{\text{N}_2\text{O}_4} = 4.5 - x = 4.0 \text{ atm}$$

- b.
The reaction must shift to reactants (shift left) to reach equilibrium.



Initial	0	9.0 atm	
Change	+x	← -2x	
Equil.	x	9.0 - 2x	

$$K_p = \frac{(9.0 - 2x)^2}{x} = 0.25, \quad 4x^2 - (36.25)x + 81 = 0$$

$$\text{Solving: } x = \frac{-(-36.25) \pm [(-36.25)^2 - 4(4)(81)]^{1/2}}{2(4)}, \quad x = 4.0 \text{ atm}$$

- The other value $x = 5.1$, though positive, is impossible because $2x = 10.2 \text{ atm}$, which will be more than 9.0 atm

$$P_{\text{N}_2\text{O}_4} = x = 4.0 \text{ atm}; \quad P_{\text{NO}_2} = 9.0 - 2x = 1.0 \text{ atm}$$

PRACTISE QUESTIONS

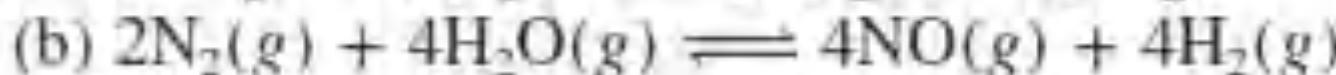
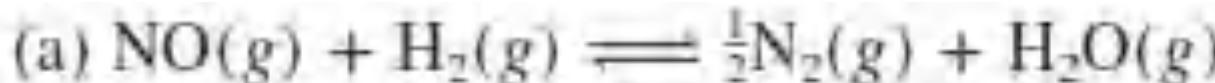
- A change in reaction conditions increases the rate of a certain forward reaction more than that of the reverse reaction. What is the effect on the equilibrium constant and on the concentrations of reactants and products at equilibrium?
- Is K very large or very small for a reaction that goes essentially to completion? Explain.
- White phosphorus, P_4 , is produced by the reduction of phosphate rock, $Ca_3(PO_4)_2$. If exposed to oxygen, the waxy, white solid smokes, bursts into flames, and releases a large quantity of heat:



- Does this reaction have a large or small equilibrium constant? Explain.
- At a particular temperature, $K_c = 1.6 \times 10^{-2}$ for



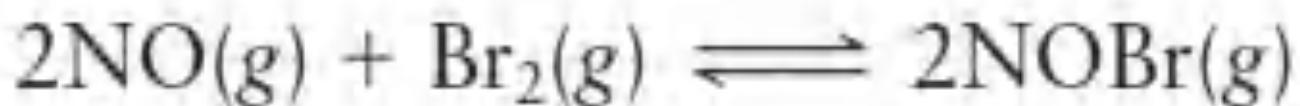
Calculate K_c for each of the following reactions:



- Ammonium hydrogen sulfide decomposes according to the following reaction, for which $K_p = 0.11$ at 250°C :



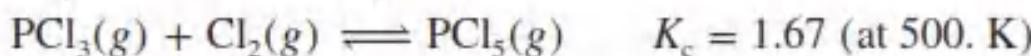
- If 55.0 g of $\text{NH}_4\text{HS}(s)$ is placed in a sealed 5.0-L container, what is the partial pressure of $\text{NH}_3(g)$ at equilibrium?
- Nitric oxide and bromine at initial partial pressures of 98.4 torr and 41.3 torr, respectively, were allowed to react at 300. K. At equilibrium the total pressure was 110.5 torr. The reaction is



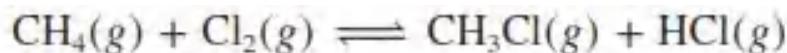
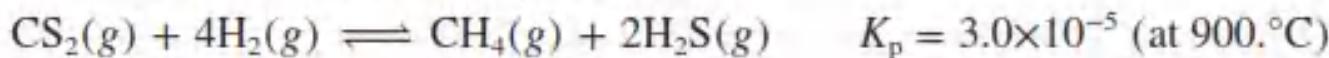
- Calculate the value of K_p .
- What would be the partial pressures of all species if NO and Br_2 , both at an initial partial pressure of 0.30 atm, were allowed to come to equilibrium at this temperature?

• 1

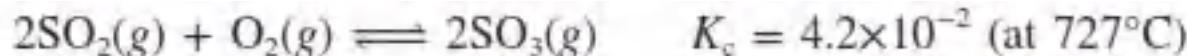
Calculate K_p for the following reaction:



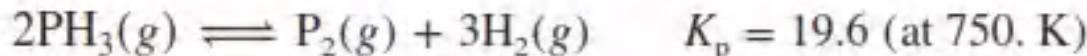
Calculate K_c for the following reaction:



At 1500 K, $K_p = 1.6 \times 10^4$. In the reaction mixture, $P_{\text{CH}_4} = 0.13$ atm, $P_{\text{Cl}_2} = 0.035$ atm, $P_{\text{CH}_3\text{Cl}} = 0.24$ atm, and $P_{\text{HCl}} = 0.47$ atm. Is CH_3Cl or CH_4 forming?



Suppose 3.4 mol of SO_2 , 1.5 mol of O_2 , and 1.2 mol of SO_3 are placed in a 2.0-L flask. Is the system at equilibrium? If not, in which direction will the reaction proceed?



In a reaction mixture at equilibrium, $P_{\text{PH}_3} = 0.112$ atm and $P_{\text{P}_2} = 0.215$ atm. What is the equilibrium partial pressure of H_2 ?

FACTORS AFFECTING EQUILIBRIUM POSITION



THE LE – CHATELIER'S PRINCIPLE



Le Châtelier's principle applies to many systems.

Source: © AfriPics.com/Alamy

- When there is a change in the conditions of a system so that a system is no longer at equilibrium, the systems has the remarkable ability to adjust itself and re-attain equilibrium. This phenomenon is described by **Le Châtelier's principle:**
 - when a chemical system at equilibrium is disturbed, it re-attains equilibrium by undergoing a net reaction that reduces the effect of the disturbance.
- How is a system “disturbed”?
 - At equilibrium, **Q equals K .** ***The system is disturbed*** when a change in conditions forces it temporarily out of equilibrium ($Q \neq K$). Three common disturbances are a change
 - in concentration,
 - in pressure (caused by a change in volume),
 - in temperature.
- Each of these will be discussed in details

- **The Effect of a Change in Concentration**
- When a system at equilibrium is disturbed by a change in concentration of one of the components, it reacts in the direction that reduces the change:
 - If the concentration of A is increased, the system reacts to consume some of that component.
 - If the concentration of A is decreased, the system reacts to produce some of it.
- Only components that appear in ***Q can have an effect, so changes in the amounts of*** pure liquids and solids cannot.
- **A Qualitative View of a Concentration Change At 523 K, the $\text{PCl}_3\text{-Cl}_2\text{-PCl}_5$ system reaches equilibrium when**

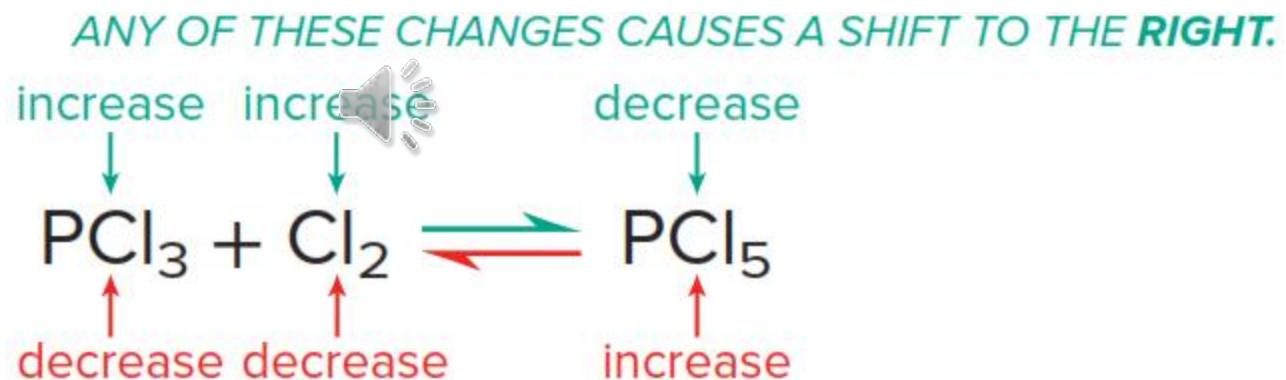


$$Q_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = 24.0 = K_c$$

- Starting with Q_c equal to K_c , let's think through some changes in concentration:
 - Adding a reactant. What happens if we disturb the system by adding some Cl_2 gas?
 - To reduce this disturbance, the system will consume some of the added Cl_2 by shifting toward product.
 - With regard to the reaction quotient, when the $[\text{Cl}_2]$ term increases, the value of Q_c decreases; thus, $Q_c < K_c$. As some of the added Cl_2 reacts with some of the PCl_3 to form more PCl_5 , the denominator becomes smaller again and the numerator larger, until eventually $Q_c = K_c$ again.
 - Notice the changes in the new equilibrium concentrations: $[\text{Cl}_2]$ and $[\text{PCl}_5]$ are higher than in the original equilibrium position, and $[\text{PCl}_3]$ is lower. Nevertheless, the ratio of values gives the same K_c .
 - Thus, the equilibrium position shifts to the right when a component on the left is added:

- ***Removing a reactant. What happens if we disturb the system by removing some PCl_3 ?***
 - To reduce this disturbance, the system will replace the PCl_3 by consuming some PCl_5 and proceeding toward reactants.
 - With regard to Q_c , ***when the $[\text{PCl}_3]$ term decreases, Q_c increases, so $Q_c > K_c$. As some PCl_5 decomposes to PCl_3 and Cl_2 , the numerator decreases and the denominator increases until $Q_c = K_c$ again.***
 - ***Once again, the new and old equilibrium concentrations are different, but the value of K_c is not.***
 - ***Thus, the equilibrium position shifts to the left when a component on the left is removed:***
- ***Adding or removing a product.***
 - ***The same points we just made for a reactant hold for a product.***
 - If we add PCl_5 , the equilibrium position shifts to the left to consume PCl_5 ;
 - if we remove some PCl_5 , the equilibrium position shifts to the right to produce PCl_5 .

- In other words, no matter how the disturbance in concentration comes about,
 - *the system reacts to consume some of the added substance or produce some of the removed substance to make $Q_c = K_c$ again*



ANY OF THESE CHANGES CAUSES A SHIFT TO THE LEFT.

Effect of Change of Volume, Pressure, or Inert Gas on Equilibrium and Product Formation

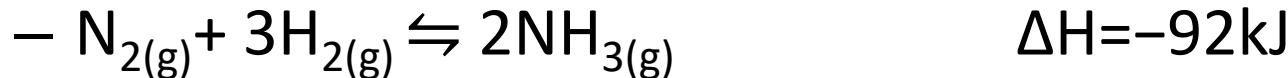
- **Change of volume, pressure, or inert gases**
 - has no effect on reactions of liquids and solids.
 - They may have an effect in gaseous reactions only when the difference in the sum of the number of reactant and product molecules (Δn) is not zero.
- **When $\Delta n = 0$:**
 - **no effect on Equilibrium and Product Formation** on changing the volume, pressure or inert gas.
- **When $\Delta n = +ve$:**
 - Increase of pressure or decrease in volume will decrease the formation of the product. Decrease of pressure or increase of volume shall have the opposite effect of increasing the product formation.
 - Inert gases do not take part in the reaction and shall increase the volume or pressure only.

- At **constant pressure**, the addition of inert gas increases the volume, so increase the product formation.
- At **constant volume**, the addition of inert gas increases the pressure, so decreases the product formation.
- In the decomposition of phosphorus pentachloride
- $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{PCl}_2$ for which $\Delta n = +1$.
 - Increase of pressure or decrease in volume decreases the decomposition of PCl_5
 - At **constant pressure**, the addition of inert gas increases the PCl_5 formation.
 - At **constant volume**, the addition of inert gas decreases the PCl_5 formation.

- **When $\Delta n = -ve$:**
 - An increase of pressure or decrease in volume will increase the formation of the product.
- **At constant pressure,**
 - the addition of inert gas increases the volume, so decrease the product formation.
- **At constant volume,**
 - the addition of inert gas increases the pressure, so increases the product formation
- In the formation of ammonia $N_2 + 3H_2 \rightleftharpoons 2NH_3$ for which $\Delta n = -2$.
 - The increase of pressure or decrease in volume increases the formation of ammonia.
- **At constant pressure,**
 - the addition of inert gas decreases ammonia formation.
- **At constant volume,**
 - the addition of inert gas increases ammonia formation.

- Effect of Change of Temperature on Equilibrium and Product Formation
 - The individual reaction in the equilibrium can be either endothermic or exothermic.
 - Likewise, at equilibrium net energy involved may make the reversible reactions either endothermic or exothermic.
- According to Le Chatelier's Principles,
 - In exothermic equilibrium,  $\text{reactants} \rightleftharpoons \text{products} + \text{energy}$
 - an increase in temperature decreases the product formation and decrease in temperature increases product formation.
 - In endothermic reactions, $\text{reactants} + \text{energy} \rightleftharpoons \text{products}$
 - an increase in temperature increases the product formation and decrease in temperature decreases the product formation
- For example:

- Consider a reaction



- Increase in Temperature

- This prefers an endothermic reaction because it takes energy.
 - An endothermic reaction is a reverse reaction and it is favoured.
 - The yield of product (NH_3) decreases.

- Decrease in Temperature



- This prefers an exothermic reaction because it gives energy.
 - An exothermic reaction is a forward reaction and it is favoured.
 - The yield of product (NH_3) increases.
- It should be noted that all the constraints considered above will only affect the position of the equilibrium. The only factor that changes the value of the equilibrium constant is **TEMPERATURE**

Effect of Catalyst on Equilibrium Position

- What is a CATALYST?
 - A substance that changes the rate of reactions (increase or decrease) without quantitatively taking part in the reaction.
 - In a reversible reaction, the change of reaction rate is the same for both forward and backward reactions.
 - The ratio of the reaction rates remains the same and so the equilibrium constant.
 - According to Le Chatelier's principles, the presence of the catalyst may speed up or delay the attainment of equilibrium but will not affect the equilibrium concentration.

EQUILIBRIA IN SOLUTION



ACID – BASE EQUILIBRIA

- Acids and bases are in many common consumer products and are indispensable in academic and industrial research.
- An *acid is a substance with H in its formula that dissociates in water to yield H_3O^+*
- A *base is a substance with OH in its formula that dissociates in water to yield OH^-*
- When an acid and a base react, they undergo neutralization. The meaning of this term has changed, as we'll see, but in the Arrhenius sense, neutralization occurs when *the H^+ from the acid and the OH^- from the base form H_2O .*

Substance	Use
Acids	
Acetic acid, CH_3COOH	Flavoring, preservative (vinegar)
Citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	Flavoring (lemon juice)
Ascorbic acid, $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	Vitamin C; nutritional supplement
Aluminum salts, $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	In baking powder, with sodium hydrogen carbonate
Bases	
Sodium hydroxide (lye), NaOH	Oven and drain cleaners
Ammonia, NH_3	Household cleaner
Sodium carbonate, Na_2CO_3	Water softener, grease remover
Sodium hydrogen carbonate, NaHCO_3	Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid
Sodium phosphate, Na_3PO_4	Cleaner for surfaces before painting or wallpapering

Source: © McGraw-Hill Education/Stephen Frisch, photographer

- Variation in Acid Strength: The Acid-Dissociation Constant (K_a)
- Acids (and bases) are classified by their ***strength***,
 - ***the amount of H_3O^+ (or OH^-) produced per mole of substance dissolved***
 - by the extent of their dissociation into ions.
- Because acids and bases  are electrolytes, their strength correlates with electrolyte strength:
 - ***strong electrolytes dissociate completely, and***
 - ***weak electrolytes dissociate slightly.***
- Strong acids dissociate completely into ions in water:



- In a dilute solution of a strong acid,



- ***HA molecules are no longer present:***
- $[\text{H}_3\text{O}^+] = [\text{A}^-] \approx [\text{HA}]_{\text{init}}$. In other words,
- $[\text{HA}]_{\text{eq}} \approx 0$,
- The value of K_c is extremely large:

$$Q_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad (\text{at equilibrium, } Q_c = K_c \gg 1)$$

- Example of such acids include HNO_3 , HCl , H_2SO_4 , HOCl , HClO_4 etc

- ***Weak acids dissociate slightly into ions in water***



- In a dilute solution of a weak acid, ***the great majority of HA molecules are undissociated.***
- Thus, $[\text{H}_3\text{O}] \ll [\text{HA}]_{\text{init}}$, and $[\text{HA}]_{\text{eq}} \approx [\text{HA}]_{\text{init}}$, so K_c is very small.

Acid Dissociation Constant, K_a

- The reaction of a weak acid, HA, with water forms a dynamic equilibrium involving H_3O^+ and a conjugate base, A^-
- The equilibrium constant is called the ACID DISSOCIATION/IONIZATION CONSTANT

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})][\text{HA}(\text{aq})]}$$

- As earlier discussed the concentration terms for pure liquids and solids are equal to 1 and do not appear in the equilibrium expression. So the acid dissociation constant becomes:

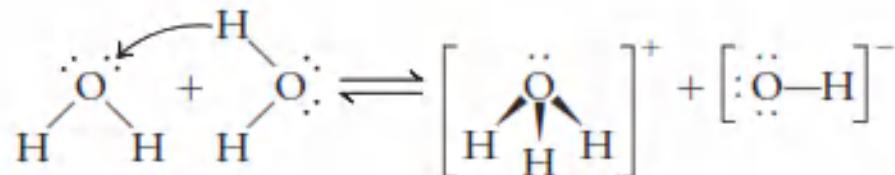
$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

– Where $[\text{H}^+_{\text{aq}}] = [\text{H}_3\text{O}^+_{\text{aq}}]$

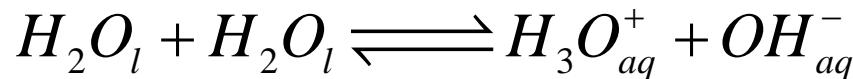
- Acid-dissociation constants of weak acids range over many orders of magnitude.

Magnitude of K_a	% Dissociation in a 1 M Solution of HA	Specific Example (K_a Value, % Dissociation)
Relatively high K_a ($\sim 10^{-2}$)	~10%	1 M chlorous acid (HClO_2) ($K_a = 1.1 \times 10^{-2}$, 10.%)
Moderate K_a ($\sim 10^{-5}$)	~0.3%	1 M acetic acid (CH_3COOH) ($K_a = 1.8 \times 10^{-5}$, 0.42%)
Relatively low K_a ($\sim 10^{-10}$)	~0.001%	1 M hydrocyanic acid (HCN) ($K_a = 6.2 \times 10^{-10}$, 0.0025%)

- Thus, for solutions of the same initial HA concentration, ***the smaller the K_a , the lower the percent dissociation of HA:***
 - Weaker acid \Rightarrow lower % dissociation of HA \Rightarrow smaller K_a
- AUTO-IONIZATION OF WATER AND THE pH SCALE
 - A substance is said to be *amphoteric* if it can behave either as an acid or as a base.
 - Water is the most common amphoteric substance.
 - This behaviour can be seen in the auto-ionization of water, which involve the transfer of proton from one water molecule to another to produce hydroxonium (H_3O^+) and hydroxide (OH^-) ions



- In this reaction one water molecule acts as an acid by furnishing a proton, and the other acts as a base by accepting the proton.



- The equilibrium constant for this auto-ionization reaction is

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

- K_w is called the ion – product of water (also known as the dissociation constant of water). At 25 °C, experiment has shown that for any aqueous system: $[H^+] = [OH^-] = 1.0 \times 10^{-7} M \Rightarrow K_w = [H^+][OH^-] = (1.0 \times 10^{-7} M)(1.0 \times 10^{-7} M) = 1.0 \times 10^{-14} M^2$
 - The unit is customarily omitted as in the case of equilibrium constant
- There are three possible situations all at 25 °C:

- A neutral solution, where $[H^+] = [OH^-]$
- An acidic solution, where $[H^+] > [OH^-]$
- A basic solution, where $[OH^-] > [H^+]$

- In each case, $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

- Illustrations
 - A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[H_3O^+] = 3.0 \times 10^{-4}$ M. Calculate the $[OH^-]$. Is the solution neutral, acidic, or basic?
- SOLUTION

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

$$\Rightarrow [OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}} = 3.3 \times 10^{-11}$$

- Since $[H^+] > [OH^-]$, the solution is acidic
- It makes sense that adding an acid to water results in an acidic solution.
- Also, since $[H_3O^+]$ is greater than 10^{-7} M, $[OH^-]$ must be less than 10^{-7} M to give a constant K_w

- Can you try this?
 - Calculate $[H_3O^+]$ in a solution that has $[OH^-] = 6.7 \times 10^{-2} M$ at **25°C**. Is the solution neutral, acidic, or basic?
- To handle numbers with negative exponents more conveniently in calculations, we convert them to positive numbers using a numerical system called a *p-scale*, the negative of the common (base-10) logarithm of the number. Applying this numerical system to $[H_3O^+]$ gives pH, the negative of the common logarithm of $[H^+]$ (or $[H_3O^+]$):

$$pH = -\log_{10} [H^+]$$

What is the pH of a $10^{-12} M$ H_3O^+ solution?

$$pH = -\log [H_3O^+] = -\log 10^{-12} = (-1)(-12) = 12$$

pH of an acidic solution < 7.00

pH of a neutral solution = 7.00

pH of a basic solution > 7.00

- A p-scale is used to express other quantities as well:

- Hydroxide ion concentration can be expressed as pOH:

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

- Acidic solutions have a higher pOH (lower $[OH^-]$) than basic solutions.
 - Equilibrium constants can be expressed as pK :

- $pK = -\log K$



- Specifically for weak acids:

$$pK_a = -\log K_a \text{ and } K_a = 10^{-pK_a}$$

- ***A low pK corresponds to a high K . So***

- a reaction that reaches equilibrium with mostly products present (proceeds far to the right) has a low pK (***high K***);
 - a reaction that has mostly reactants present at equilibrium has a high pK (***low K***).

- An important relationship:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

$$-\log K_w = (-\log [\text{H}_3\text{O}^+]) + (-\log [\text{OH}^-]) = -\log (1.0 \times 10^{-14})$$

$$\text{p}K_w = \text{pH} + \text{pOH} = 14.00 \quad (\text{at } 25^\circ\text{C})$$

- pH for Strong Acids and Bases:

- The equilibrium concentration of H_3O^+ is equal to the initial concentration of a strong acid:
 - **0.200 M HCl dissociates to produce 0.200 M H_3O^+ .**
 - The equilibrium concentration of OH^- is equal to the initial concentration of an alkali metal hydroxide:
 - **0.200 M KOH dissociates to produce 0.200 M OH^- .**

- Example:
- Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH for each solution at 25°C:
 - (a) 0.20 M HCl
 - (b) 0.0012 M Mg(OH)₂, used as an antacid in the treatment of heartburns
- **SOLUTION**
- **For 0.20 M HCl:**
 - $[H_3O^+] = 0.20 \text{ M}$
 - $pH = -\log_{10}[H_3O^+] = -\log_{10}0.20 = 0.70$
 - $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.20} = 5 \times 10^{-14} \text{ M}$
 - $pOH = -\log_{10}[OH^-] = -\log_{10}(5 \times 10^{-14}) = 13.3$



- For 0.0012 M $Mg(OH)_2$
- $Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$
 - $[OH^-] = 2 \times 0.0012\text{ M} = 0.0024\text{ M}$
 - $pH = -log_{10}[OH^-] = -log_{10}0.0024 = 2.62$
 - $[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0024} = 4.17 \times 10^{-12}\text{ M}$
 - $pH = -log_{10}[H^+] = -log_{10}(4.17 \times 10^{-12}) = 11.38$
- The strong acid has $pH < 7$ and the strong base has a $pH > 7$, as expected. In each case, $pH + pOH = 14$, so the arithmetic seems correct.
- TRY THIS!!!
 - Sodium hydroxide is used to clear clogged drains. A solution of NaOH has a pOH of 4.48 at 25°C . What are its pH , $[OH^-]$, and $[H_3O^+]$?

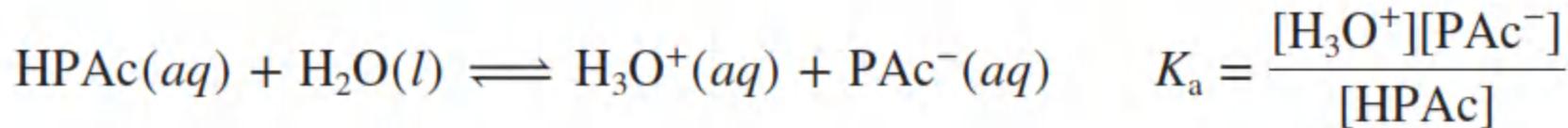
SOLVING PROBLEMS ON ACID-BASE EQUILIBRIA

- Problem Phenylacetic acid ($C_6H_5CH_2COOH$, simplified here to HPAc) builds up in the blood of persons with phenylketonuria, an inherited disorder that, if untreated, causes mental retardation and death. A study of the acid shows that the pH of 0.12 M HPAc is 2.62. **What is the K_a of phenylacetic acid?**



- **SOLUTION**

- **Given that $pH = 2.62 \Rightarrow [H^+] = 10^{-2.62} = 0.0024\text{ M}$**
- Equation for the dissociation of HPAc is



- Let us set up a ICE Table

Concentration	HPAc_{aq}	\rightleftharpoons	H^+_{aq}	+	PAc^-_{aq}
Initial	0.12		0		0
Change	-x		+x		+x
Equilibrium	$0.12 - x$		x		x

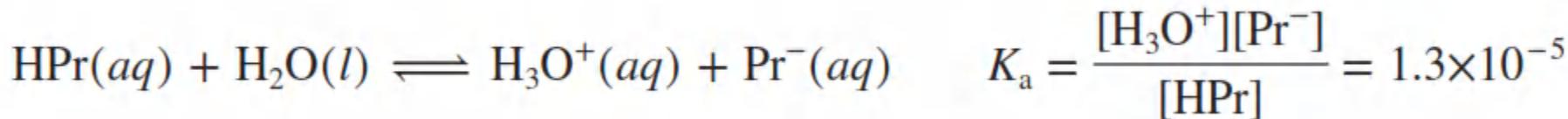
- But $[\text{H}^+] = 0.0024 \text{ M} = [\text{PAc}^-] = x$



$$K_a = \frac{[\text{H}^+][\text{PAc}^-]}{[\text{HPAc}]} = \frac{(x)(x)}{(0.12 - x)} = \frac{0.0024^2}{0.12 - 0.0012} = 4.84 \times 10^{-5}$$

Example 2:

- Propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, which we simplify to HPr) is a carboxylic acid whose salts are used to retard mold growth in foods. What are the $[\text{H}_3\text{O}^+]$ and the pH of 0.10 M HPr ($K_a = 1.3 \times 10^{-5}$)
- The equation for the dissociation and the dissociation constant is:**



Concentration	HPr_{aq}	\rightleftharpoons	H^+_{aq}	+	Pr^-_{aq}
Initial	0.10		0		0
Change	-x		+x		+x
Equilibrium	$0.10 - x$		x		x

$$K_a = \frac{[H^+][Pr^-]}{[HPr]} = \frac{(x)(x)}{(0.10-x)} = \frac{x^2}{0.10-x}$$

- A trick to avoid solving a quadratic equation for this kind of problem is to assume that since the acid is a weak acid (from the value of the K_a) and also that the initial concentration is very high(0.10 M, relatively), the amount of it dissociated is negligibly small compared to the initial concentration such that $0.10 - x \approx 0.10$.
- This assumption will be reasonable if the % dissociation < 5%, otherwise, the quadratic equation will need to be solved to find x

- Using the assumption above

$$K_a = \frac{[H^+][\text{Pr}^-]}{[H\text{Pr}]} = \frac{(x)(x)}{(0.10-x)} = \frac{x^2}{0.10-x} \approx \frac{x^2}{0.10}$$

$$\Rightarrow x^2 = 0.10 \times K_a = 0.10 \times 1.3 \times 10^{-5} = 1.3 \times 10^{-6}$$

$$\Rightarrow x = [H^+] = [\text{Pr}^-] = \sqrt{(1.3 \times 10^{-6})} = 1.14 \times 10^{-3} M$$

- Is our assumption reasonable? Let us find out

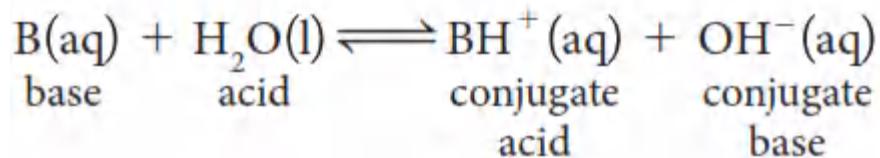
$$\begin{aligned}\text{Percent dissociation} &= \frac{\text{amount dissociated}}{\text{initial amount}} \times 100\% \\ &= \frac{1.14 \times 10^{-3}}{0.10} \times 100\% \\ &= 1.14\%\end{aligned}$$

- Since this is less than 5%, it is a reasonable one

$$pH = -\log_{10} [H^+] = -\log_{10} (1.14 \times 10^{-3}) = 2.94$$

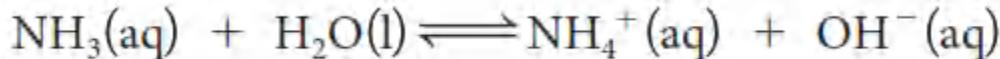
- Base Dissociation Constant

- Many compounds are bases even though they do not contain the hydroxide ion.
- These compounds increase the concentration of hydroxide ions in aqueous solution because of their reaction with water.



- In other words, these bases are Brønsted–Lowry bases.

- For example, according to the Brønsted–Lowry theory, ammonia, $\text{NH}_3(\text{aq})$, is a base because it reacts with water to form aqueous hydroxide ions:



- The equilibrium position of this reaction is far to the left, ammonia is considered to be a weak base.
- Compounds that react with water as ammonia does are generally weak bases.

For the reaction of a generic base with water, the equilibrium law equation, K , is written as follows:

$$K = \frac{[\text{OH}^-(\text{aq})][\text{BH}^+(\text{aq})]}{[\text{B}(\text{aq})][\text{H}_2\text{O}(\text{l})]}$$

- However, since the concentration (density) of water is a constant, it can be incorporated into the value of K (just as it was in the equilibrium law equation for K_a). This yields a new constant, K_b , called the base ionization constant:

$$K_b = \frac{[\text{BH}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{B}(\text{aq})]}$$

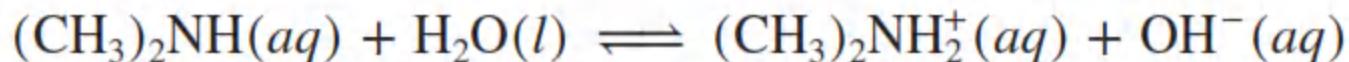
- For the ammonia – water equilibrium; the K_b for the reaction is:

$$K_b = \frac{[\text{OH}^-(\text{aq})][\text{NH}_4^+(\text{aq})]}{[\text{NH}_3(\text{aq})]}$$

Base-dissociation constants can be expressed as $\text{p}K_b$ values:

$$\text{p}K_b = -\log K_b \quad \text{and} \quad 10^{-\text{p}K_b} = K_b$$

- Problem Dimethylamine, $(\text{CH}_3)_2\text{NH}$, a key intermediate in detergent manufacture, has a K_b of 5.9×10^{-4} . What is the pH of 1.5 M $(\text{CH}_3)_2\text{NH}$?
- **SOLUTION:** Writing the balanced equation and K_b expression:



$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$

- Setting up the ICE table as usual

Concentration (M)	$(\text{CH}_3)_2\text{NH}(aq)$	$\text{H}_2\text{O}(l)$	$(\text{CH}_3)_2\text{NH}_2^+(aq)$	$\text{OH}^-(aq)$
Initial	1.5	—	0	0
Change	$-x$	—	$+x$	$+x$
Equilibrium	$1.5 - x$	—	x	x

- Making similar assumption as we did under acid dissociation (assuming x is negligibly small as compared to the initial concentration of the base) i. e. $1.5 - x \approx 1.5$. Substituting into the K_b expression to have

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} = 5.9 \times 10^{-4} \approx \frac{x^2}{1.5}$$

$$x = [\text{OH}^-] \approx 3.0 \times 10^{-2} M$$

- How reasonable is our assumption? Let us check

$$\begin{aligned}\text{Percent dissociation} &= \frac{\text{amount dissociated}}{\text{initial amount}} \times 100\% \\ &= \frac{3.0 \times 10^{-2}}{1.5} \times 100\% \\ &= 2.00\% < 5\%; \text{ assumption justified}\end{aligned}$$

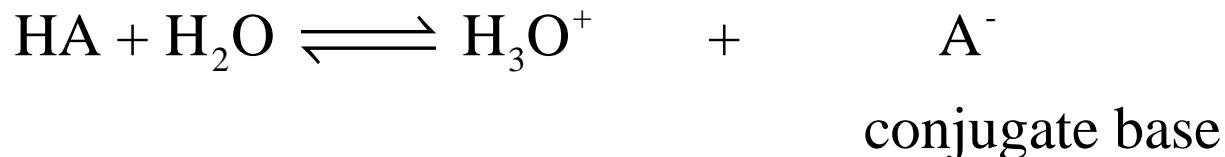
Calculating pH:

$$\begin{aligned}[\text{H}_3\text{O}^+] &= \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-2}} = 3.3 \times 10^{-13} M \\ \text{pH} &= -\log(3.3 \times 10^{-13}) = 12.48\end{aligned}$$

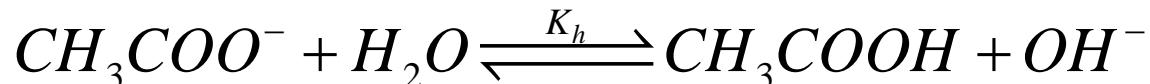
HYDROLYSIS OF IONS



- For an ion in solution, hydrolysis is the reaction of the ion with water in which proton transfer occurs
 - Most ionic salts dissolve in water to form oppositely charged ions which are hydrated.
 - The subsequent reaction of these ions with water is hereto refers as hydrolysis
- It is not every ion that undergoes hydrolysis. There are only two types of ion to be considered here:
 - An anion that is a conjugate base of a weak acid
 - A cation that is conjugate acid of a weak base
- Consider the reaction of a weak acid with water represented thus:



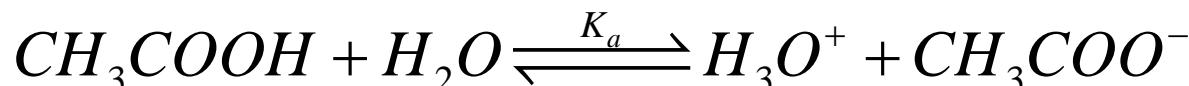
- For example, the acetate ion (CH_3COO^-) is the conjugate base of acetic acid (CH_3COOH). In the hydrolysis of the acetate ion, proton is transferred from water to the acetate ion to become acetic acid



- The equilibrium constant for the process is

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$


- The above can also be called hydrolysis constant, K_h .
- Consider the dissociation of acetic acid itself;



- The associated dissociation constant K_a is

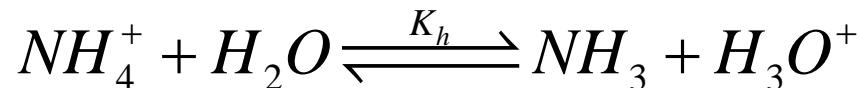
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

- If both numerator and denominator of the last equation are both multiplied by $[OH^-]$:

$$\begin{aligned}
 K_a &= \frac{[CH_3COO^-][H_3O^+][OH^-]}{[CH_3COOH][OH^-]} = \frac{[CH_3COO^-]}{[CH_3COOH][OH^-]} \times K_w \\
 &= \frac{1}{K_h} \times K_w = \frac{K_w}{K_h} \\
 \Rightarrow K_w &= K_a K_h
 \end{aligned}$$

- Thus, the extent to which  hydrolysis of the acetate ion (conjugate base of acetic acid) occurs is inversely proportional to the strength of its conjugate acid (acetic acid)
 - Generally, the extent of hydrolysis of the conjugate base of an acid is inversely proportional to the strength of the acid.
- Now, consider the hydrolysis of positively charged metal ions from sparingly soluble salts (formed from the reaction of a strong acid and a weak base) such as ammonium chloride (NH_4Cl)

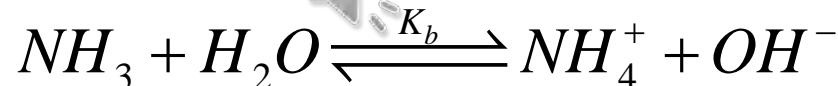
- The cation, NH_4^+ reacts with water (hydrolysis) as:



- The hydrolysis constant is obtained as

$$K_h = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

- Now, consider the dissociation of the weak base, NH_3 :



- The equilibrium expression for the above is

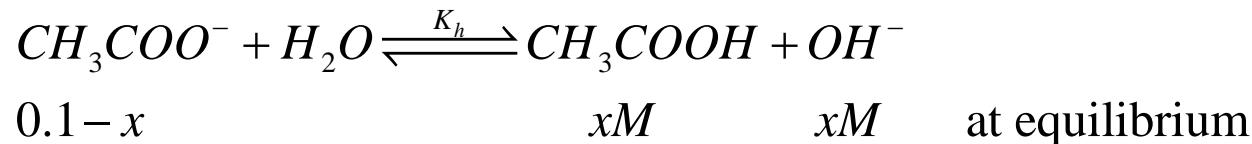
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

- Multiplying both the numerator and denominator of the hydrolysis constant expression above by $[\text{OH}^-]$ to give

$$\begin{aligned}
 K_h &= \frac{[NH_3][H_3O^+][OH^-]}{[NH_4^+][OH^-]} = \frac{[NH_3]}{[NH_4^+][OH^-]} \times K_w \\
 &= \frac{1}{K_b} \times K_w \\
 \Rightarrow K_w &= K_b K_h
 \end{aligned}$$

- To illustrate the applications of the above, Consider the following:
 
- Calculate the pH and percent hydrolysis occurring in the following
 - 0.100 M NaAc (Ac = acetate; $K_a = 1.8 \times 10^{-5}$ for CH_3COOH)
 - 0.200 M NH_4Cl ($K_b = 1.8 \times 10^{-5}$ for NH_3)

- SOLUTIONS
- In the NaAc solutions, the hydrolysis of Na^+ is negligible since the conjugate base, NaOH is very strong. Considering the hydrolysis of the acetate ion as



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{(x)(x)}{0.1 - x}$$


- Assuming $0.1 - x \approx 0.1$, since the acetate ion is a conjugate base of a very weak acid (acetic acid). Then,

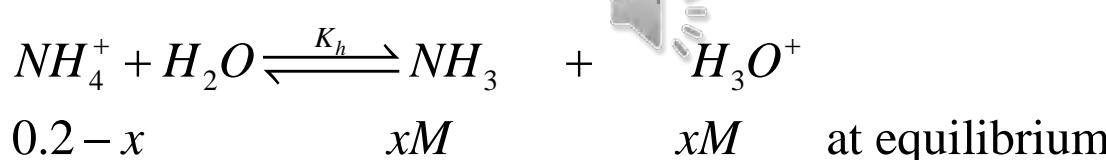
$$5.6 \times 10^{-10} = \frac{x^2}{0.1} \Rightarrow x^2 = 5.6 \times 10^{-11} \Rightarrow x = \sqrt{5.6 \times 10^{-11}} = 7.48 \times 10^{-6} M$$

- $\Rightarrow [\text{OH}^-] = 7.48 \times 10^{-6} M$
- $\therefore p\text{OH} = -\log[\text{OH}^-] = -\log(7.48 \times 10^{-6}) = 5.13$
- $\therefore pH = 14 - p\text{OH} = 14 - 5.13 = 8.87$

- Percent hydrolysis = $\frac{\text{amount hydrolysed}}{\text{initial amount}}$
 $= \frac{7.48 \times 10^{-6}}{0.1} \times 100\% = 7.48 \times 10^{-3}\%$

- The assumption is justified since $7.48 \times 10^{-3}\% < 5\%$

- For the NH_4Cl solutions, the hydrolysis of the Cl^- is negligible because the conjugate acid, HCl is very strong. Therefore, considering the hydrolysis of NH_4^+ as follows:



$$K_h = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{(x)(x)}{0.2 - x}$$

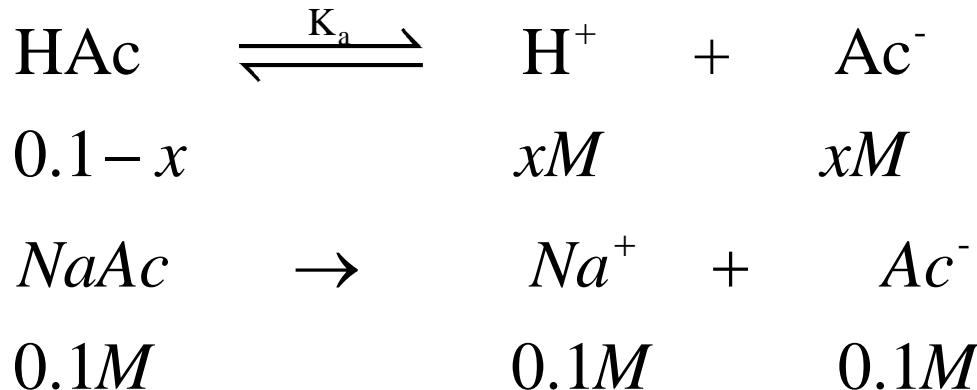
- Assuming $0.2 - x \approx 0.2$, since the ammonium ion is a conjugate base of a very weak base (ammonia). Then,

$$5.6 \times 10^{-10} = \frac{x^2}{0.2} \Rightarrow x^2 = 1.12 \times 10^{-10} \Rightarrow x = \sqrt{1.12 \times 10^{-10}} = 1.06 \times 10^{-5} M$$

- $\Rightarrow [H^+] = 1.06 \times 10^{-5} M$
- $\therefore pH = -\log[H^+] = -\log(1.06 \times 10^{-5}) = 4.98$
- $$\begin{aligned} \text{Percent hydrolysis} &= \frac{\text{amount hydrolysed}}{\text{initial amount}} \\ &= \frac{1.06 \times 10^{-5}}{0.2} \times 100\% = 5.30 \times 10^{-3}\% \end{aligned}$$
- The assumption is justified since $5.30 \times 10^{-3}\% < 5\%$
- CAN YOU TRY THESE?
- Calculate the pH and percent hydrolysis in the following solutions:
 - a) Sodium formate, 0.60 M (K_a for formic acid = 1.8×10^{-4})
 - b) Potassium propionate, 0.023 M (K_a for propionic acid = 1.3×10^{-5})
 - c) Ethylammonium chloride, $C_2H_5NH_3^+Cl^-$ (K_b for ethylamine = 4.3×10^{-4})

BUFFER SOLUTION

- One of the most important applications of the acid – base equilibria is in the preparation of a buffer solution
- A buffer solution is one that resists change in its pH despite the addition of a small amount of an acid, a base or other electrolytes.
 - The most important practical example of a buffered solution is human blood, which can absorb the acids and bases produced by biological reactions without changing its pH.
- What constitutes a buffer?
 - A mixture of a weak acid with one of it's salt – acid buffer
 - A mixture of a weak base and one of it's salt – base buffer
- Consider a mixture of 0.10 M acetic acid (HAc) and 0.10 M sodium acetate (NaAc). The two processes in the mixture are:



- Note the following:
 - NaAc is a very strong electrolyte (an ionic salt) and so, ionizes completely to give 0.10 M Ac⁻. This fixes the concentration of Ac⁻ ion
 - If there is only acetic acid initially, it will dissociate partially (sparingly) into Ac⁻ and H⁺
 - The presence of 0.10 M Ac⁻ from NaAc will suppress the dissociation of HAc and so, HAc may be regarded as being present in its undissociated form (Le Chatelier's Principle). This fixes the concentration of acetic acid

- For the dissociation of the acid, the dissociation constant expression is:

$$K_a = \frac{[Ac^-][H^+]}{[HAc]}$$

- This can be written as

$$[H^+] = K_a \frac{[HAc]}{[Ac^-]}$$

- Taking negative logarithm of both sides of the expression above gives

$$-\log_{10} [H^+] = -\log_{10} K_a + \left(-\log_{10} \frac{[HAc]}{[Ac^-]} \right)$$


- The above finally gives

$$pH = pK_a + \left(\log_{10} \frac{[Ac^-]}{[HAc]} \right) = pK_a + \log_{10} \frac{[Salt]}{[Acid]}$$

- Since $[Ac^-] = [NaAc]$ i.e. sodium acetate fixes the concentration of Ac^-
- The last equation above is known as Henderson – Hasselbach equation. It is commonly used to determine the pH of a buffer solution

- For a base buffer, consider a mixture of ammonia and ammonium chloride
- $$NH_3 + H_2O \xrightleftharpoons{K_b} NH_4^+ + OH^-$$



- According to Le Chatelier's principle,

- the presence of NH_4^+ from the completely ionized NH_4Cl suppresses the formation of the same ion (ammonium ion) from NH_3 , such that
- the bulk of the ammonium ion in solution is exclusively from NH_4Cl (salt) and that NH_3 remains fairly undissociated

- This expression for the dissociation of NH_3 is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$\Rightarrow [OH^-] = K_b \frac{[NH_3]}{[NH_4^+]}$$

- Taking negative logarithm of both sides of the equation above gives

$$pOH = pK_b + \left(\log_{10} \frac{[NH_4^+]}{[NH_3]} \right) = pK_a + \log_{10} \frac{[Salt]}{[Base]}$$

- Illustrations:
- Calculate the pH:
 - a. of a buffer solution consisting of 0.50 M HClO ($K_a = 2.9 \times 10^{-8}$) and 0.60 M NaClO ;
 - b. after adding 0.020 mol of solid NaOH to 1.0 L of the buffer solution in part (a); [assume that the addition of NaOH causes negligible volume change.]
 - c. after adding 30.0 mL of 1.5 M HCl to 0.50 L of the buffer solution in part (a).



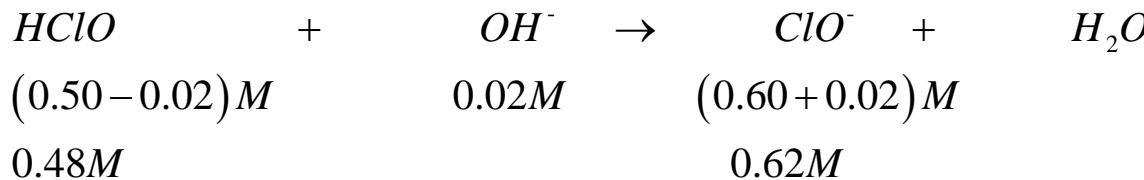
- SOLUTION
- For an acid buffer as above

$$pH = pK_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} = -\log_{10}(2.9 \times 10^{-8}) + \log_{10} \left(\frac{[\text{NaClO}]}{[\text{HClO}]} \right)$$

(a)

$$\begin{aligned}
 &= 7.54 + \log_{10} \left(\frac{0.6}{0.5} \right) \\
 &= 7.54 + 0.08 \\
 &= 7.62
 \end{aligned}$$

- In the presence of 0.020 mole/L of NaOH, the following are the processes within the system:

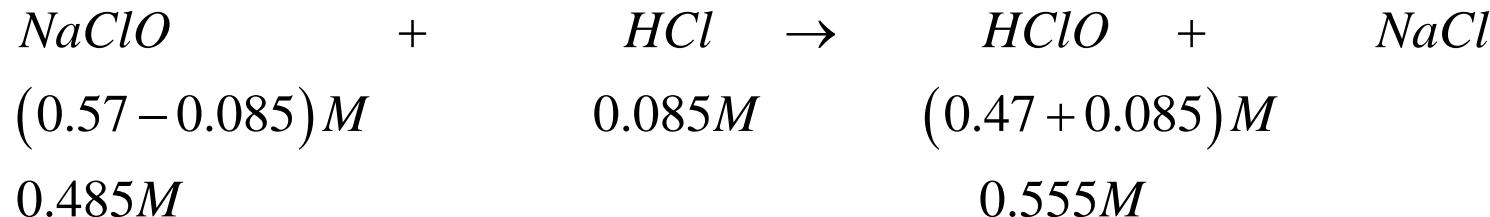


$$\begin{aligned}
 pH &= pK_a + \log_{10} \frac{[Salt]}{[Acid]} = -\log_{10}(2.9 \times 10^{-8}) + \log_{10} \left(\frac{[NaClO]}{[HClO]} \right) \\
 &= 7.54 + \log_{10} \left(\frac{0.62}{0.48} \right) \\
 &= 7.54 + 0.11 \\
 &= 7.65
 \end{aligned}$$



- The addition of strong base increased the concentration of the basic buffer component at the expense of the acidic buffer component.
- Note especially that the pH *increased only slightly, from 7.62 to 7.65.*

- The addition of 30 mL of 1.5 M HCl to 0.5 L of the buffer gives the following
- $Mole\ of\ HCl\ added = 1.5\ molL^{-1} \times (0.5 + 0.03)L = 0.045\ mole$
- The new concentrations are
 - $[HCl] = 0.045\ mole / 0.53\ L = 0.085\ M$
 - $[HClO] = (0.50\ M \times 0.50\ L) / (0.53\ L) = 0.47\ M$
 - $[NaClO] = (0.60\ M \times 0.50\ L) / (0.53\ L) = 0.57\ M$
- The following processes will then take place:



$$\begin{aligned}
 pH &= pK_a + \log_{10} \frac{[Salt]}{[Acid]} = -\log_{10}(2.9 \times 10^{-8}) + \log_{10} \left(\frac{[NaClO]}{[HClO]} \right) \\
 &= 7.54 + \log_{10} \left(\frac{0.485}{0.555} \right)
 \end{aligned}$$

$$= 7.54 - 0.06$$

$$= 7.48$$

- Can you try the following?
- Calculate the pH of a buffer consisting of 0.50 M HF and 0.45 M KF
 - (a) before and
 - (b) after addition of 0.40 g of NaOH to 1.0 L of the buffer (K_a of HF = 6.8×10^{-4}).
- Calculate the pH of a buffer consisting of 0.25 M $(CH_3)_2NH_2Cl$ and 0.30 M $(CH_3)_2NH$
 - (a) before and
 - (b) after addition of 50.0 mL of 0.75 M HCl to 1.0 L of the buffer [pK_b of $(CH_3)_2NH$ = 3.23].

**CHM 101
(INTRODUCTORY CHEMISTRY I)**

THERMOCHEMISTRY



Introduction

- Thermochemistry is the study of heat changes associated with chemical process either at constant volume or at constant pressure.

The following sub-topics will be discussed:

- Balancing of intermolecular forces.
- Order-disorder phenomenon,
- Entropy, free energy, energy effect,
- exothermic and endothermic changes,
- Enthalpy of reaction. Hess's law of enthalpy summation (with relevant calculations),
- Heats of neutralization, combination and formation,
- Bond dissociation energies (with relevant calculations)
- Free energy and spontaneous change.



INTERMOLECULAR FORCES



What are intermolecular forces?

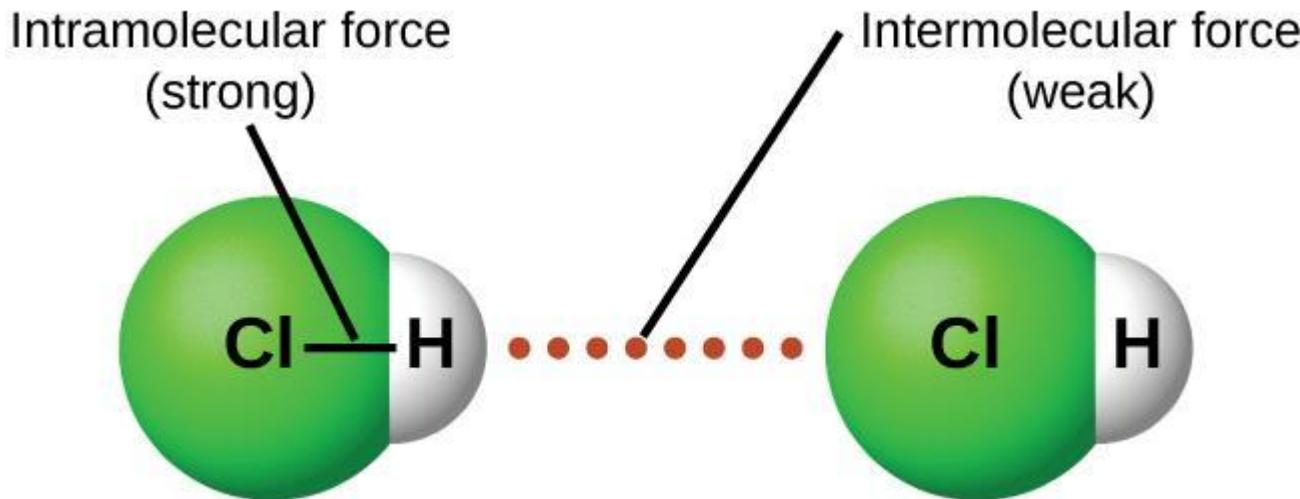
- Intermolecular forces are the forces that exist between molecules or particles. They are the noncovalent attractive force between atoms, molecules, and/or ions, which determine many of the physical properties of a substance.
- The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule.
- Properties like melting point and boiling points are a measure of how strong the attractive forces are between atoms or molecules.

Intramolecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms.



Intermolecular forces (cont'd)

Let's consider HCl molecules as an example.....



Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.



Balancing of Intermolecular Forces

Two factors determine whether a substance is a solid, liquid or gas.

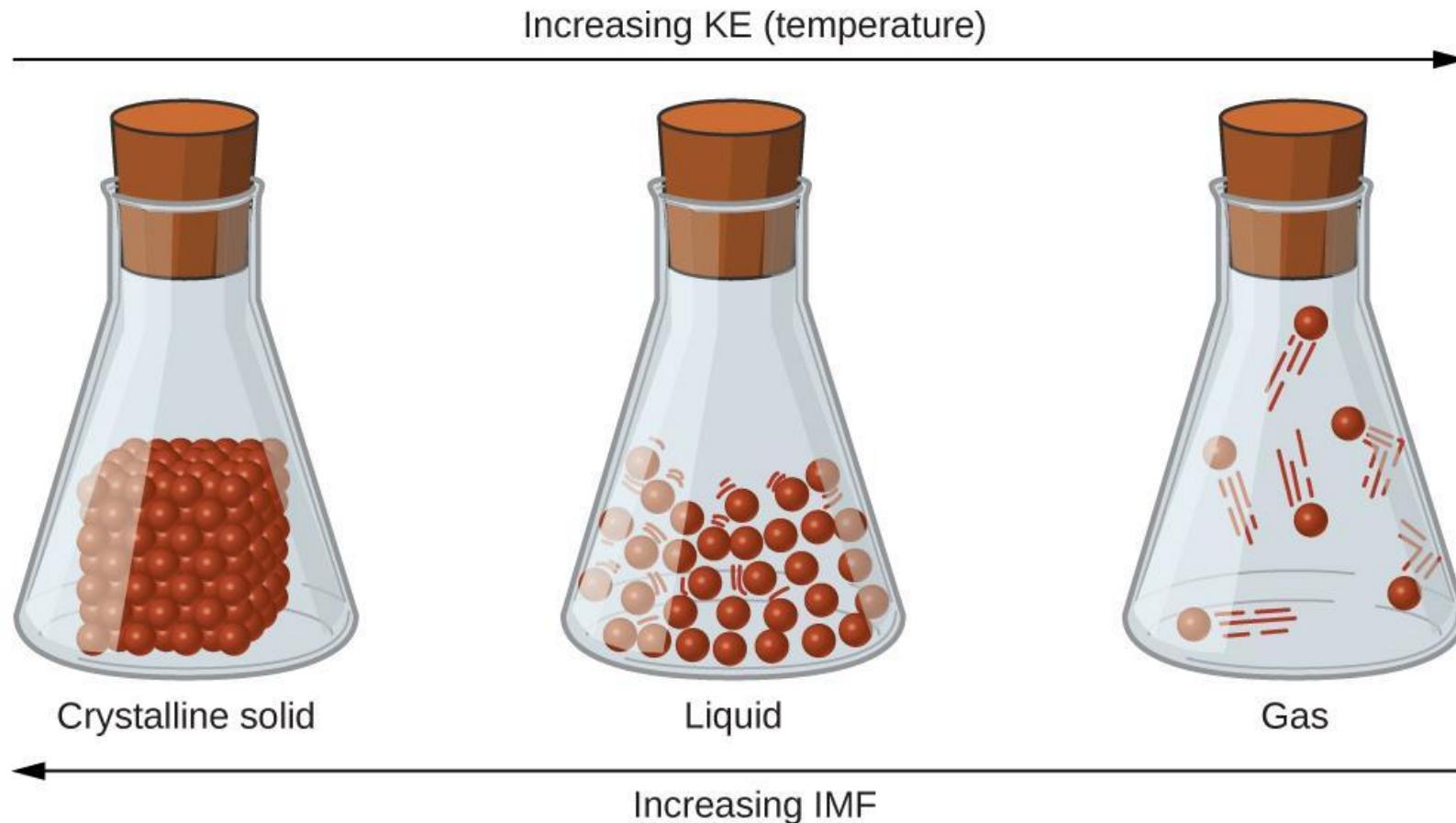
1. The kinetic energy of the particles (atoms, molecules or ions) that make up the substance.
→ This keeps particles moving apart.
2. The attractive intermolecular forces between particles.
→ This keeps particles close together.

The balance between these 2 factors determines the phase of a substance. i.e. the preferred phase of substance depends on the strength of the intermolecular forces and the energy of the particles.

- If the K.E is > the attractive forces, a gas phase is preferred.
- If the K.E < the attractive forces, a liquid or solid is formed.



Balancing of Intermolecular Forces (cont'd)



Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces.

(Note: The space between particles in the gas phase is much greater than shown.)

Source: <https://cooljargon.com/ebooks/chemistry/m51077/index.cnxml.html>



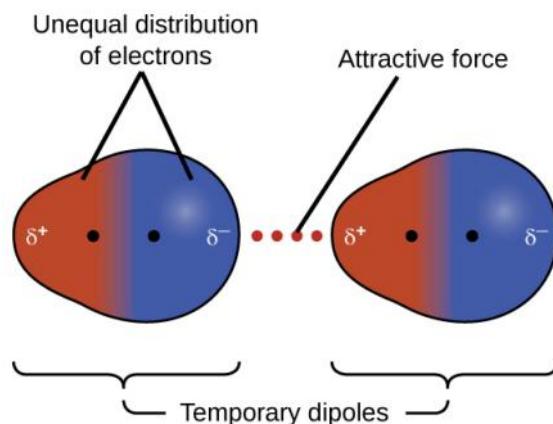
- At low temperatures, most substances are solids (except helium, a liquid at absolute zero).
- As temperature increases, substances with very weak intermolecular forces become gases directly (sublimation); substances with weak interaction can become liquids as temperature increases.
- As temperature increases, all substances progress from solid to liquid to gas.
- As bonds become more polarized, the charges on the atoms become greater, the intermolecular attractions become greater leading to higher boiling points.



TYPES OF INTERMOLECULAR FORCES.

1). Dispersion forces (also called London dispersion)

Instantaneous position of an e^- in a molecule makes that point of the molecule **negatively charged** and the rest **positively charged**. Dispersion is the only IMF that occur between non-polar molecules. It is the weakest IMF. It is Present in all substances with electrons



Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

E.g



London dispersion force (I_2 bond)

- Dispersion forces increase with molecular weight. The greater the number of electrons in a species, the stronger the dispersion forces. E.g

Halogen	Boiling Point	Melting Point
F_2	85K	53K
Cl_2	238K	172K
Br_2	332K	226K

- And sometimes, smaller molecules are gases and larger molecules are solid at the same temperature

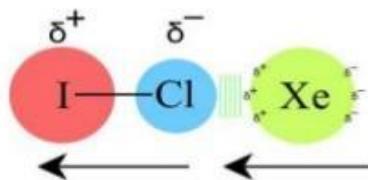


2. Dipole-induced dipole forces

- These forces occur between permanent dipoles and polarisable electron cloud.

A dipole can *induce* (cause) a temporary dipole to form in a non-polar molecule

The molecules then line up to match $\delta+$ and $\delta-$ charges

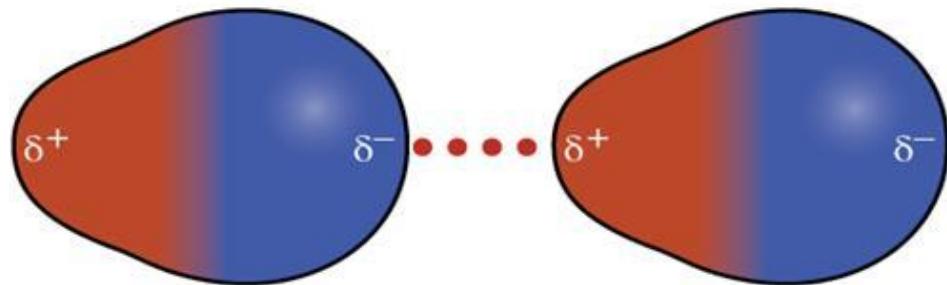


- Another example is carbondioxide in ethylene
- *They are weak but stronger than London forces*
- Dispersion forces and dipole-induced forces are generally referred to as van der Waal forces

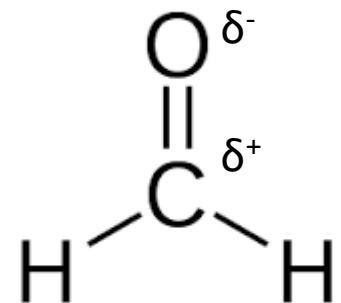


3. Dipole – Dipole attraction (Permanent Dipoles)

The oppositely charged ends of a polar molecule which have partial on them attract each other. E. g polar molecules like HCl.



Formaldehyde has permanent dipoles (based on the polarized carbon-oxygen bond) and thus shows dipole-dipole interaction.



- CH_2Cl_2 has a higher boiling point than CF_4 (non-polar) even though it has a lower molar mass.
- The larger the dipole, the greater the dipole – dipole intermolecular interaction.
- They are stronger than van der Waal forces

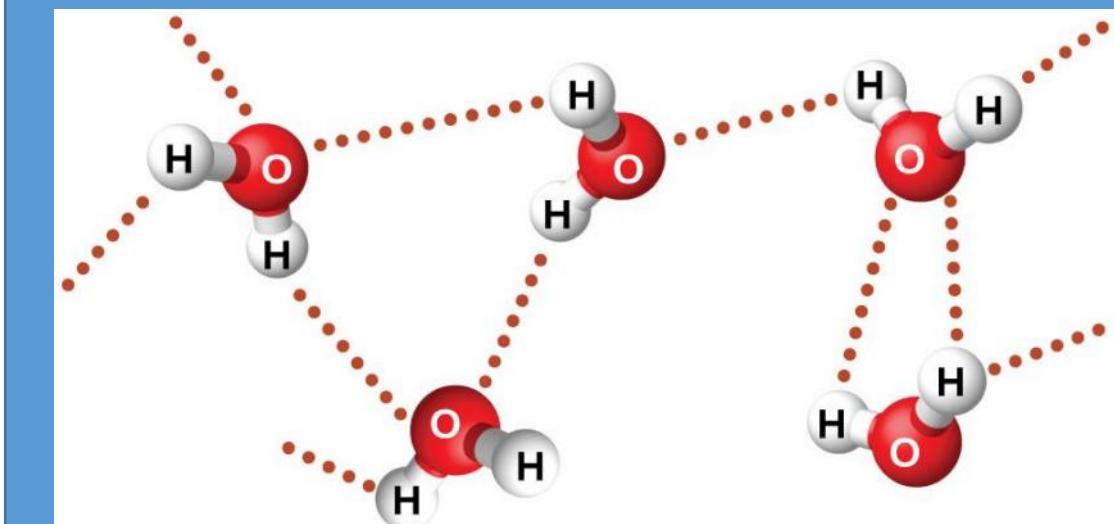


4. Hydrogen Bonding

This is a special case of dipole-dipole forces. Molecules with H covalently bonded to F, N, or O have hydrogen bonding which are very strong. **F, N and O** have high EN

- It is stronger than dispersion forces, dipole-induced dipole forces and permanent dipoles.
- The dipole – dipole interactions between these bonds are unusually strong.
- Examples of hydrogen bonds include $\text{HF}\cdots\text{HF}$, $\text{H}_2\text{O}\cdots\text{HOH}$, and $\text{H}_3\text{N}\cdots\text{HNH}_2$, acetic acid, acetone in water, etc

- Water, H_2O has relatively high melting and boiling point while H_2S molecules do not. This strong attraction between H_2O requires additional energy to separate its molecules.

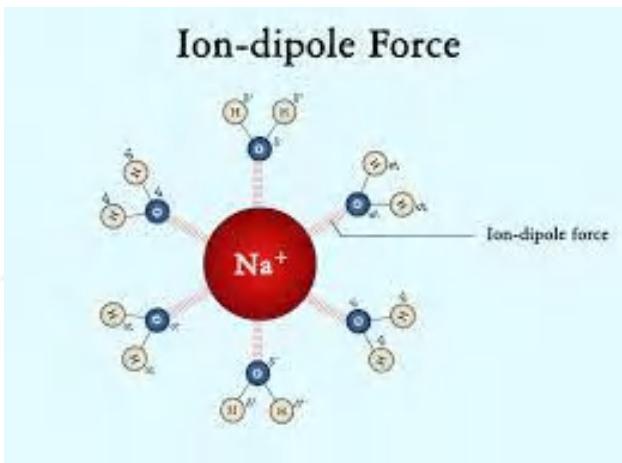
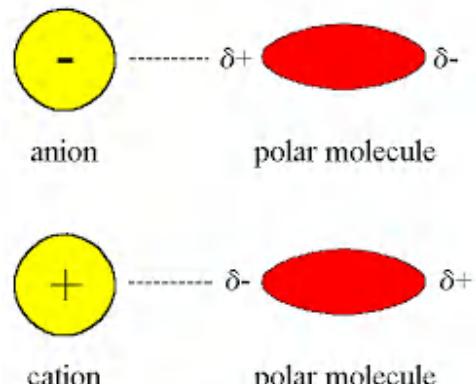


Hydrogen Bonding (cont'd)

- Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), H₂O has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, H₂S, is 233 K (-60°C). This is because H₂O molecules experience hydrogen bonding, while H₂S molecules do not.
- This strong attraction between H₂O molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected.
- H- bonding in water is responsible for water's ability as a solvent, its high heat capacity and its ability to expand when freezing

5. Ion-dipole and Ion-induce dipole

Ion-dipole : Force between an ion and a dipole (full charge and a partial charge). An example is seen when salt dissolves in water (since water molecules have permanent dipoles).



- Ion-dipole interaction increases as the charge increases and also increases with smaller size of ion involved.
- They are stronger than dipole-dipole forces

Example: compare dissolving MgCl₂ and KCl in water.

Solution: For Mg²⁺ and K⁺, charge +2 is higher.

Hence, ion – dipole interaction is greater when MgCl₂ is dissolved in water than when KCl is dissolved in water.

Exercise: 1) Contrast between KCl and C_sCl dissolved in water.

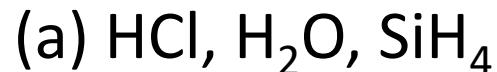
Ion-induced dipole force consists of an ion and a non-polar molecule interacting. Like a dipole-induced dipole force, the charge of the ion causes distortion of the electron cloud on the non-polar molecule



Practice Questions

1. What type of intermolecular force do all substances have?
2. What is necessary for a molecule to experience dipole-dipole interactions?
3. What is necessary for a molecule to experience hydrogen bonding?
4. How does varying the temperature change the preferred phase of a substance?
5. Identify the strongest intermolecular force present in each substance.
 - He, CHCl₃, HOF
6. Identify the strongest intermolecular force present in each substance.
 - CH₃OH, (CH₃)₂CO, N₂
7. Identify the strongest intermolecular force present in each substance.
 - HBr, C₆H₅NH₂, CH₄
8. Identify the intermolecular forces present in the following solids:
 - (a) CH₃CH₂OH
 - (b) CH₃CH₂CH₃
 - (c) CH₃CH₂Cl

9. Arrange each of the following sets of compounds in order of increasing boiling point temperature:



10. O₂, NO, N₂ Neon and HF have approximately the same molecular masses.

(a) Explain why the boiling points of Neon and HF differ.

(b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

11. On the basis of intermolecular attractions, explain the differences in the boiling points of *n*-butane (-1 °C) and chloroethane (12 °C), which have similar molar masses.

12. Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

**CHM 101
(INTRODUCTORY CHEMISTRY I)**

THERMOCHEMISTRY (2)



ORDER – DISORDER PHENOMENON



ENTROPY

Entropy: A thermodynamic function that measures the degree of randomness or disorder in a system. It is denoted as **S**. Its unit is $\text{J.K}^{-1}.\text{mol}^{-1}$

- Entropy is a **state function** and an **extensive property**.

(State function: property whose value doesn't depend on the path taken to reach that specific value is known to as state functions or point functions- they depend on the state of the substance like temperature, pressure or the amount or type of the substance. An extensive property is a property that depends on the amount of matter in a sample.)

- During change of state, systems tend to a state of greatest disorder (high entropy)
 - **Second Law of Thermodynamics**

$$\uparrow \text{entropy} = \uparrow \text{disorder}$$

The greater the randomness, the higher the entropy. As the solid changes through the liquid to the gaseous state. i.e., gaseous systems show much greater disorder than liquid systems, which in turn show greater disorder than solid systems.



To determine the direction of change in entropy.....

➤ Second law of thermodynamics states that all closed system tend to maximize entropy (Reversing the ever increasing tendency requires the input of energy)

e.g. Solid → Liquid → Gas.

Lump of ice → liquid (heat is absorbed from the surroundings,
disorderliness increases, **higher energy**)

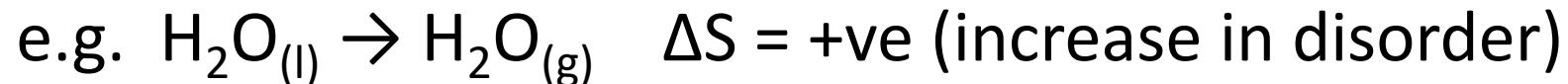
$$\Delta S = S_{\text{product}} - S_{\text{reactant}}$$

- When $S_{\text{product}} < S_{\text{reactant}}$, $\Delta S = -\text{ve}$
- When $S_{\text{product}} > S_{\text{reactant}}$, $\Delta S = +\text{ve}$



1. Change of State :

When a substance changes to a state of higher energy, the entropy increases ($\Delta S = +ve$). But if the change is to a state of lower energy, entropy decreases ($\Delta S = -ve$).

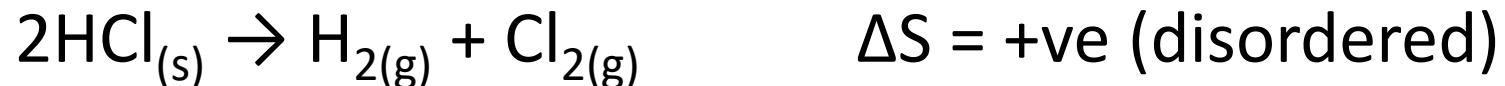
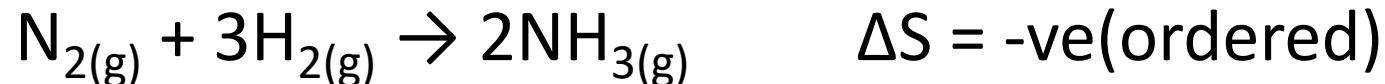
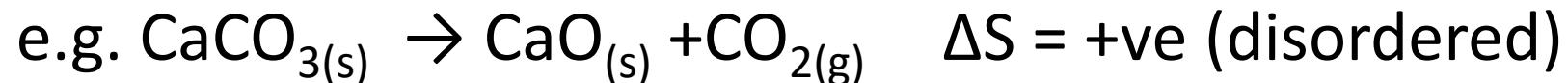


....Positive entropy therefore indicates spontaneity of the process
(following this law)



2. Decomposition or Composition:

When a substance decomposes into 2 or more substances, entropy increases i.e. $\Delta S = +ve$. But if two or more substances compose into a single substance, entropy decreases i.e. $\Delta S = -ve$



3. Change in Volume Occupied:

when a gaseous substance decomposes into another gas of smaller volume, entropy decreases; but entropy increases if the product is of higher volume.

- Example, $N_2O_4 \rightleftharpoons 2NO_2$

Here, volume changes from 1 vol. in N_2O_4 to 2 vols. in NO_2 , therefore, entropy increases. i.e. $\Delta S = +ve$.

Note in summary:

- The entropy change involved when a system changes from an orderly state to a disorderly state is always positive ($\Delta S = +ve$).
- From a disorderly state to an orderly state, entropy is always negative ($\Delta S = -ve$).

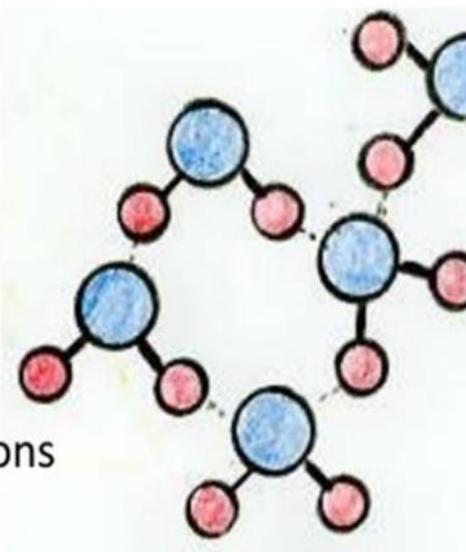


ENTHALPY

ENTHALPY

Chemical energy is stored in:

- moving electrons
- vibration of chemical bonds
- rotation and translation of molecules
- stored nuclear energy of protons & neutrons
- energy stored in chemical bonds



Enthalpy (H) is expressed as

$$H = U + PV$$

U = internal energy

P = Pressure

V = Volume

- When a process occurs at constant pressure, the heat flow (q or Q) (either released or absorbed) for the process is equal to the change in enthalpy.
i.e $\Delta H = q$
- Enthalpy is a **state function** which depends entirely on the state functions T , P and U .
- The unit of molar enthalpy is $J \cdot mol^{-1}$.

Source: <https://www.slideshare.net/mrtangextrahelp/tang-01b-enthalpy-entropy-and-gibbs-free-energy>



ENTHALPY CHANGES: Exothermic and endothermic reactions

- Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states

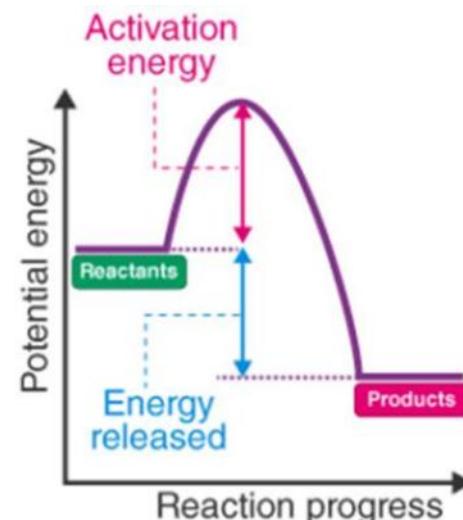
change in enthalpy (ΔH) – change in heat of a system

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

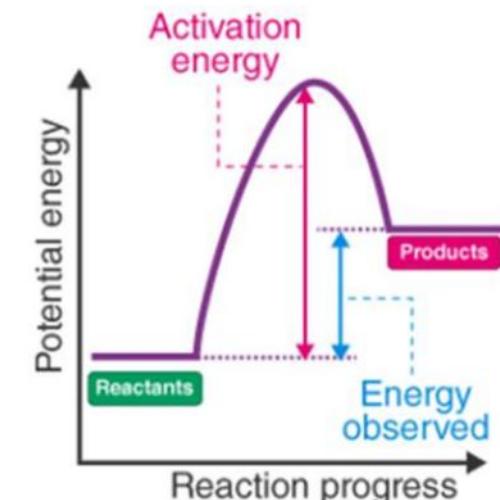
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- When a system (reaction) loses heat to the surrounding, the reaction is exothermic. i.e. ΔH is $-ve$ ($\Delta H_{\text{product}} < \Delta H_{\text{reactant}}$)

- When a system (reaction) absorbs heat from the surrounding, the reaction is endothermic i.e. $\Delta H = +ve$ ($\Delta H_{\text{product}} > \Delta H_{\text{reactant}}$)



Exothermic Reaction



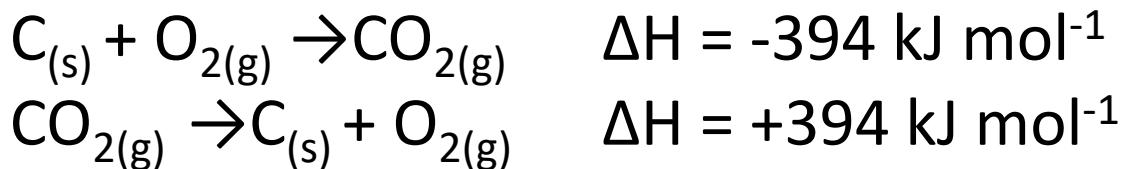
Endothermic Reaction

<https://cdn1.byjus.com/wp-content/uploads/2016/06/Energy-Level-Diagram-of-an-Endothermic-Reaction-700x410.png>



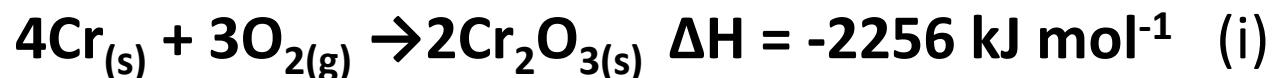
ENTHALPY OF REACTION

- When energy needs to be added to a material to change its phase from a liquid to a gas, that amount of energy is called the enthalpy (or latent heat) of vaporization
- Other phase transitions have similar associated enthalpy changes, such as the enthalpy (or latent heat) of fusion for changes from a solid to a liquid
- Enthalpy of reaction is the enthalpy change accompanying a reaction represented by a balanced chemical equation.
- For any physical or chemical process where there is an enthalpy change, the reverse process will be accompanied by the reverse enthalpy change (i.e. **change in sign**)
e.g.



ΔH can be related to the number of moles of each reactant.....

e.g.

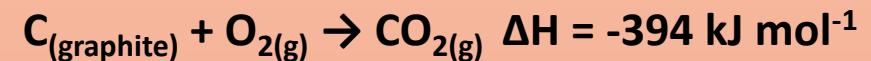


This should be written as:



Note: The stoichiometry coefficient of the reaction in (ii) is a fraction of reaction (i).
Hence, **ΔH value changes**

The phase (or state) of each substance (gas, liquid or solid) taking part in the reaction must be specified.



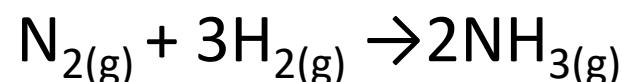
ΔH depends on the state of substances.

e.g.



Example 1:

How much heat is evolved when 500 kg of ammonia is produced according to the following equation?



$$\Delta H = -91.8 \text{ kJ mol}^{-1}$$

$$[\text{N} = 14.0, \text{H} = 1.00 \text{ g mol}^{-1}]$$

Solution:

$$\text{No of moles of NH}_3 = \frac{\text{mass given}}{\text{molar mass of NH}_3}$$

$$\text{molar mass of NH}_3 = 14 + 3(1.00) = 17 \text{ g mol}^{-1}$$

$$\text{mass given} = 500 \text{ kg} = 500 \times 10^3 \text{ g}$$

$$\therefore n_{\text{NH}_3} = \frac{500 \times 10^3 \text{ g}}{17 \text{ g mol}^{-1}} = 2.94 \times 10^4 \text{ mol}$$

From the balanced chemical equation,

2 moles of NH_3 gave $-91.8 \text{ kJ mol}^{-1}$.

$\therefore 2.94 \times 10^4 \text{ mol of NH}_3$ will give:

$$\frac{-91.8 \text{ kJ mol}^{-1}}{2 \text{ mol}} \times 2.94 \times 10^4 \text{ mol}$$

$$= -1.35 \times 10^6 \text{ kJ mol}^{-1}$$



ΔH , $\Delta H^\circ_{\text{reaction}}$ and the Standard state

Δ = represents the change in the enthalpy;

$^\circ$ = signifies that the reaction is a standard enthalpy change,

$^{\text{reaction}}$ = denotes that this change is the enthalpy of reaction

$$\Delta H_{\text{reaction}} = \sum n \Delta H_p - \sum m \Delta H_r$$

where:

Σ represents summation

n and m are the coefficients of the substances in the product(s) and reactant(s) respectively

H_p = enthalpies of the product(s)

H_r = enthalpies of the reactant(s)

The Standard State:

- The standard state of a substance is the pure substance in a specified state (solid or liquid or gas) at 1 atm pressure.
- Standard conditions are:
 - gases at a pressure of 1 atm (10^5 Pa)
 - solutions in unit concentration
 - substances in their standard state
- The $\Delta H^\circ_{\text{reaction}}$ is the standard heat of reaction or standard enthalpy of a reaction, and like ΔH also measures the enthalpy of a reaction. However, $\Delta H^\circ_{\text{reaction}}$ takes place under "standard" conditions, meaning that the reaction takes place at 25°C and 1 atm.
- The benefit of a measuring ΔH under standard conditions lies in the ability to relate one value of ΔH° to another, since they occur under the same conditions.



Enthalpy Change Accompanying a Change in State

A change in state involves a change in enthalpy

1. Enthalpy of fusion or enthalpy of melting (ΔH_{fusion})

- the enthalpy change when one mole of a substance melts.

e.g For example, for one mole of ice the enthalpy is given as:

$$\Delta H_{fusion} = 6.01 \text{ kJ at } 273.15 \text{ K}$$

2. Enthalpy of freezing ($\Delta H_{freezing}$)

- Enthalpy change when one mole of a substance freezes.

$$\Delta H_{freezing} = -\Delta H_{fusion}$$

3. Enthalpy of vaporization (ΔH_{vap})

-heat required to vaporize one mole of a substance.

$$\Delta H_{vap} = \Delta H_{vapor} - \Delta H_{liquid}$$

e.g for one mole of water, $\Delta H_{vap} = 44.0 \text{ kJ at } 298 \text{ K}$

4. Enthalpy of condensation ($\Delta H_{condensation}$)

$$\Delta H_{condensation} = -\Delta H_{vap}$$

5. Enthalpy of sublimation

$$\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vap}$$

Specific temperatures the change takes place are stated in all enthalpies of phase changes

Relationship between Temperature and Heat

- When the temperature increases, the amount of molecular interactions also increases.
- As the number of interactions increase, the internal energy of the system rises.
- if the internal energy (U) increases then, the ΔH increases as temperature rises. (since $H = U + PV$)

Specific heat capacity (c) is the heat required to raise the temperature of a unit mass of substance by $1^{\circ} C$ (unit is $J K^{-1} g^{-1}$ or $J ^{\circ}C^{-1}g^{-1}$)

$$\text{Specific heat capacity, } c = \frac{\text{heat capacity}}{\text{mass } (m)} \quad (1)$$

$$\text{Heat capacity} = \frac{\text{Quantity of heat } (Q)}{\text{Rise in temp } (\Delta T)} \quad (2)$$

Combining equations (1) and (2) we obtain,

$$Q = mc\Delta T \quad (3)$$



Examples

(1) Water has specific heat $4.18 \text{ J K}^{-1}\text{g}^{-1}$. 100 g of water rise in temperature by 2.0 K. Calculate the heat quantity absorbed by water.

Solution:

$$\begin{aligned} q &= mc\Delta T \\ &= 100\text{g} \times 4.18 \text{ J K}^{-1}\text{g}^{-1} \times 2.0 \text{ K} \\ &= 9.36 \text{ J} \end{aligned}$$

(2) 293.7 J of heat is removed from 5g of Aluminum causing the temperature to drop from 85°C to 19°C . What is the specific heat capacity of Aluminum?

Solution:

$$\begin{aligned} q &= mc\Delta T \\ -293.7 \text{ J} &= (5\text{g}) (c)(292-358 \text{ K}) \\ -293.7 \text{ J} &= -330 c \text{ (g. K)} \\ c &= 0.89 \text{ J K}^{-1} \text{ g}^{-1} \end{aligned}$$



3. A 50g of an unknown material at 200°C was added to 100g of water at 25°C . The final temp of the mixture was 41.8°C . What is the specific heat capacity of the unknown material? (Water has the sp. heat capacity of $4.18 \text{ J } ^{\circ}\text{C}^{-1}\text{g}^{-1}$),

$$\frac{\text{metal}}{200^{\circ}\text{C}} \quad 41.8^{\circ}\text{C} \quad (q = -\text{ve})$$

$$\frac{\text{H}_2\text{O}}{25^{\circ}\text{C}} \quad 41.8^{\circ}\text{C} \quad (q = +\text{ve}).$$

$$\text{But, } Q_m = Q_{\text{H}_2\text{O}}$$

$$\therefore -Q_m = Q_{\text{H}_2\text{O}}$$

$$-mc\Delta T = -mc\Delta T$$

$$-mc(T_f - T_i) = -mc(T_f - T_i).$$

$$-50(c)(25 - 200 \text{ } ^{\circ}\text{C}) = 100(4.184)(41.8 - 25 \text{ } ^{\circ}\text{C})$$

$$7910(c) = 7029.12$$

$$c = 0.8895 \text{ J.}$$

specific heat capacity of the material is $0.8895 \text{ J } ^{\circ}\text{C}^{-1}\text{g}^{-1}$



**CHM 101
(INTRODUCTORY CHEMISTRY I)**

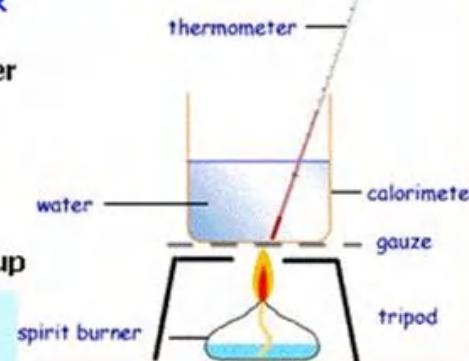
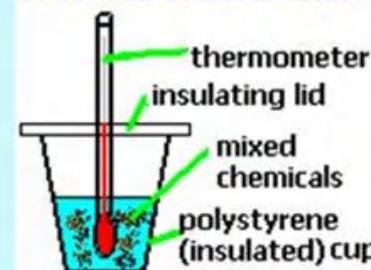
THERMOCHEMISTRY (3)



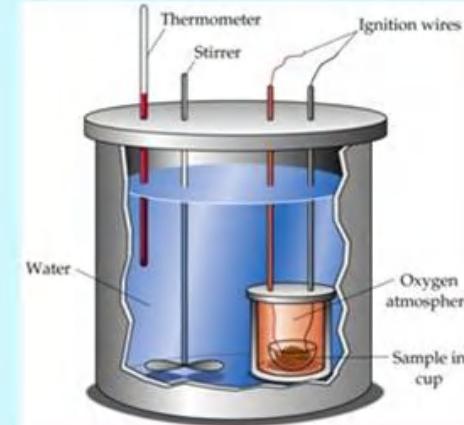
MEASURING ENTHALPY CHANGES

HOW CAN WE CALCULATE ENTHALPY CHANGES?

A SIMPLE CALORIMETER



Simple calorimeters



Bomb calorimeter

There are two ways of measuring enthalpy changes:

- Measuring enthalpy changes of combustion
- Measuring enthalpy changes of reaction

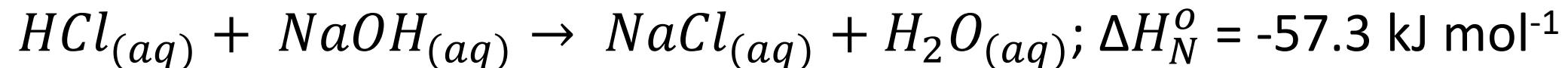


- In an elementary laboratory, enthalpy changes are often measured in a “coffee-cup calorimeter” such as that shown as simple calorimeter . Suppose the reaction to be measured is between two solutions. One of these solutions is introduced into the coffee cup, and the temperature of both solutions is measured.
 - The second solution is now introduced, the mixture stirred, and the rise in temperature recorded.
 - Since the cup is made of polystyrene foam, a very good insulator, very little or no heat energy escapes. Heat lost by the solution = heat gained by the calorimeter.
 - The heat capacity of the calorimeter is the amount of heat absorbed by the calorimeter per unit change in temperature.
- *Heat capacity* =
$$\frac{\text{Quantity of heat } (Q)}{\text{Rise in temp } (\Delta T)}$$
- $$Q = mc\Delta T$$
- where m = mass of the substance



Standard Enthalpy of Neutralization (ΔH_N^o or ΔH_{neut}^o)

-Enthalpy of Neutralization is the heat evolved when one mole of hydrogen ion (from an acid) reacts with a mole of OH⁻ (from a base) to produce one mole of water.



Standard Enthalpy of Formation (ΔH_f^o)

-This is the enthalpy change when one mole of a compound is formed from its constituent elements in their standard states at 298 K and 1 atm pressure.

$$\Delta H_{reaction}^o \equiv \Delta H_f^o$$

- For elements and compounds, their standard states are simply the states in which they exist under standard condition of 298K and 1 atom pressure.

Standard States:

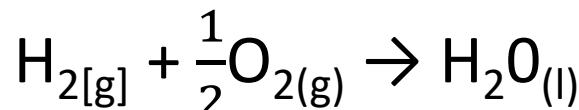
- Solid for elements (except H_g and Br_2)
- Some as diatomic gaseous molecules (H_2 , N_2 , O_2 , F_2 , Cl_2) or monoatomic gases (H_e , N_e , Ar , Kr , X_e , Rn).
- ΔH_f^o of an element is its standard state under standard condition is zero.

Standard Enthalpy of Formation

- ΔH_f^0 of an element in its most stable form under standard conditions is zero.

For example, the standard enthalpies of formation of carbon (graphene), diatomic oxygen gas, diatomic nitrogen gas, sodium metal, and liquid mercury are zero under standard conditions.

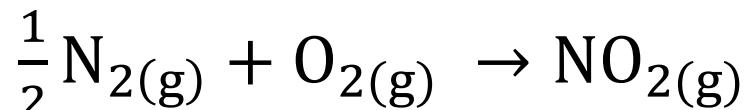
E.g.



- $\Delta H_f^0[H_2O_{(l)}] = -285.9 \text{ kJ mol}^{-1}$



- $\Delta H_f^0[CH_{4(g)}] = -74.9 \text{ kJ mol}^{-1}$



- $\Delta H_f^0 = \Delta H^0 = +33 \text{ kJ mol}^{-1}$ (endothermic reaction)

Note:

$$\Delta H_f^0(O_{2(g)}) = \Delta H_f^0(H_{2(g)}) = \Delta H_f^0(C_{(s)}) = 0$$

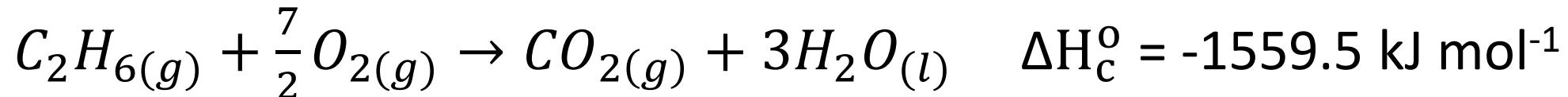
I mole of the product is formed in each case.



Standard Enthalpy of Combustion (ΔH_c°)

- of an element or compound is the enthalpy change when a mole of that compound reacts with oxygen to form product specified by balanced equations at standard conditions.

- For example:

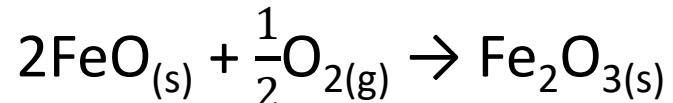


ΔH_c° is always exothermic in nature



Examples

1. Calculate ΔH^0 for the reaction



Given: $\Delta H_f^0[\text{FeO}] = -266 \text{ kJ mol}^{-1}$

$$\Delta H_f^0[\text{Fe}_2\text{O}_3] = -821 \text{ kJ mol}^{-1}$$

Solution:

- Recall: $\Delta H_{\text{reaction}}^0 = \sum n \Delta H_f^0(\text{product}) - \sum m \Delta H_f^0(\text{reactant})$

$$\Delta H_f^0(\text{O}_2) = 0.$$

$$\begin{aligned}\therefore \Delta H_{\text{reaction}}^0 &= [(1)(-821 \text{ kJ mol}^{-1}) - [(2)(-266) + \frac{1}{2}(0)] \\ &= -821 - (-532) = \underline{-289 \text{ kJ.}}\end{aligned}$$

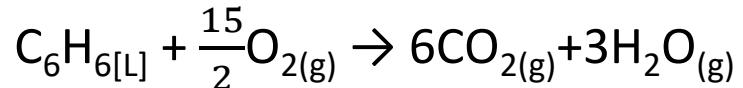
Exothermic



Example 2

- When one mole of benzene, $C_6H_{6(l)}$ is burned to give $CO_{2(g)}$ and $H_2O_{(l)}$, 782 kcal heat is evolved. Calculate ΔH_f° of benzene in $kJmol^{-1}$ and $kcal mol^{-1}$ given H_f° for CO_2 and H_2O to be -394 and -286 $kJmol^{-1}$ respectively. Comment on your answer.
- Solution:

Balance equation of reaction is



Since 782 kcal is evolved in the process

$$(1 \text{ cal} = 4.184 \text{ J})$$

$$\begin{aligned}\Delta H_f^\circ_{\text{reaction}} &= -782 \text{ kcal} = (-782) (4.184) \\ &= 3.27 \times 10^3 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta H_f^\circ_{\text{reaction}} &= 3.27 \times 10^3 \text{ kJ} \\ &= [\sum n \Delta H_f^\circ_{\text{products}} - \sum m \Delta H_f^\circ_{\text{reactants}}] \\ &= [(6)(-394) + (3)(-286) - (\Delta H_f^\circ_{C_6H_6} + 0)] \\ &= -3.27 \times 10^3 \text{ kJ} = -3.22 \times 10 \text{ kJ} - \Delta H_f^\circ_{C_6H_6} \\ \Delta H_f^\circ(C_6H_6) &= -3.22 \times 10 \text{ kJ} + (-3.22 \times 10^3 \text{ kJ}) \\ &= 0.05 \times 10^3 \text{ kJ} = +50 \text{ kJ mol}^{-1}\end{aligned}$$

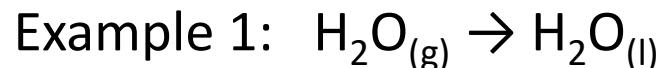
$$\text{In kcal mol}^{-1}, \Delta H_f^\circ = \frac{50}{4.184} = +1.2 \text{ kcal mol}^{-1}$$

Comment : The reaction is Endothermic



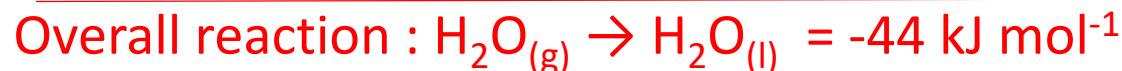
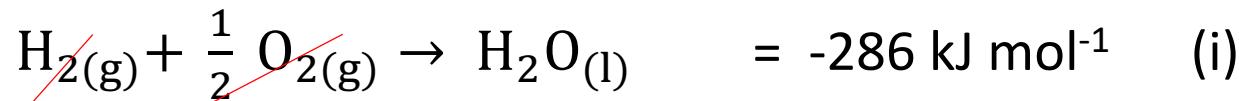
Hess's Law of Enthalpy Summation

- States that: The enthalpy change for a given reaction is a constant (under given condition of temperature and pressure) and is independent of the number of steps by which the reaction occurs.



$$\Delta H = -286 - (-242) = -44 \text{ kJ mol}^{-1} \text{ (since } \Delta H_{\text{condensation}} = \sum n \Delta H_{\text{products}} - \sum m \Delta H_{\text{reactants}})$$

The step by step process:

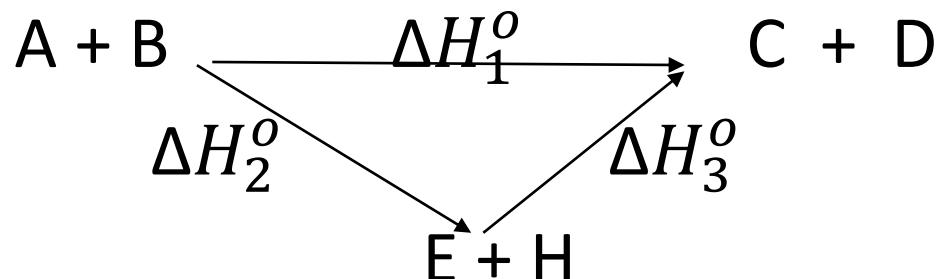


(Adding equations (i) and (ii), H_2 and O_2 cancel out , enthalpy values are added together and the overall reaction is given)



Hess's Law of Enthalpy Summation

- This law states that the total heat change accompanying a chemical reaction is independent of the path taken



$$\Delta H_1^o = \Delta H_2^o + \Delta H_3^o$$

Example 2:

	$\Delta H \text{ (kJ)}$
(i) $\frac{1}{2}\text{N}_2\text{[g]} + \frac{1}{2}\text{O}_2\text{[g]} \rightarrow \text{NO}_{\text{[g]}}$	+90
(i) $\text{NO}_{\text{[g]}} + \text{O}_{\text{[g]}} \rightarrow \text{NO}_2\text{[g]}$	-56
(ii) $2\text{NO}_2\text{[g]} \rightarrow \text{N}_2\text{O}_4\text{[g]}$	-58

Evaluate ΔH for the reaction (iv) $\text{N}_2\text{[g]} + 2\text{O}_2\text{[g]} \rightarrow \text{N}_2\text{O}_4\text{[g]}$



Solution:

Producing N_2O_4 through NO and NO_2 we require we double equating (i) and (ii)

		$\Delta H \text{ (kJ)}$
$2 \times \text{(i)}$	$\text{N}_{2[\text{g}]} + \text{O}_{2[\text{g}]} \rightarrow 2\text{NO}_{2[\text{g}]}$	+180
$2 \times \text{(ii)}$	$2\text{NO}_{[\text{g}]} + \text{O}_{2[\text{g}]} \rightarrow 2\text{NO}_{2[\text{g}]}$	-112
	$2\text{NO}_{2[\text{g}]} \rightarrow \text{N}_{2[\text{g}]} \text{O}_{4[\text{g}]}$	-58

Adding the three equations, the intermediates NO and NO_2 cancel out to give equation(iv)

$$\therefore \Delta H = +190 - 112 - 58 = +10 \text{ kJ.}$$



**CHM 101
(INTRODUCTORY CHEMISTRY I)**

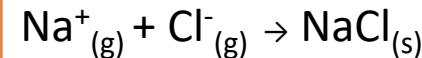
THERMOCHEMISTRY (4)



Born-Haber Cycle:

- This is a technique for applying Hess's law to the standard enthalpy changes which occur when an ionic compound is formed.
- For example, lattice energy is the enthalpy change when one mole of an ionic compound is formed from its constituent ions in gaseous state..

E.g.



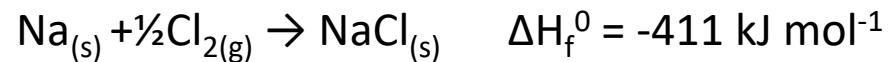
ΔH_L = Lattice energy.

- The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids which are difficult to determine experimentally (but are calculated by means of Born-Haber Cycle).



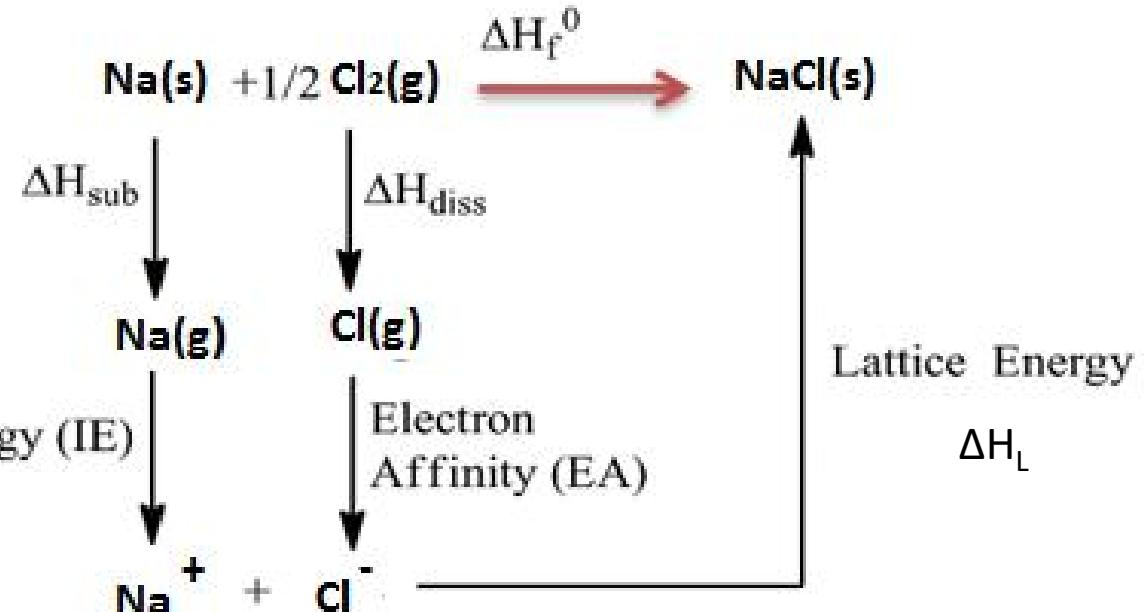
Born-Haber Cycle for Sodium chloride

.....The heat of formation of sodium chloride (ΔH_f^0) from the sodium metal and chlorine gas can be experimentally measured.



The formation of ionic solid sodium chloride from solid sodium metal and gaseous chlorine is not a single step process but goes through several processes. Heat changes of all the processes except the lattice energy can be experimentally measured.

Born Haber Cycle for Sodium Chloride



The steps involved are:

(1) Solid sodium atom sublimes to gaseous atom by absorbing heat energy ($\Delta H_{\text{sub}}^{\circ}$)

$\text{Na}_{[\text{s}]} \rightarrow \text{Na}_{[\text{g}]} : \Delta H_{\text{sub}}^{\circ}$ = Standard enthalpy of sublimation or vaporization.

(2) Gaseous sodium atom absorbs the ionization energy to release one electron and forms gaseous sodium ion.

$\text{Na}_{[\text{s}]} \rightarrow \text{Na}^{+} + \text{e}^{-} : \text{I.E}$ = Ionization energy.

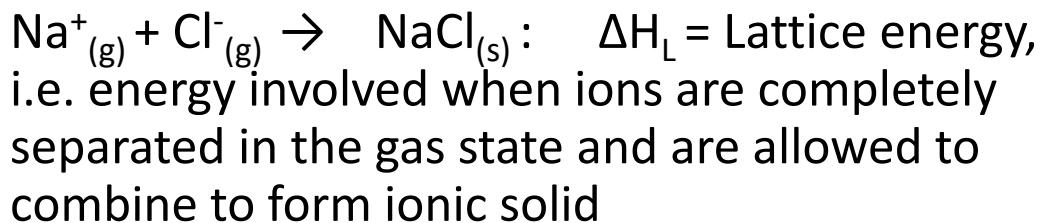
(3) Diatomic gaseous chlorine breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of chlorine molecule

$\frac{1}{2}\text{Cl}_{2(\text{g})} \rightarrow \text{Cl}_{(\text{g})} : \frac{1}{2} \Delta H_{\text{diss}}^{\circ}$ = Heat of dissociation

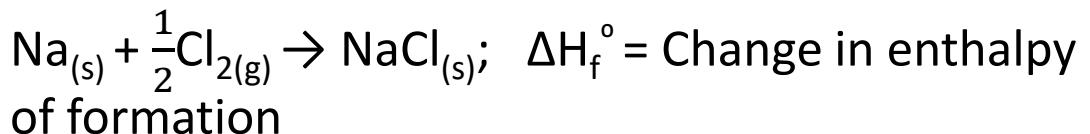
(4) Chlorine atom accepts an electron to form chloride ion and releases energy equivalent to electron affinity.



(5) Gaseous sodium ion and gaseous chloride ion combine to form solid sodium chloride molecule and releases energy equivalent to lattice energy.



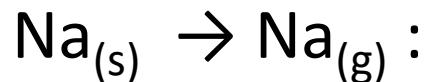
Recall:



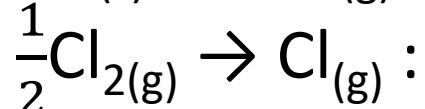
Using Hess's Law for NaCl:

$$\Delta H_f^{\circ} = \Delta H_{\text{sub}}^{\circ} + I.E + \Delta H_{\text{diss}}^{\circ} + E.A + \Delta H_L$$

$$\Delta H_L = \Delta H_f^{\circ} - \Delta H_{\text{sub}}^{\circ} - I.E - \frac{1}{2}\Delta H_{\text{diss}}^{\circ}$$



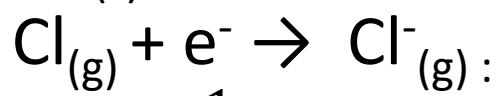
$$\Delta H_{\text{sub}}^{\circ} = 109 \text{ kJ mol}^{-1}$$



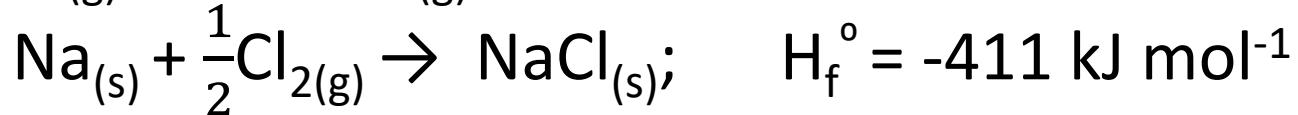
$$\frac{1}{2}\Delta H_{\text{diss}}^{\circ} = 121 \text{ kJ mol}^{-1}$$



$$I.E = 494 \text{ kJ mol}^{-1}$$



$$E.A = -364 \text{ kJ mol}^{-1}$$



$$H_f^{\circ} = -411 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\therefore \Delta H_L &= \Delta H_f^{\circ} - \Delta H_{\text{sub}}^{\circ} - I.E - \frac{1}{2}\Delta H_{\text{diss}}^{\circ} \\ &= -411 - 109 - 494 - 121 - (-364) \\ &= -771 \text{ kJ mol}^{-1}\end{aligned}$$



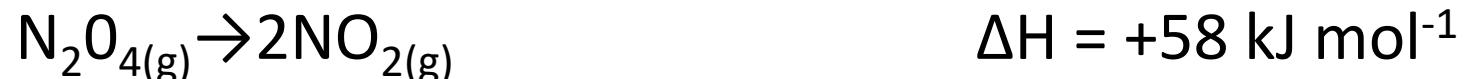
BOND DISSOCIATION ENERGY

- When bonds are formed, energy is released but when bonds are broken, energy is absorbed.
- The bond energy (B.D.E) for a given bond in a molecule is ΔH for the process in which that bond is broken in the molecule in the gas phase and the resulting fragments are separated by an infinite distance.



ΔH here $\equiv \Delta H_{\text{atomisation}}$.

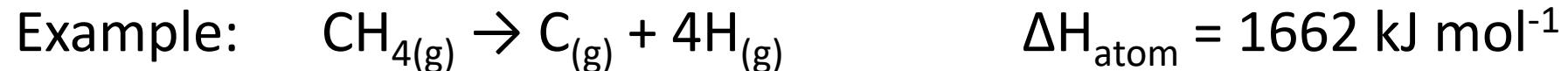
For the dissociation of N_2O_4 ,



$\Delta H \equiv$ Bond energy of the N – N bond in N_2O_4

Note that Bond energy is not the negative of ΔH_f^0





- 4 C-H bonds are broken.

$$\therefore \text{Average C-H bond energy} = \frac{\Delta H_{\text{atom}}}{4} = \frac{1662}{4} = 415.5 \text{ kJ mol}^{-1}$$

$$\Delta H^0_{\text{reaction}} = -\sum m \Delta H^0_{\text{[bond formed]}} + \sum m \Delta H^0_{\text{[bond broken]}}$$

Since ΔH^0 is **+ve** when bonds are broken and ΔH^0 is **-ve** when bonds are formed,

$$\Delta H^0_{\text{reaction}} = \sum n B.E_{\text{reactants}} - \sum m B.E_{\text{products}}$$

- B.E = Bond energy terms of the products and reactants involved in a chemical reaction
- n & m are number of bonds broken and formed in the reactant(s) and product(s) respectively.



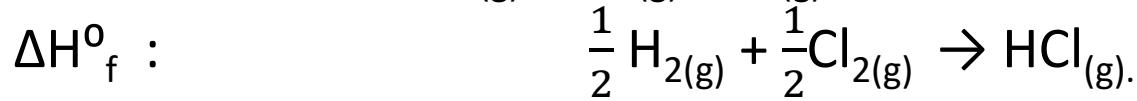
- The sum of the bond energy terms in a particular compound approximately equals the enthalpy of atomization of that compound.

Bond	$\Delta H^\circ \text{ kJ mol}^{-1}$	Bond	$\Delta H^\circ \text{ kJ mol}^{-1}$
C – H	412	C – I	218
C – C	348	N – H	391
H – H	436	O – H	463
C – Cl	327	S – H	344
C – Br	284	C = C	612

- Bond energies represent in enthalpy between a molecule and the atoms. Heat of formation, on the other hand refers to the enthalpy difference between the compound and the elements in their standard states. Hence, a bond energy is not the negative of ΔH_f° .



In HCl, for example, the two processes are



Example (1):

Calculate the bond energy in the HCl molecule from the following information.

$$\Delta H_f^0 \text{ for HCl} = -92.4 \text{ kJ mol}^{-1}$$

Bond energies: H_2 , 432 kJ mol⁻¹

Cl_2 , 238 kJ mol⁻¹

Solution

Hint: B.E can help us to work out ΔH_f^0 values for H atoms and Cl atoms.

$$\Delta H_f^0 \text{ for H} = \frac{432}{2} = 216 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0 \text{ for Cl} = \frac{238}{2} = 119 \text{ kJ mol}^{-1}$$

- The bond energy of HCl is ΔH for the reaction $\text{HCl}_{(\text{g})} \rightarrow \text{H}_{(\text{g})} + \text{Cl}_{(\text{g})}$ (atomization)

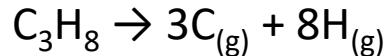
$$\Delta H = (216 + 119) - -(92.4) = 427 \text{ kJ mol}^{-1}$$



Example 2:

Calculate the B.E of C – C in C_3H_8 given that ΔH_{atom} of H = 218 kJ mol^{-1} , ΔH_{atom} of C = 715 kJ mol^{-1} ; $\Delta H_f = -98.7 \text{ kJ mol}^{-1}$ and Bond energy of C – H = 412 kJ mol^{-1}

Solution:



$$\begin{aligned}\Delta H_{atom(C_3H_8)} &= [3\Delta H_{atom(C)} + 8\Delta H_{atom(H)}] - [\Delta H_f(C_3H_8)] \\ &= [(3 \times 715) + (8 \times 218)] - [-98.7]\end{aligned}$$

$$\Delta H_{atom(C_3H_8)} = 3987.7 \text{ kJ mol}^{-1}$$

$$\Delta H_{atom(C_3H_8)} = \Delta H_{reaction} = 3987.7 \text{ kJ mol}^{-1}$$

In C_3H_8 we have,

8 C – H bonds and 2 C – C bonds, which account for the B.E of C_3H_8 .

$$\therefore 3987.7 = 2B.E(C - C) + 8B.E(C - H).$$

$$\begin{aligned}2B.E(C - C) &= 3987.7 - 8B.E(C - H) \\ &= 3987.7 - 8(412) \\ &= 3987.7 - 3296\end{aligned}$$

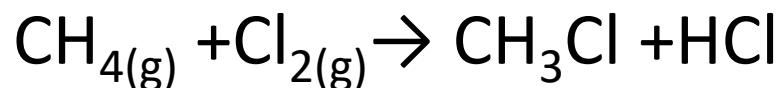
$$2B.E(C - C) = 691.7$$

$$\therefore B.E(C - C) = \frac{691.7}{2} = 345.8 \text{ kJ mol}^{-1}.$$

Example 3:

Calculate the ΔH^0 for the reaction below, given the following bond enthalpies at 298 K

Bonds	$\Delta H^0 \text{ kJ mol}^{-1}$
C-H	+411
Cl-Cl	+243
C-Cl	+327
H-Cl	+431



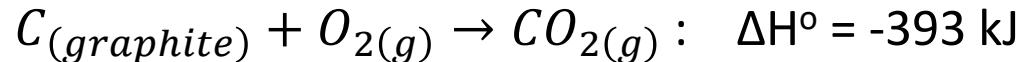
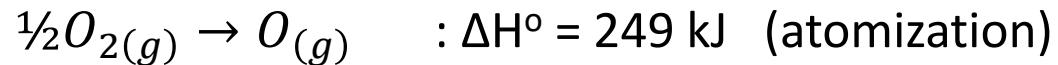
Solution

$$\begin{aligned}\Delta H^0_{\text{reaction}} &= \sum n B.E_{\text{reactants}} - \sum m B.E_{\text{products}} \\ &= [4(\text{C-H}) + 1(\text{Cl-Cl})] - [3(\text{C-H}) + 1(\text{C-Cl}) + 1(\text{H-Cl})] \\ &= [4(411) + 1(243)] - [3(411) + 1(237) + 1(431)] \\ &= -104 \text{ kJ mol}^{-1}\end{aligned}$$

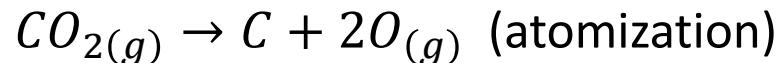


Example 4

Determine the bond energy of CO_2 and hence the average bond energy of C=O in CO_2 given the following information:



Solution



$$\begin{aligned} \text{B.E (or } \Delta H^\circ_{\text{atom}} \text{)} &= [\Delta H^\circ_{(\text{sub})} \text{C}_{(\text{graphite})} + 2 \Delta H^\circ_{\text{atom(O}_2\text{)}}] - [\Delta H^\circ_f \text{CO}_{2(g)}] \\ &= [715 + 2(249)] - [-393] \\ &= 1606 \text{ kJ mol}^{-1} \end{aligned}$$

The structure of CO_2 is O=C=O

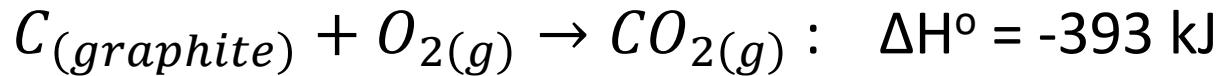
\therefore there are 2 C=O in CO_2

$$\text{Average bond energy of C=O in CO}_2 = \frac{\text{B.E(CO}_2\text{)}}{2}$$

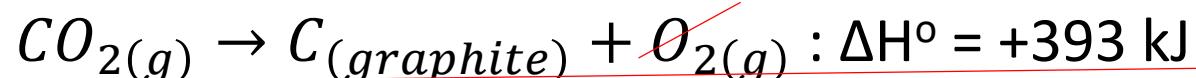
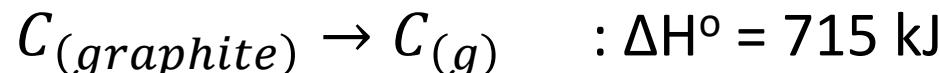
$$= \frac{1606}{2} = \boxed{803 \text{ kJ mol}^{-1}}$$



- Alternative method: from the information provided.....



To determine bond energy of CO_2 (i.e ΔH_{atom} of CO_2); we rearrange the equations to ensure CO_2 appears on the LHS of the equation and apply Hess's law.....



$$\text{Average bond energy of C=O in } \text{CO}_2 = \frac{B.E(\text{CO}_2)}{2}$$

$$= \frac{1606}{2} = 803 \text{ kJ mol}^{-1}$$



**CHM 101
(INTRODUCTORY CHEMISTRY I)**

THERMOCHEMISTRY (5)

Additional Note on Entropy – Ideal gas systems

- Like enthalpy, change in entropy of a reaction can be determined using the expression:

$$\Delta S = \sum n \Delta S_{\text{(products)}} - \sum m \Delta S_{\text{(reactants)}}$$

where n and m are coefficients of the substances in the product(s) and reactant(s) respectively.

For an isothermal expansion of n moles of an ideal gas from state 1 to state 2,

$$\Delta S = n R \ln \frac{V_2}{V_1} \quad (1)$$

For an ideal gas:

$$p_1 V_1 = p_2 V_2$$

$$\frac{p_1}{p_2} = \frac{V_2}{V_1} \quad (2)$$

Therefore,

$$\Delta S = n R \ln \frac{p_1}{p_2} \quad (3)$$

Equations (1) and (3) are applicable when volume changes and pressure changes are involved respectively

Calculating entropy for ideal gas systems.....

- Example:

Calculate the entropy change accompanying a two hundred fold expansion of 5 moles of an ideal gas [$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$].

Solution: Using equation (1) given earlier,

$$\Delta S = n R \ln \frac{V_2}{V_1}$$

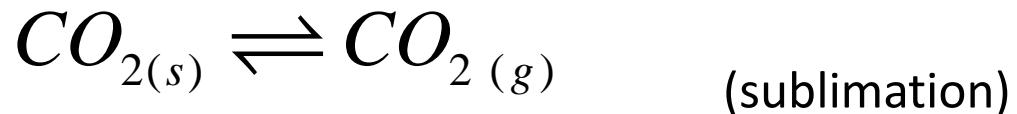
If $V_1 = x \text{ dm}^3$, $V_2 = 100x \text{ dm}^3$

$$\Delta S = (5 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{100x}{x}$$

$$\Delta S = 220.2 \text{ J K}^{-1}$$

Entropy for Phase Transition

- Consider the phase transition:



All phase transitions are always in equilibrium with each other, hence,

$$\Delta G = 0$$

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

$$\Delta G = 0 = \Delta H_t - T\Delta S_t \quad \text{for phase transition,}$$

t denotes phase transition

$$\therefore \Delta S_t = \frac{\Delta H_t}{T_t}$$

where, ΔS_t = entropy change accompanying transition

ΔH_t = enthalpy change accompanying transition

T_t = temperature of transition

Exercise 1.

The heat of vaporization ΔH_{vap} of carbon tetrachloride, CCl_4 at $25^\circ C$ is 43 kJ mol^{-1} . If 1 mole of liquid CCl_4 at $25^\circ C$ has an entropy of 214 J K^{-1} . What is the entropy of 1 mole of the vapor in equilibrium with the liquid at this temperature?

Exercise 2.

Calculate the entropy change when 4.6 grams of nitrogen (IV) oxide gas is allowed to expand isothermally from a volume of 240 cm^3 to volume of 1050.54 dm^3 at $38^\circ C$ [$N=14.00$; $O = 16.0 \text{ g mol}^{-1}$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$]

FREE ENERGY

Free energy has the dimensions of energy. Free energy is used to determine how systems change and how much work they can produce

Two forms exist:

1. Helmholtz free energy F – called work function
2. Gibb's free energy G

Expressed as.....

$$F = U - TS$$

$$G = U + PV - TS$$

$$G = H - TS,$$

$$\text{and } H = U + PV.$$

where:

U = Internal energy

T = Temp above Zero

H = Enthalpy

S = Entropy

- Free energy is an extensive property (i.e. Its magnitude depends on the amount of substance in a given thermodynamic state).
- Since chemical reactions release energy when energy-storing bonds are broken, how is the energy associated with chemical reactions quantified and expressed? How can the energy released from one reaction be compared to that of another reaction?
- A measurement of free energy is used to quantitate these energy transfers.

Calculating ΔG

- Free energy is called Gibbs free energy (G) after Josiah Willard Gibbs, the scientist who developed the measurement.
- Every chemical reaction involves a change in free energy, called delta G (ΔG).
- The change in free energy can be calculated for any system that undergoes a change, such as a chemical reaction.
- To calculate ΔG , subtract the amount of energy lost to entropy (denoted as ΔS) from the total energy change of the system (ΔH).

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

- Change in free energy ΔG is the amount of energy available to do work. Hence, ΔG is useful in determining the direction of spontaneous change and evaluating the maximum work that can be obtained from thermodynamic process.

Like enthalpy and entropy, Gibb's free energy (G) depends on the initial and final state of the system undergoing change (i.e. **Gibb's free energy is also a state function**).

$$\Delta G = G_{\text{(products)}} - G_{\text{(reactants)}}$$

and

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

For any chemical reaction,

$$\Delta G = \sum n \Delta G_{\text{(products)}} - \sum m \Delta G_{\text{(reactants)}}$$

when,

$\Delta G = -ve$ -Reaction is spontaneous (the reaction will occur as written)

$\Delta G = 0$ -Reaction is at equilibrium (i.e. two phases are in equilibrium, no useful work)

$\Delta G = +ve$ -Reaction is not spontaneous (reaction cannot do work)

e.g. $\Delta G = -ve$ for $T > 273.16K$ i.e. ice changes to water

$\Delta G = +ve$ for $T < 273.16K$ i.e. reverse reaction of freezing taken place.

- Under standard conditions (25°C and 1 atmosphere pressure),

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

- Free energy of formation of an element in its standard state is zero.

Estimation of Free Energy

Gibb's free energy is also related to the equilibrium constant (K) by the expression.

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

$$\Delta G = -2.303 RT \log_{10} K$$

R = Gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

T = Temperature in Kelvin

K = Equilibrium constant

- Using the equation $\Delta G = \Delta H - T\Delta S$
 - (a) At low temperatures: $T\Delta S$ becomes small and ΔH controls the sign of ΔG . Exothermic reactions are thus feasible at low temperature.
 - (b) At high temperatures: $T\Delta S$ becomes large and more important.
 - i. *For Endothermic reactions*, ΔS must be large enough for ΔG to be –ve
 - ii. *Endothermic reactions* become explosive and favourable at high temperatures.

Spontaneity and Non-spontaneity (ΔG values)

- Enthalpy and Entropy can be combined to predict reaction spontaneity

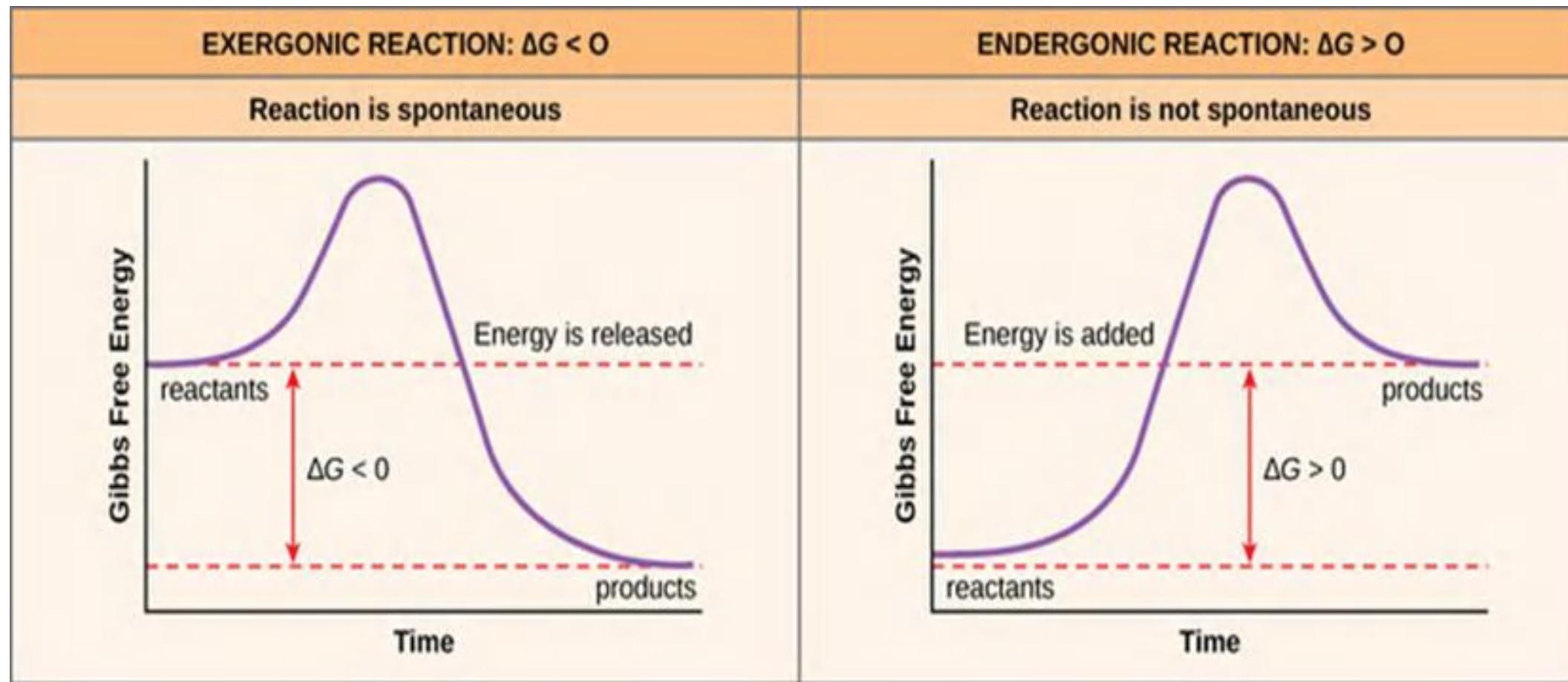
$$\Delta G = \Delta H - T\Delta S$$

ΔH	ΔS	ΔG	Comments on Reaction
-	+	-	Always spontaneous
+	+	+ or -	Spontaneous at high temperatures
-	-	+ or -	Spontaneous at low temperatures
+	-	+	Never spontaneous

Endergonic and Exergonic Reactions

- Reactions that release energy have $\Delta G < 0$.
- A negative ΔG also means that the products of the reaction have less free energy than the reactants because they gave off some free energy during the reaction.
- Reactions that have a negative ΔG are called exergonic reactions. Exergonic means energy is exiting the system.
- These reactions are also referred to as spontaneous reactions because they can occur without the addition of energy into the system (e.g, rusting of iron is a spontaneous reaction that occurs slowly, little by little, over time.)
- If a chemical reaction requires an input of energy rather than releasing energy, then the ΔG for that reaction will be a positive value.
- In this case, the products have more free energy than the reactants. Thus, the products of these reactions can be thought of as energy-storing molecules. These chemical reactions are called endergonic reactions; they are non-spontaneous.
- An endergonic reaction will not take place on its own without the addition of energy.

Energy Diagram: Exergonic and Endergonic Reactions

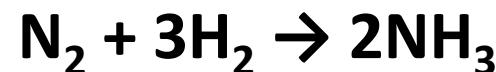


Source: <https://www.google.com/url?sa=i&url=https%3A%2F%2Fwww.khanacademy.org%2Fscience%2Fbiology%2Fenergy-and-enzymes%2Ffree-energy-tutorial%2Fa%2Fgibbs-free-energy&psig=AOvVaw2Cys6Tt8sVqDDkJ3NLajRX&ust=1616805450486000&source=images&cd=vfe&ved=0CAIQjRxqFwoTCIDW6ufbzO8CFQAAAAAAdAAAAABAD>

EXAMPLES

Example 1.

Determine the standard free energy change for the following reaction at 25°C.



Given ΔH and ΔS are -81.5 kJ and -189.0 J/K

- **Solution:**

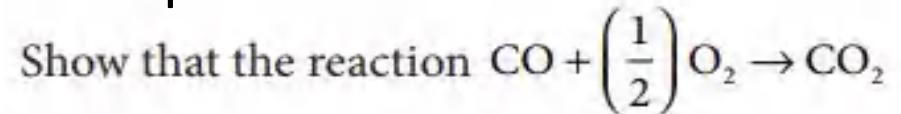
We have an equation, $\Delta G = \Delta H - T\Delta S$

Substitute the above values in this equation

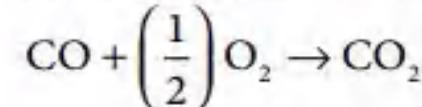
$$\Delta G = -81.5 \text{ kJ} - (298 \text{ K}) (-0.1890 \text{ kJ/K})$$

$$\Delta G = -24.7 \text{ kJ}$$

Example 2



at 300K is spontaneous. The standard Gibbs free energies of formation of CO_2 and CO are -394.4 and -137.2 kJ mole⁻¹ respectively.



$$\Delta G_{(\text{reaction})}^0 = \sum G_f^0(\text{products}) - \sum G_f^0(\text{reactants})$$

$$\Delta G_{(\text{reaction})}^0 = \left[G_{\text{CO}_2}^0 \right] - \left[G_{\text{CO}}^0 + \frac{1}{2} G_{\text{O}_2}^0 \right]$$

$$\Delta G_{(\text{reaction})}^0 = -394.4 + [137.2 + 0]$$

$$\Delta G_{(\text{reaction})}^0 = -257.2 \text{ kJ mol}^{-1}$$

$\Delta G_{(\text{reaction})}$ of a reaction at a given temperature is negative hence the reaction is spontaneous.

Source: [https://www.brainkart.com/article/Solved-Example-Problems--Gibbs-free-energy-\(G\)_34806/](https://www.brainkart.com/article/Solved-Example-Problems--Gibbs-free-energy-(G)_34806/)

Practice Questions:

For practice questions, go to [Entropy and Gibb's free energy](#)
(right click on the link and choose **open Hyperlink**)

For more practice question with solutions, go to [Enthalpy, Entropy and
Gibb's free energy](#)

ELECTROCHEMISTRY (MODULE 1)

COURSE OUTLINE

Electrical units, ohm's law, Faraday's law of electrolysis, Electrochemical cells, Galvanic cells, Standard Hydrogen Electrode (Half Cell) Standard Electrode Potentials and Reactions Concentration effects (Nernst equation) Redox Reaction. Oxidation Potentials treated in terms of free Energy change.

Objectives

At the end of this topic, students will be able to

- Describe the relationship between time, current and the amount of substance produced or consumed in an electrolytic cell
- Solve problems using Faraday's law
- Describe an electrochemical cell and differentiate between galvanic cell and electrolytic cells
- Describe the oxidation and reduction half cells for some galvanic cells and be able to determine the direction of current flow.
- Determine the relationship between cell potential and Gibbs free energy
- Examine relationship between the standard cell potential and the equilibrium constant, K
- Apply Nernst equation for calculating the emf of galvanic cell and define standard potential of cell.

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry that deals with the interchange of chemical and electrical energy.

- It is primarily concerned with two processes that involve oxidation-reduction reaction
 - i. The use of current to produce chemical change – **Electrolytic cell**
 - ii. The generation of an electric current from a chemical reaction – **Galvanic cells or Voltaic cell**

Electrochemistry constitutes one of the most important interfaces between chemistry and everyday life.

- it provides techniques for monitoring chemical reactions
- Used in measuring properties of solution e.g pH of solution, the pKa of an acid
- Helps in monitoring the activity of our brain and heart
- Used in measuring the pH of our blood and the presence of pollutants in our water supply.
- Used in batteries and in solving corrosion of ion
- Manufacturing of some chemicals e.g. NaOH, extraction of Al, Mg and Calcium. Purification of Cu

Electrical Units

There are few electrical units which we should understand before taking up study of quantitative aspects of electrochemistry

- **Coulomb (C)**

A coulomb is a unit quantity of electricity.

- *it is the amount of electricity that passes when a current of 1 ampere (A) flows from 1 second*

- **Ampere (I)**

An ampere is a unit rate of flow of electricity

- An ampere is a current of one coulomb per second

- **Ohm (R)**

An ohm is a unit of electricity resistance

- **Volt (V)**

A volt is a unit of electromotive force.

- It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.

Ohms Law

This law states that current (I) is inversely proportional to the resistance (R)

$$\therefore I \propto \frac{1}{R}$$

$$I = \frac{V}{R} \quad \text{or} \quad V = IR$$

where V is the voltage in volt

I is the current in amperes

R is the resistance in ohms

The quantity of electricity called coulombs (Q) is related to current by

$$Q = I \times t$$

where t = time in second

I = current in amperes

The quantity of electricity presented in one mole of electron is 96,500 coulombs and is called a **Faraday**.

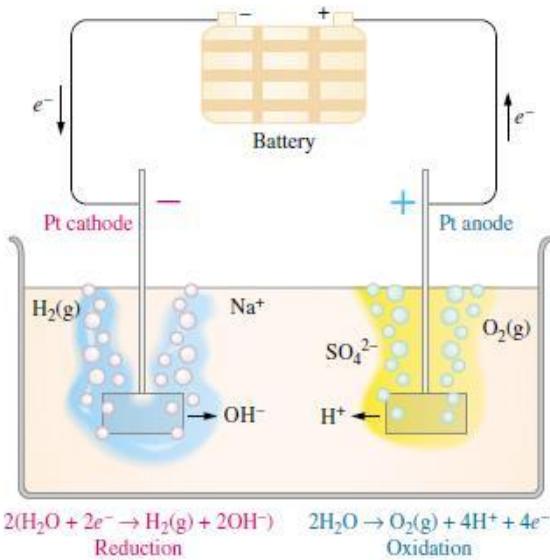
$$\text{i.e. } 1 \text{ Faraday} = 96,485 \text{ coulombs} \approx 96,500 \text{ coulombs} \approx 9.65 \times 10^4 \text{ coulombs}$$

Hence

96,500 coulombs per mole of electron is called Faraday constant

Electrolysis

- This deals with the production of chemical reaction by means of an electric current.
- The conduction if electricity is always accompanied by decomposition of the electrolyte
- Electrolysis takes place in an electrolytic cell



The **electrolytic cell** contains two electrodes and either a molten salt solution or some other type of solution (e.g. aqueous)

- The external emf is provided by a source of direct current (sometimes another voltaic cell, or battery)
- This external current acts as an **electron pump** to **push electrons into one electrode** (and **drive a reduction reaction**) and **to withdraw electrons from the other electrode** (and **drive an oxidation reaction**)
 - The electrode where **oxidation** occurs is still called the **anode**. However, **for an electrolytic cell it is labeled as "+"** to indicate that this is the electrode where electrons are being withdrawn by the external EMF
 - The electrode where **reduction** occurs is still called the **cathode**. However, **for an electrolytic cell it is labeled as "-"** to indicate that this is the electrode where electrons are being pumped into by the external EMF

Definitions

Electrolytes – are compounds which when in molten form or dissolved in a suitable solvent, will conduct electivity.

Note that *an electrolyte always contain ions*. Hence they are usually ionic compounds
e.g Na₂SO₄ solution: 2Na⁺_(aq) and SO₄²⁻_(aq)

Non-electrolytes – are compounds which does not conduct electric current either in molten form or solution.

- They contain no ions. They are usually covalent compounds (Always in molecular form)

Electrodes

These are two poles or rods through which electric current enters or leave an electrolyte. **The positive electrodes** are known as **ANODE**.

- It is the electrode through which electrons leave the electrolytes

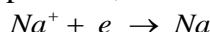
The negative electrode is called **CATHODE**

- It is the electrode through which electrons enter the electrolyte.

Quantitative Electrolysis and Electrolytic Cells

One important aspect of electrolysis reactions is their stoichiometry

- Suppose we pass a current through a solution or a molten salt, how much substance will be liberated from the solution at electrode?
- For this problem, we work on a **mole basis**. e.g.



One electron reduces one sodium ion to an atom.

Therefore one mole electron reduces one mole sodium ion to produce one mole sodium atom.

This is done by knowing the charge on the electron and the value of Avogadro number.

Hence the quantity of electricity that produce one mole is

$$\begin{aligned} &= (1.602 \times 10^{-19} \text{ coulomb}) \times (6.023 \times 10^{23} \text{ mole}^{-1}) \\ &\quad \text{charge on one electron} \qquad \qquad \text{No of electron in one mole} \\ &= 96,490 \text{ coulomb mole}^{-1} \end{aligned}$$

A coulomb (C) is the quantity of electricity that passes when a current of 1 ampere (A) flows from 1 second.

Hence, to pass one mole of electron through an electrode, we would have to pass 1 ampere for 96,490 seconds or 26.80 hrs.

- The quantity of electricity is known as Faraday constant (F) $\approx 96,500 \text{ C mole}^{-1}$ (three significant figures)
- This came from Michael Faraday law of electrolysis

Faraday's First Law

The mass of a product of electrolysis is proportional to the quantity of electricity pass.

$$\begin{aligned} i.e. m &\propto Q \\ m &\propto It \end{aligned} \tag{1}$$

Since $Q = It$.

$m = \text{mass of product of electrolysis}$

$I = \text{current and } t = \text{seconds}$

Faraday's Second Law

If the same quantity of electricity is passed through a series of electrolytes in separate cells, then the mass of the different products are proportional to the chemical equivalents.

$$i.e. m \propto E \tag{2}$$

where E = chemical equivalent

$$E = \frac{M_r}{n}$$

M_r = Atomic mass

n = unit charge of ion (valency of the ion)

Combining equations (1) and (2)

$$m \propto EIt$$

$$m = \frac{EIt}{95,000} \text{ grams}$$

$$m = ZIt \quad (3)$$

where Z = the electrochemical equivalent

$$Z = \frac{E}{96,500}$$

Substituting, $E = \frac{M_r}{n}$

$$Z = \frac{M_r}{96,500}$$

substituting in equation (3) gives

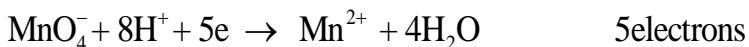
$$m = M \frac{M_r}{96,500 n}$$

This equation is used to calculate the mass of a product of electrolysis if all other quantities are known.

The reduction of Na^+ is a one electron process



Other oxidation or reduction processes may involve the transfer of more than one electron e.g.



- The relationship between the amount of substance undergoing gain or loss of electrons and the quantity of electricity passed will depend on the number of electrons required to effect the change on each ion or molecule.
- Hence, the number of moles of a substance oxidized or reduced at an electrode is equal to the number of moles of electrons passed divided by the number of electrons involved in the electrodes reaction for each ion or molecule or the substance.

- If we pass a current i ampere for a period of t seconds through an electrode at which an n electron change is occurring, the amount of substance undergoing the reaction at the electrode will be

$$\frac{it}{nF} = \frac{it}{96,500} \text{ moles}$$

- The quantity of substances undergoing reaction when one mole of electron passes will obviously be $\frac{1}{n}$ moles

- This is often referred to as one equivalent of the substance.

Hence value of equivalent will depend on n (i.e. in the reaction that is occurring)

∴ it is not fixed for a given substance

e.g In Fe,

- it could enter into reaction where $n=2$ or $n=3$

Note: we cannot speak on an equivalent of substance without specifying the reaction it undergoes.

For this CHM 101, this concept will not be used, but instead the mole concept coupled with the value of n derived from the half-cell reaction equation will be used.

Example 1: How much Br_2 is liberated by electrolysis of molten KBr for 30 minutes at a current of 2.0A?

Solution

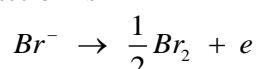
$$30 \text{ mins} = 30 \times 60 \text{ s} = 1800 \text{ s}$$

At a current of 2.0A (2.0 C s^{-1})

The amount of electricity passed is

$$2.0 \times 1800 = 3600 \text{ C} = \frac{3600}{96,500} = 0.0373 \text{ mole of electron}$$

The anode reaction is



From the above reaction, in one electron process, $\frac{1}{2}$ mole of Br_2 is liberated

∴ 1 mole of electron liberates $\frac{1}{2}$ mole of Br_2

$$\begin{aligned} \text{Hence 1 mole of electron liberates } & \frac{1}{2} \times 2 (79.9 \text{ g}) \\ & = 79.9 \text{ g} \end{aligned}$$

0.0373 mole of electron liberates $0.0373 \text{ moles} \times 79.9 \text{ g/mole} = 3.0 \text{ g Br}_2$

CHM 101

ELECTROCHEMISTRY

Prof. O.O.SORIYAN

MODULE 1

COURSE OUTLINE

Module 1: Electrical units, ohm's law, Faraday's law of electrolysis.

Module 2: Electrochemical cells, Galvanic cells, Standard Hydrogen Electrode (Half Cell)
Standard Electrode Potentials and Reactions

Module 3: Concentration effects (Nernst equation) Redox Reaction.
Oxidation Potentials treated in terms of free Energy change.

MODULE 1

Electrical units,
ohm's law,
Faraday's law of
electrolysis.

Objectives

At the end of this module, students will be able to

- Describe the relationship between time, current and the amount of substance produced or consumed in an electrolytic cell
- Solve problems using Faraday's law of electrolysis.

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry that deals with the interchange of **chemical** and **electrical energy**.

ELECTROCHEMISTRY (contd)

- ▶ It is primarily concerned with two processes that involve oxidation-reduction reaction
- ▶ The use of current to produce chemical change – **Electrolytic cell**
- ▶ The generation of an electric current from a chemical reaction – **Galvanic cells or Voltaic cell**

Application of Electrochemistry

- ▶ it provides techniques for monitoring chemical reactions
- ▶ Used in measuring properties of solution e.g pH of solution, the pKa of an acid
- ▶ Helps in monitoring the activity of our brain and heart
- ▶ Used in measuring the pH of our blood and the presence of pollutants in our water supply.
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ELECTRICAL UNITS

Coulomb (C)

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Ampere (I)

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- ▶ *An ampere is a current of one coulomb per second*

Ohm (R)

- ❖ An ohm is a unit of electricity resistance

Volt (V)

- ❖ A volt is a unit of electromotive force.
- ▶ *It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.*

Ohms Law

- ▶ This law states that current (I) is inversely proportional to the resistance (R)

$$I \propto \frac{1}{R}$$
$$I = \frac{V}{R} \quad or \quad V = IR$$

- ▶ where V is the voltage in volt
- ▶ I is the current in amperes
- ▶ R is the resistance in ohms

- ▶ The quantity of electricity called coulombs (Q) is related to current by

$$Q = I \times t$$

where t = *time in seconds*

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The quantity of electricity presented in one mole of electron is 96,500 coulombs and is called a **Faraday**.

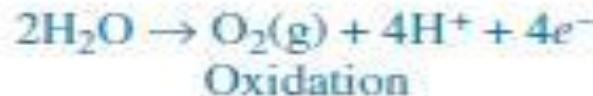
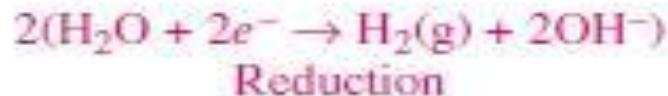
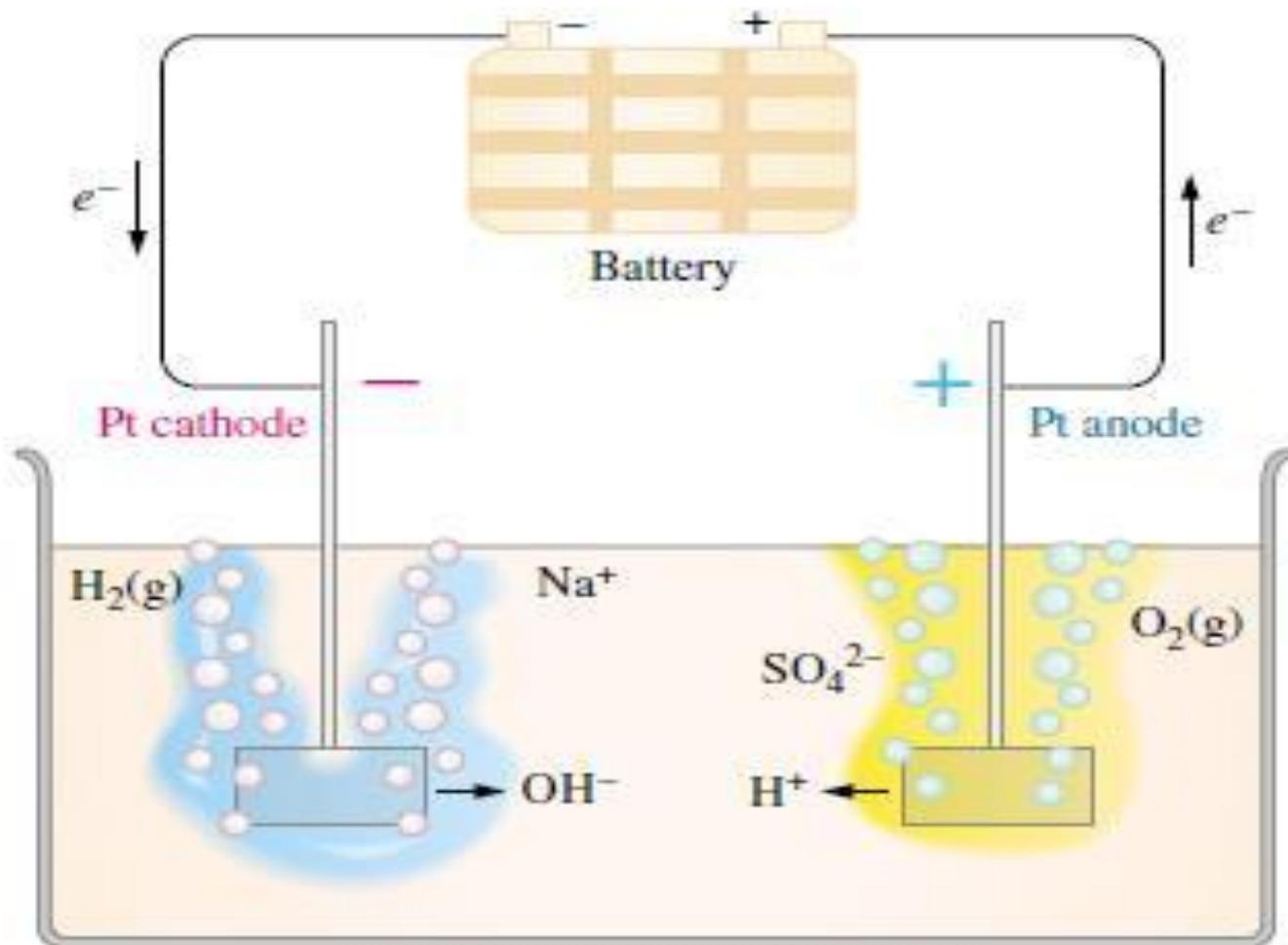
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Hence, 96,500 coulombs per mole of electron is called Faraday constant

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- ▶ The conduction if electricity is always accompanied by decomposition of the electrolyte
- ▶ Electrolysis takes place in an electrolytic cell

Electrolytic Cell



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- . The external emf is provided by a source of direct current (sometimes another voltaic cell, or battery)
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- The electrode where *oxidation* occurs is still called the *anode*. However, *for an electrolytic cell it is labeled as "+"* to indicate that this is the electrode where electrons are being withdrawn by the external EMF
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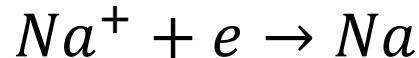
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- ▶ **Non-electrolytes** – are compounds which does not conduct electric current either in molten form or solution.
- ▶ **Electrodes** –These are two poles or rods through which electric current enters or leave an electrolyte.
The positive electrodes are known as **ANODE**.
 - ❖ It is the electrode through which electrons leave the electrolytes**The negative electrode** is called **CATHODE**
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Quantitative Electrolysis and Electrolytic Cells

One important aspect of electrolysis reactions is their stoichiometry

- Suppose we pass a current through a solution or a molten salt, how much substance will be liberated from the solution at electrode?
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- ▶ One electron reduces one sodium ion to an atom.
- ▶ Therefore one mole electron reduces one mole sodium ion to produce one mole sodium atom.
- ▶ This is done by knowing the charge on the electron and the value of Avogadro number.

Hence the quantity of electricity that produce one mole is
= $(1.602 \times 10^{-19} \text{ Coulomb}) \times (6,023 \times 10^{23} \text{ mole}^{-1})$
= *charge on one electron* \times *No of electron in one mole*
= 96,490 coulomb mole $^{-1}$

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Hence, to pass one mole of electron through an electrode, we would have to pass 1 ampere for 96,490 seconds or 26.80 hrs.

- The quantity of electricity is known as Faraday constant (F)
 $\approx 96,500 \text{ C mole}^{-1}$ (three significant figures)
- This came from Michael Faraday law of electrolysis

Faraday's laws of electrolysis

Faraday's First Law

States that:

The mass of a product of electrolysis is proportional to the quantity of electricity pass.

$$m \propto Q$$
$$m \propto It \quad (1)$$

where m = mass of product of electrolysis

I = current and t = time (in seconds)

Faraday's Second Law

States that:

If the same quantity of electricity is passed through a series of electrolytes in separate cells, then the mass of the different products are proportional to the chemical equivalents.

$$m \propto E \quad (2)$$

where E = chemical equivalent

$$E = \frac{M_r}{n}$$

M_r = Atomic mass

n = unit charge of ion (valency of the ion)

Combining equations (1) and (2)

$$m \propto EIt$$

$$m = \frac{EIt}{95,000} \text{ grams}$$

$$m = ZIt \quad (3)$$

where $Z = \text{the electrochemical equivalent}$

$$Z = \frac{E}{96,500}$$

Substituting, $E = \frac{M_r}{n}$

$$Z = \frac{M_r}{96,500}$$

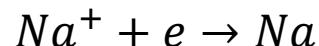
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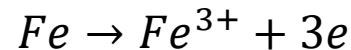
The reduction of Na^+ is a one electron process



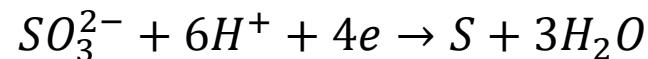
Other oxidation or reduction processes may involve the transfer of more than one electron e.g.



2 electrons



3 electrons



4 electrons

- The relationship between the amount of substance undergoing gain or loss of electrons and the quantity of electricity passed will depend on the number of electrons required to effect the change on each ion or molecule.

- Hence, the number of moles of a substance oxidized or reduced at an electrode is equal to the number or moles or electrons passed divided by the number of electrons involved in the electrode's reaction for each ion or molecule or the substance.
- If we pass a current i ampere for a period of t seconds through an electrode at which an n electron change is occurring, the amount of substance undergoing the reaction at the electrode will be

$$\frac{it}{nF} = \frac{it}{96,500} \text{ moles}$$

The quantity of substances undergoing reaction when one mole of electron passes will obviously be $\frac{1}{n}$ moles

This is often referred to as one equivalent of the substance.

Hence value of equivalent will depend on n (i.e. in the reaction that is occurring)

Therefore it is not fixed for a given substance

e.g In Fe,

Therefore it could enter into reaction where $n = 2$ or $n = 3$

Note: we cannot speak on an equivalent of substance without specifying the reaction it undergoes.

For this CHM 101, this concept will not be used, but instead the mole concept coupled with the value of n derived from the half-cell reaction equation will be used.

Example 1: How much Br_2 is liberated by electrolysis of molten KBr for 30 minutes at a current of 2.0A?

Solution

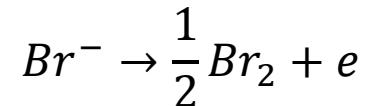
$$30 \text{ mins} = 30 \times 60 \text{ s} = 1800 \text{ s}$$

At a current of 2.0A (2.0 C s^{-1})

The amount of electricity passed is

$$2.0 \times 1800 = 3600 \text{ C} = \frac{3600}{96500} = 0.0373 \text{ mole of electrons}$$

The anode reaction is



From the above reaction, in one electron process, $\frac{1}{2}$ mole of Br_2 is liberated
1 mole of electron liberates $\frac{1}{2}$ mole of Br_2

$$\begin{aligned} \text{Hence 1 mole of electron liberates} & \quad \frac{1}{2} \times 2 (79.9\text{g}) \\ & = 79.9\text{g} \end{aligned}$$

$$0.0373 \text{ mole of electron liberates } 0.0373 \text{ moles} \times 79.9\text{g/mole} = 3.0\text{g Br}_2$$

ELECTROCHEMISTRY

MODULE 2

Electrochemical cells, Galvanic cells,
Standard Hydrogen Electrode (Half Cell) Standard Electrode Potentials and Reactions

Objectives of Module 2

At the end of Module 2, students will be able to

- Describe an electrochemical cell and differentiate between galvanic cell and electrolytic cells
- Describe the oxidation and reduction half cells for some galvanic cells and be able to determine the direction of current flow.

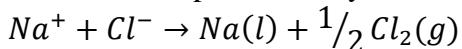
Electrochemical Cell

Electrochemical cell is a device in which an electric current (flow of electrons) is either produced by a spontaneous chemical reaction or is used to bring about a non-spontaneous reaction.

Recall in Thermodynamic (or Thermochemistry) A spontaneous reaction is a reaction that has a natural tendencies to occur on its own without external influences.

- i.e. the free energy of such reaction must be negative ($\Delta G_{rxn} = -ve$)
- We have discussed electrolysis reaction occurring in cells called Electrolytic cells. This is an example of electrochemical cell.

The reaction is carried out by using an external potential difference to supply the necessary energy, since the electrolysis reaction will not occur spontaneously.



- ❖ This requires considerable energy input to go as written.

Note: *The products of the reaction at each electrode must be kept apart to prevent spontaneous reaction occurring in the reverse direction.*

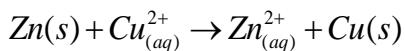
Voltaic Cells (or Galvanic Cells)

A voltaic (galvanic cells) is an electrochemical cell in which a spontaneous chemical reaction is used to generate an electrical current.

- Galvanic cell name to honors Luigi, Galvani (1737 – 1798) an Italian credited with discovery of electricity.
- Voltaic cell-after Aleksandra Volta (1745 – 1829) who constructed cell of this type -1800.

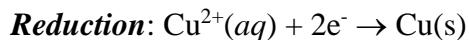
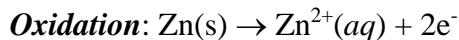
They take advantage of a spontaneous reaction. e.g. batteries.

To understand how redox reaction can be used to generate a current, let consider reaction between Zn(s) and Cu²⁺(aq)



- The reaction as shown is spontaneous. The Zinc metal is *oxidized*, and the Copper ion is *reduced*
- The reverse reaction, the oxidation of Copper and the reduction of Zinc ion, *is not spontaneous*

The **redox half-reactions** for the above reaction would be:

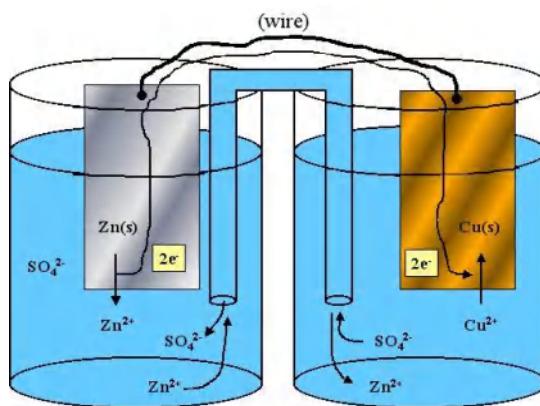


- The oxidation of a Zinc atom releases 2 electrons
- The reduction of a Copper ion is achieved by the acceptance of 2 electrons

Thus, there would appear to be a movement, or flow, of electrons from the Zinc metal to the Copper ions

According to the above equation, if Zinc metal is placed in an aqueous solution containing Cu^{2+} ions (e.g. a solution of copper sulfate salt), the following will occur:

The oxidizing agent can be separated from the reducing agent as below

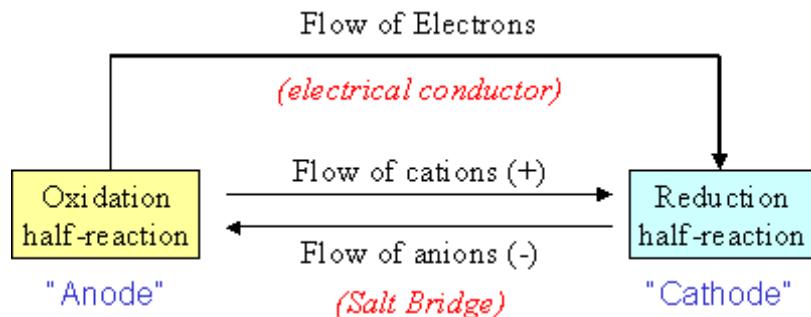


- If the electrons flowed from right to left component, then the left component (receiving electrons) would be **negatively charged** while the right component (losing electrons) would be **positively charged**.
- In consideration of keeping the overall concentration of ions in balance between the two sides, cations will also be moving to the right:
- Thus, in the connecting tube of solution we have net movement of both types of ions:
 - anions are going into the oxidation side
 - cations going into the reduction side
- *The connecting tube of solution is called a Salt Bridge*
- Electrons flow through the wire from reducing agent to oxidizing agent

The two solid metals in the different half-reactions are called **electrodes**

- The metal in the half-reaction where **oxidation** is occurring is called the **Anode**
- The metal in the half-reaction where **reduction** is occurring is called the **Cathode**
- The **cathode** is often labeled with a "+"; "this electrode **"attracts electrons"**"
- The **anode** is often labeled with a "-"; "this electrode **"repels electrons"**"

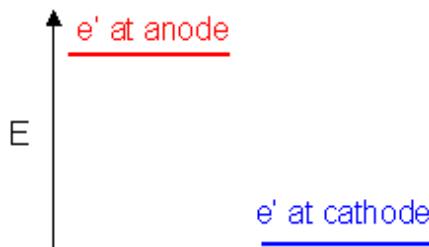
Summary of the movement of ions, electrons and the redox half-reactions in a voltaic cell:



Cell Potential

A key question is: what causes the electrons to flow from the anode to the cathode?

- The electrons flow from the anode to the cathode because of a **difference in the potential energy** of the electrons at the anode compared to the cathode
- In particular, the potential energy of the electrons is higher at the anode than at the cathode



- The potential difference between two electrodes is called the **electromotive force**, or **emf**
- The emf of a voltaic cell is called the **cell potential**, or the **cell voltage**
- The cell voltage of a voltaic cell will be positive value
- Unit of electrical potential is volt (V) is define as 1 joule of work per coulomb of charge transfer
- Instrument use in measurement of the cell potential is volt meter.

When current flow through a wire, the frictional heating that occurs waste some of the useful energy.

∴ A voltmeter will measure a potential that is lower than the maximum cell potential. The instrument that measures an accurate measurement is a potentiometer (since no energy is wasted heating the wire).

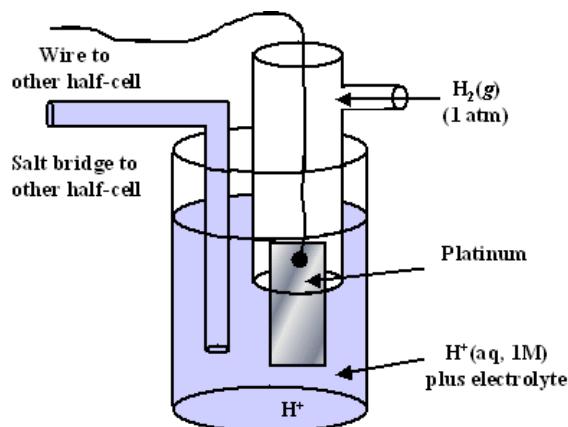
- With advances in electronic technology we now have digital voltmeters (which draw a negligible amount of current).

- This instrument are more convenient to use, they have replaced potentiometers in the modern laboratory.

The standard hydrogen electrode (SHE)

The absolute potential of single metal/metal ion system cannot be measured directly.

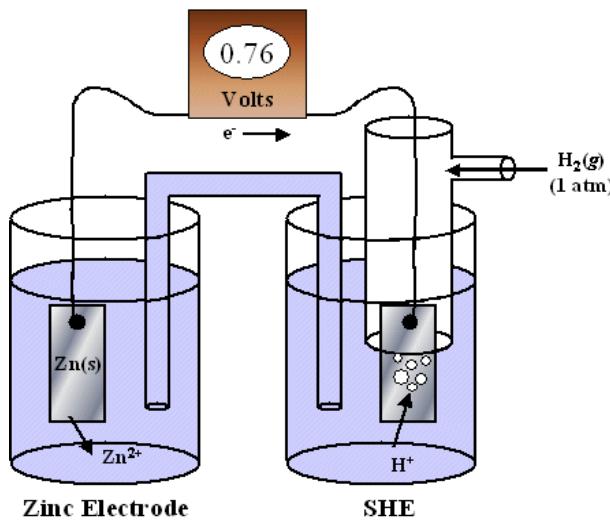
- For conveniences in working with cell potentials there is a universal accepted convention for measuring cell potentials.
- We construct a standard hydrogen electrode, which is an electrode in which gaseous hydrogen at one atmosphere pressure is in equilibrium with hydrogen ions in solution, concentration 1M at 25°C over a platinum surface.



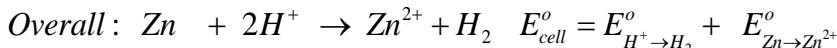
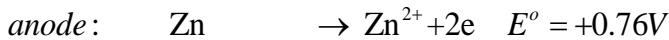
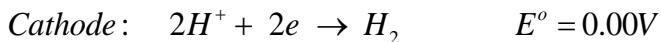
Hence the standard hydrogen potential is the reference potential against which all half-reaction potentials are assigned.

Example

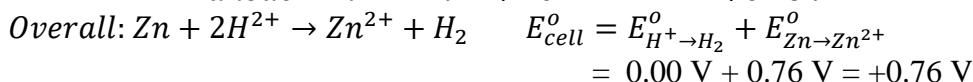
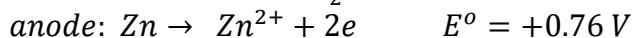
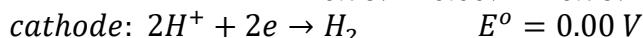
Suppose we assemble a cell by combining a standard hydrogen electrode with a zinc metal electrode immersed in 1M ZnSO₄ Solution.



We can write down the equation for each half-cell reaction with its accompanying standard electrode potential, given the symbol E^o

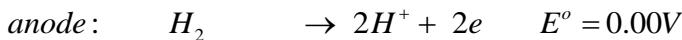
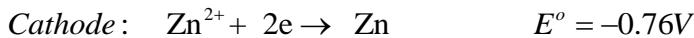


$$0.76V = 0.00V + 0.76V$$



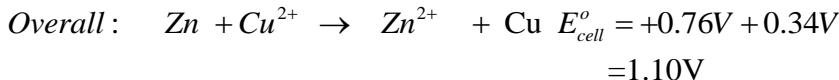
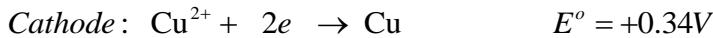
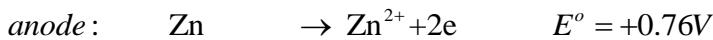
The superscript o indicates that standard states are used (**This will be discussed later**).

- a) When a half-reaction is reversed, the sign of E^o is reversed. e.g.

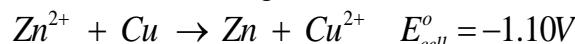


Note: Reaction will spontaneously proceed in the direction for which the overall cell potential is positive.

- If we now assemble a cell by taking one Cu/Cu²⁺ electrode and one Zn/Zn²⁺ electrode
- We can use this to forecast the overall cell potential and the direction in which the reaction will spontaneously proceed. e.g.



For the reverse reaction, E^o is negative.

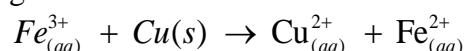


Hence, the reaction is non spontaneous since E_{cell}^o is negative.

- b) When a half-reaction is multiplied by an integer, E^o remain the same.

- This is because standard reduction is an intensive properties (**it does not depend on how many times the reaction occurs**)
- The potential is not multiplied by the integer required to balance the cell reaction e.g.

Consider a galvanic cell on the redox reaction.



Half reactions are



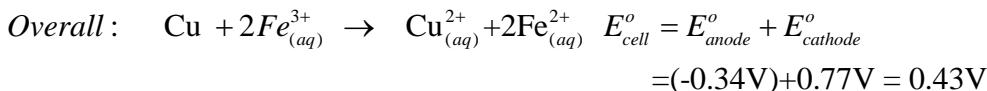
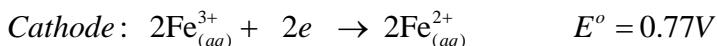
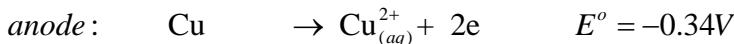
Since Cu^{2+}/Cu has the lower positive E° value it will be forced to run in reverse (anode reaction)



- Each Fe^{3+} ion accepts only one electron,
 - Hence reaction (i) must be multiplied by 2



to obtain a balanced equation



- The measurement of the half-cell potentials of a whole variety of electrodes with reference to standard hydrogen electrode can be done easily.
- Hence overall cell potential of any pair of can be worked out like this.

Note that all half-reactions are given as reduction processes in standard tables in most text books. These E° values are measured under standard conditions which are defined as follows:

Definitions of Standard State

- For a gas, the standard state is a pressure of exactly 1 atm (H_2 , O_2 , Cl_2 etc)
- For a substance present in a solution, the standard state is a concentration of exactly 1M at an applied pressure of 1 atm (e.g. Cu^{2+} , H^+ , Cl^- etc)
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid. e.g. Cu, Zn, Mg
- A temperature of 25°C

The half-cell potentials are all given as reductions

- This is the usual practice.
- The table is referred to as standard reduction potential.

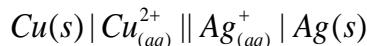
Cell Notation

Chemists have devised a short hand way of describing the make-up of a galvanic cell.

- By convention, in standard cell notation, the anode half-cell is specified on the left, with electrode material of the anode given first.

anode electrode | anode electrolyte || cathode electrolyte | cathode electrode

e.g. for a copper – silver cell, it is represented as

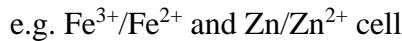


In this case,

- Anode electrode is copper metal
- the single vertical bar represents **phase boundary** between copper electrodes and the solution
- the double vertical bars represent **the two phase boundaries one at each end of the salt bridge**
- on the right is the cathode half cell

Sometimes, both the oxidized and reduced forms of the reactants in a half-cell are soluble and cannot be used as an electrode

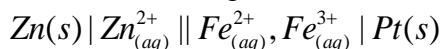
- in such cases, an inert electrode compound of platinum or gold is used to provide a site for electron transfer.



The cell reaction is given as



The cell notation for the galvanic cell is

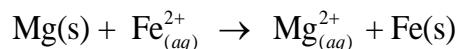


where we have separated the formulas for the two iron ions by a comma.

- The reduction of the Fe^{3+} to Fe^{2+} takes place at the surface of the inert platinum electrode.

Home work

- (i) Sketch and label galvanic cell that makes use of the following spontaneous redox reaction.

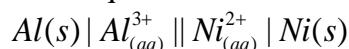


Write the half-reactions for the anode and cathode. Give the standard cell notation.

(Hint: determine which half-reaction represents oxidation and which represents reduction)

- (ii) Write the anode and cathode half-reaction for the following galvanic cell.

Write the equation for the overall cell reaction.



Sketch and label a galvanic cell that corresponds to the standard cell notation.

CHM 101

ELECTROCHEMISTRY

Prof. O.O.SORIYAN

MODULE 2

MODULE 2

**Electrochemical cells,
Galvanic cells,
Standard Hydrogen
Electrode (Half Cell)
Standard Electrode
Potentials and Reactions**

Objectives of Module 2

At the end of Module 2, students will be able to

- Describe an electrochemical cell and differentiate between galvanic cell and electrolytic cells
- Describe the oxidation and reduction half cells for some galvanic cells and be able to determine the direction of current flow.

Electrochemical Cell

Electrochemical cell is a device in which an electric current (flow of electrons) is either produced by a spontaneous chemical reaction or is used to bring about a non-spontaneous reaction.

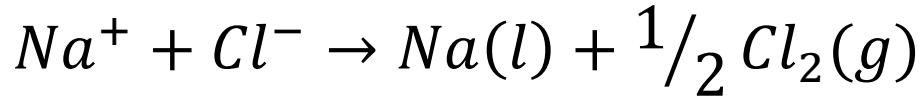
Recall in Thermochemistry: A spontaneous reaction is a reaction that has a natural tendencies to occur on its own without external influences.

**i.e. the free energy of such reaction must be negative
 $(\Delta G_{rxn} = -ve)$**

We have discussed electrolysis reaction occurring in cells called Electrolytic cells.

This is an example of electrochemical cell.

The reaction is carried out by using an external potential difference to supply the necessary energy, since the electrolysis reaction will not occur spontaneously.



- ❖ This requires considerable energy input to go as written.

Note: *The products of the reaction at each electrode must be kept apart to prevent spontaneous reaction occurring in the reverse direction.*

Voltaic Cells (or Galvanic Cells)

A voltaic (galvanic cells) is an electrochemical cell in which a spontaneous chemical reaction is used to generate an electrical current.

- Galvanic cell name to honors Luigi, Galvani (1737 – 1798) an Italian credited with discovery of electricity.
- Voltaic cell-after Aleksandra Volta (1745 – 1829) who constructed cell of this type -1800.

They take advantage of a spontaneous reaction. e.g. batteries.

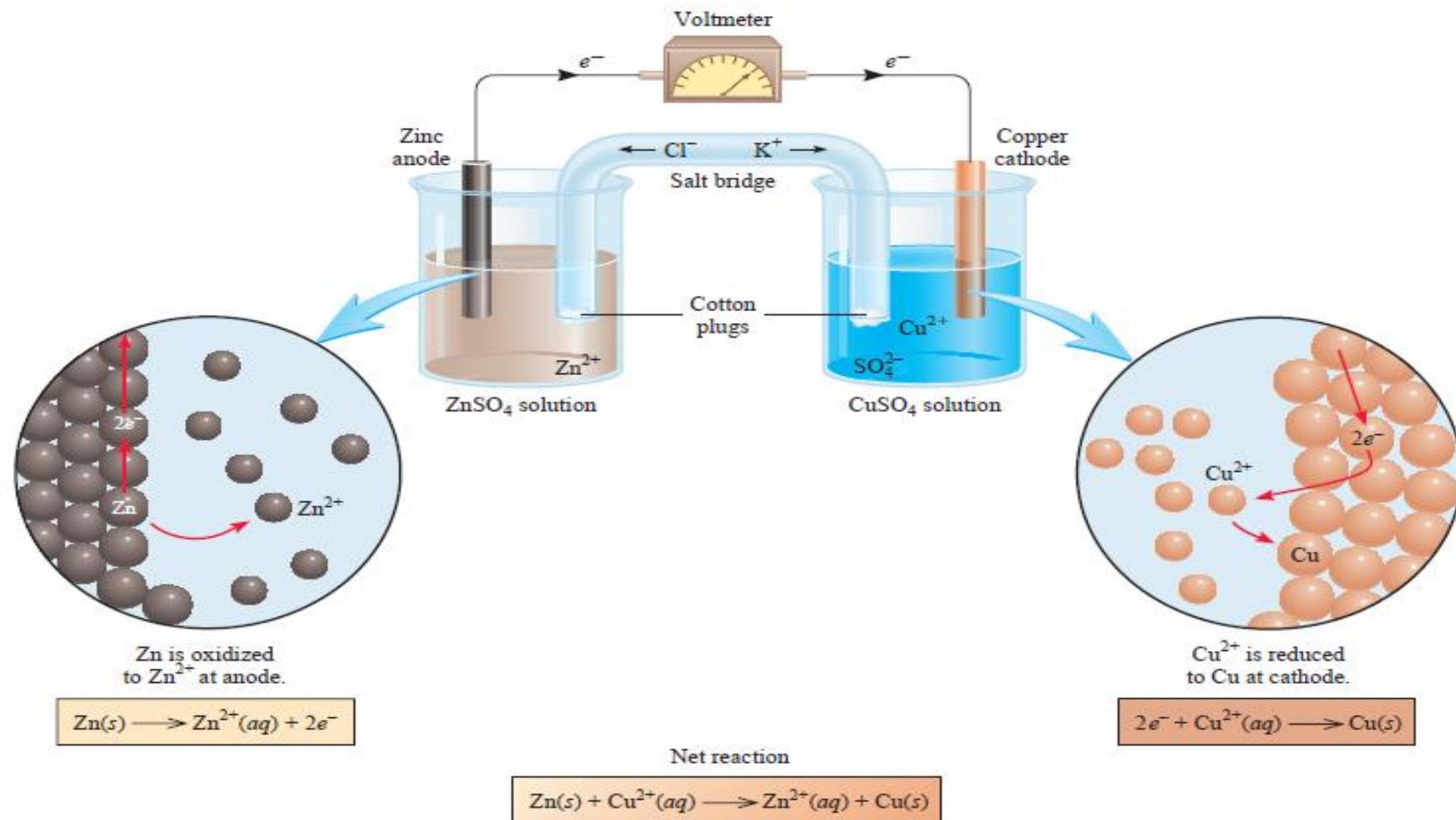
- ▶ How redox reaction can be used to generate a current, let consider reaction between Zn(s) and Cu²⁺(aq)



- The reaction as shown is spontaneous. The Zinc metal is *oxidized*, and the Copper ion is *reduced*
 - The reverse reaction, the oxidation of Copper and the reduction of Zinc ion, *is not spontaneous*
- The *redox half-reactions* for the above reaction would be:
- ▶ *Oxidation:* $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(aq) + 2\text{e}^-$
 - ▶ *Reduction:* $\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu(s)}$

- The oxidation of a Zinc atom releases 2 electrons
 - The reduction of a Copper ion is achieved by the acceptance of 2 electrons
- *Thus, there would appear to be a movement, or flow, of electrons from the Zinc metal to the Copper ions*
- According to the above equation, if Zinc metal is placed in an aqueous solution containing Cu^{2+} ions (e.g. a solution of copper sulfate salt), the following will occur:
- The oxidizing agent can be separated from the reducing agent as below

Voltaic Cell



- If the electrons flowed from right to left component, then the left component (receiving electrons) would be **negatively charged** while the right component (losing electrons) would be **positively charged**.
- In consideration of keeping the overall concentration of ions in balance between the two sides, cations will also be moving to the right:
- Thus, in the connecting tube of solution we have net movement of both types of ions:
 - anions are going into the oxidation side
 - cations going into the reduction side
- *The connecting tube of solution is called a **Salt Bridge***
- Electrons flow through the wire from reducing agent to oxidizing agent

The two solid metals in the different half-reactions are called *electrodes*

- The metal in the half-reaction where *oxidation* is occurring is called the *Anode*
- The metal in the half-reaction where *reduction* is occurring is called the *Cathode*
- The *cathode* is often labeled with a "+"; "this electrode *attracts electrons*"
- The *anode* is often labeled with a "-"; "this electrode *repels electrons*"

Movement of ions, electrons and the redox half-reactions in a voltaic cell

Flow of Electrons

(electrical conductor)

Oxidation
half-reaction

"Anode"

Flow of cations (+)

Reduction
half-reaction

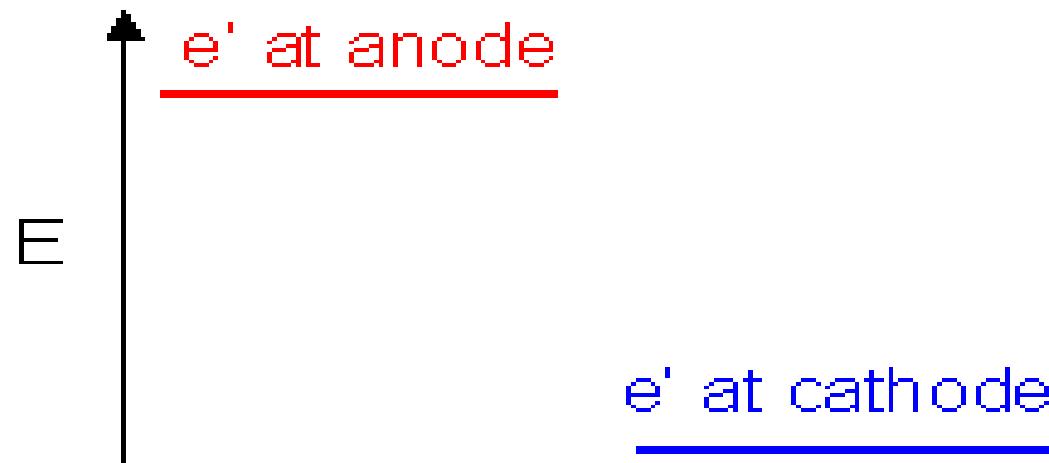
"Cathode"

Flow of anions (-)

(Salt Bridge)

Cell Potential

- ▶ A key question is: what causes the electrons to flow from the anode to the cathode?
- The electrons flow from the anode to the cathode because of a *difference in the potential energy* of the electrons at the anode compared to the cathode
- In particular, the potential energy of the electrons is higher at the anode than at the cathode



The standard hydrogen electrode (SHE)

The absolute potential of single metal/metal ion system cannot be measured directly.

- For conveniences in working with cell potentials there is a universal accepted convention for measuring cell potentials.
- We construct a **standard hydrogen electrode**, which is an electrode in which gaseous hydrogen at one atmosphere pressure is in equilibrium with hydrogen ions in solution, concentration 1M at 25°C over a platinum surface.

- The potential difference between two electrodes is called the ***electromotive force***, or **emf**
- The emf of a voltaic cell is called the ***cell potential***, or the **cell voltage**
- The cell voltage of a voltaic cell will be positive value
- Unit of electrical potential is volt (V) is define as 1 joule of work per coulomb of charge transfer
- Instrument use in measurement of the cell potential is **voltmeter**.

When current flow through a wire, the frictional heating that occurs waste some of the useful energy.

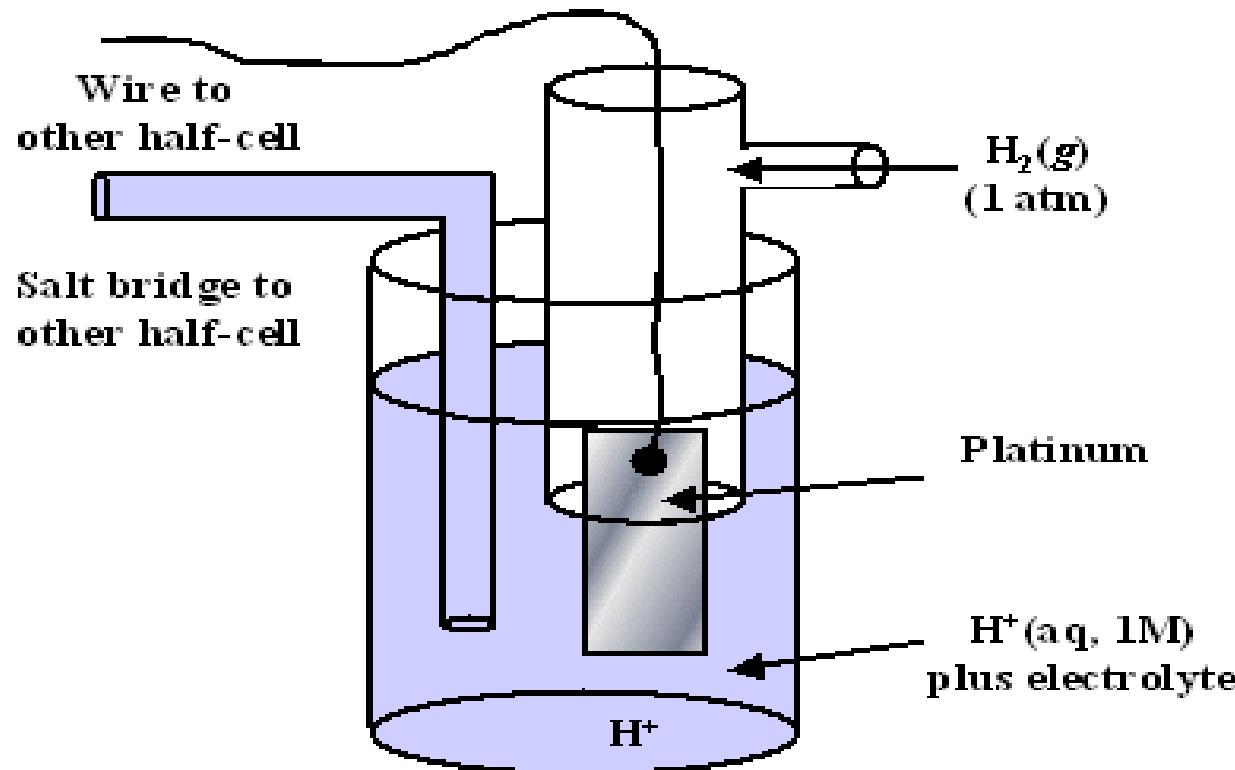
The instrument that measures an accurate measurement is a **potentiometer** (since no energy is wasted heating the wire).

The standard hydrogen electrode (SHE)

The absolute potential of single metal/metal ion system cannot be measured directly.

- For conveniences in working with cell potentials there is a universal accepted convention for measuring cell potentials.
- We construct a **standard hydrogen electrode**, which is an electrode in which gaseous hydrogen at one atmosphere pressure is in equilibrium with hydrogen ions in solution, concentration 1M at 25°C over a platinum surface.

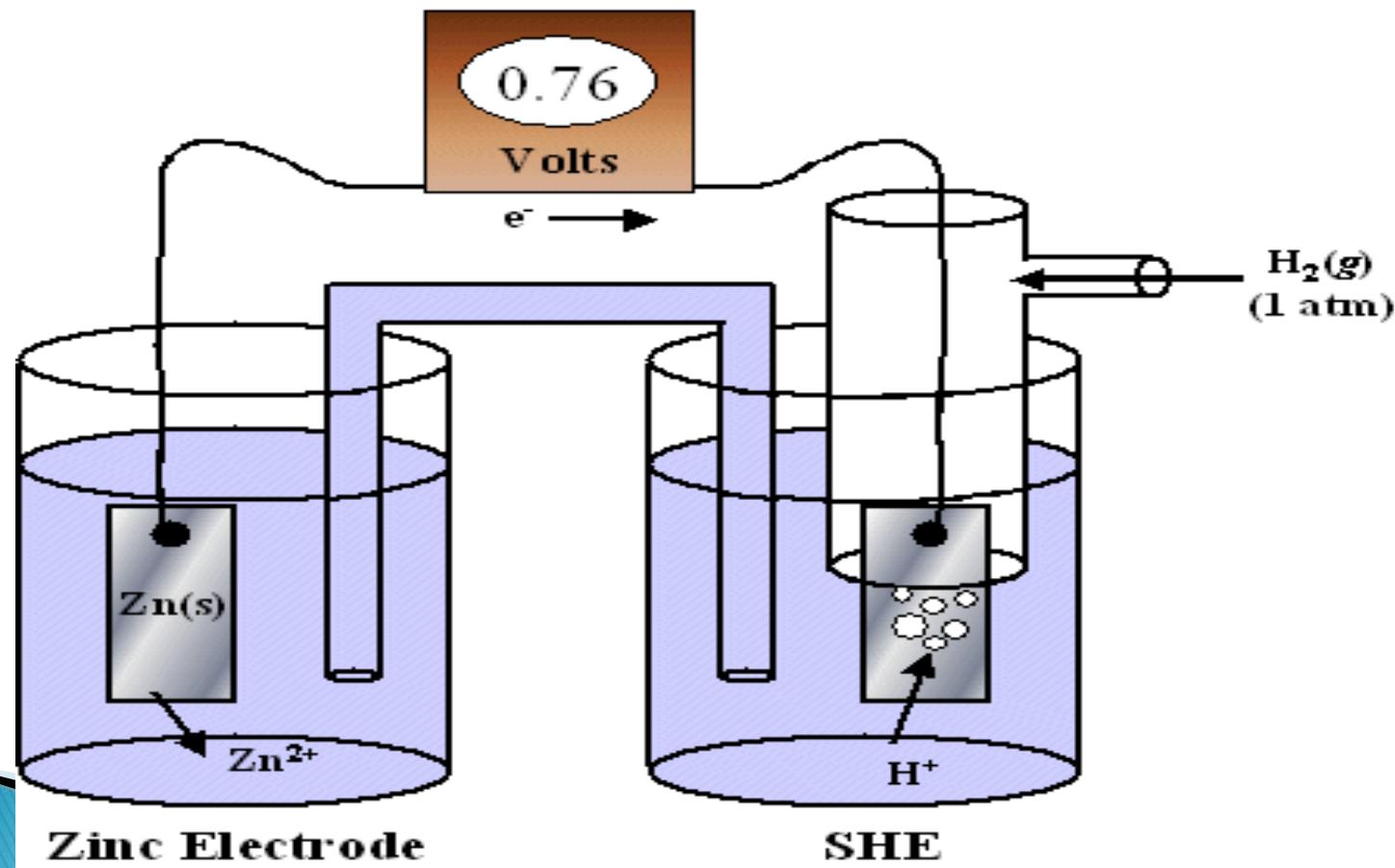
The standard hydrogen electrode (SHE)

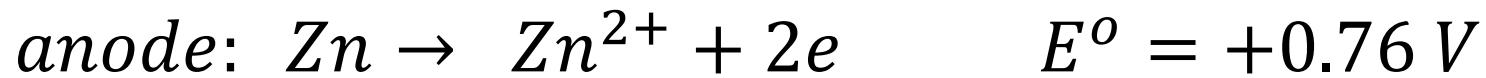


Hence the standard hydrogen potential is the reference potential against which all half-reaction potentials are assigned.

A standard hydrogen electrode with a zinc metal electrode

Suppose we assemble a cell by combining a standard hydrogen electrode with a zinc metal electrode immersed in IM ZnSO_4 Solution.

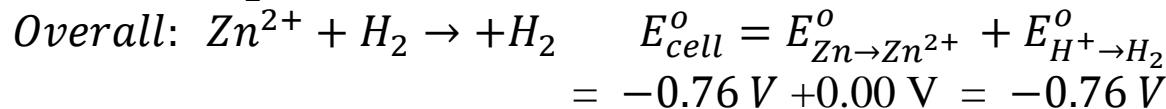
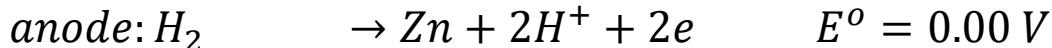




$$\begin{aligned} E_{cell}^o &= E_{H^+ \rightarrow H_2}^o + E_{Zn \rightarrow Zn^{2+}}^o \\ &= 0.00 \text{ V} + 0.76 \text{ V} = +0.76 \text{ V} \end{aligned}$$

The superscript ^o indicates that standard states are used
(This will be discussed later).

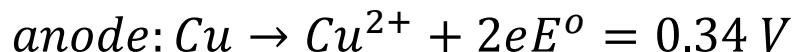
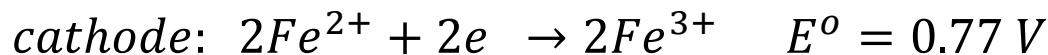
a. When a half-reaction is reversed, the sign of E^o is reversed. e.g.



Note: Reaction will spontaneously proceed in the direction for which the overall cell potential is positive.

b. When a half-reaction is multiplied by an integer, E^o remain the same.

- ▶ This is because standard reduction is an intensive properties (**it does not depend on how many times the reaction occurs**)
- ▶ The potential is not multiplied by the integer required to balance the cell reaction



$$E_{\text{cell}}^o = E_{\text{anode}}^o + E_{\text{cathode}}^o$$

Definitions of Standard State

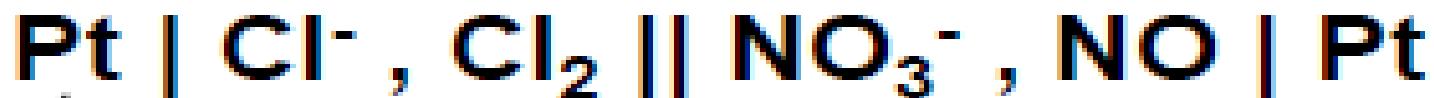
- ▶ For a gas, the standard state is a pressure of exactly 1 atm (H_2 , O_2 , Cl_2 etc)
- ▶ For a substance present in a solution, the standard state is a concentration of exactly 1M at an applied pressure of 1 atm (e.g. Cu^{2+} , H^+ , Cl^- etc)
- ▶ For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid. e.g. Cu, Zn, Mg
- ▶ A temperature of 25°C

Cell Notation

- ▶ A short hand way of describing the make-up of a galvanic cell
 - ▶ anode electrode | anode electrolyte || cathode electrolyte | cathode electrode
 - ▶ for in copper – silver cell, it is represented as
- ▶ $\text{Cu(s)}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$

Cell Notation

More complex abbreviated cell notations



Platinum
Electrode

Species in the
same phase



Oxidation (or reduction)
species in different phases

ELECTROCHEMISTRY

MODULE 3

Concentration effects (Nernst equation) Redox Reaction. Oxidation Potentials treated in terms of free Energy change.

Objectives of Module 3

At the end of this topic, students will be able to

- Determine the relationship between cell potential and Gibbs free energy
- Examine relationship between the standard cell potential and the equilibrium constant, K
- Apply Nernst equation for calculating the emf of galvanic cell and define standard potential of cell.

Relationship between cell potential and free energy

From thermochemistry or thermodynamics, we know for a reaction to be spontaneous, free energy ΔG must be negative

$$\Delta G = -ve$$

$$i.e \Delta G = -ve$$

and cell potential for the reaction E_{cell}^o must be positive

$$E_{cell}^o = +ve$$

$$i.e E_{cell}^o = +ve$$

for an electrochemical cell, the energy change for a chemical reaction is given by

$$\Delta G^o = nFE_{cell}^o$$

$$\Delta G = -nFE_{cell}^o$$

n = number of moles of electrons transfer in the reaction as given by the balanced equation.

F = Faraday constant - it is measured by charge per mole of electrons .

F = 96500 coulomb/mole or $9.6485 \times 10^4 C/mole$

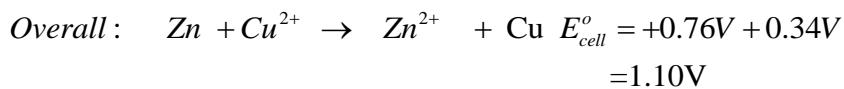
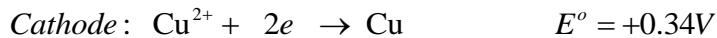
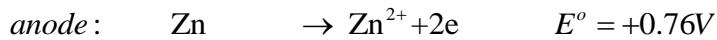
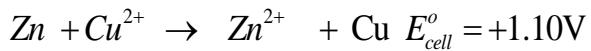
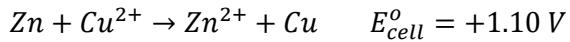
From this equation, the following conclusions can be obtained:

- When E_{cell}^o is positive , the cell reaction is feasible
- When E_{cell}^o is negative; the cell reaction is not feasible.
- When E_{cell}^o is zero, the cell reaction is in equilibrium.

Question 7: Calculate the free energy of Daniel Cell?

Solution:

The cell reaction is



From the half reaction, the number of mole of electron is

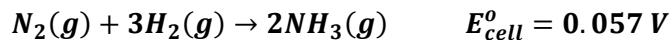
$$\therefore n = 2$$

$$\begin{aligned}\Delta G &= -nFE_{cell}^o \\ &= -(2)99.65 \times 10^4 C / mole)(1.10 V) \\ &= -2.10 \times 10^5 CV / mole\end{aligned}$$

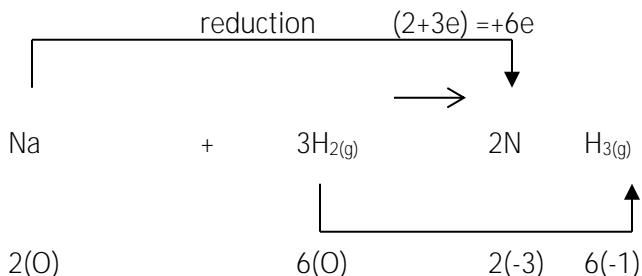
Note: $1CV = 1J$

$$\begin{aligned}\Delta G &= -2.10 \times 10^5 J / mole \\ \therefore &= -210 kJ / mole\end{aligned}$$

Question 8: Calculate the free energy for the following reaction



Solution



$$\therefore n = 6 \quad E_{cell}^o = 0.057V$$

$$\begin{aligned}\Delta G &= -nFE_{cell}^o \\ &= -(6)(9.65 \times 10^4 \text{ C/mole})(0.057V) \\ &= -3.30 \times 10^4 \text{ CV/mole} = -3.30 \times 10^4 \text{ J/mole} \\ &= -3.3.0 \text{ kJ/mole}\end{aligned}$$

If the reaction is under standard condition

$$\Delta G_{reaction}^o = -nFE_{cell}^o$$

Where E_{cell}^o = cell potential under standard conditions

At standard condition, all reactants/products and under standard condition as discussed before.

Note:

$\Delta G_{reaction}$ or $\Delta G_{reaction}^o$ is an extensive property.

An extensive property depends on the amount of substance (mass)

Cell potential E_{cell} or E_{cell}^o is an intensive property which is independent on substance (mass)

Electro chemical series

The electrochemical series is the arrangement of various electrode systems in the increasing order of their standard reduction potentials. The electrochemical series consisting of some electrode systems along with their half-cell reactions is give below.

Important features of electrochemical series:

- the electrode systems having negative values of standard reduction potentials act as anode when connected to a standard hydrogen electrode whiles those having positive values as cathode.

- The metal placed at the top (Li) of the series has the minimum value of standard reduction potential i.e. it has the minimum tendency to get reduced or maximum tendency to get oxidized. Therefore it is the strongest oxidizing agent and can reduce any other substance placed below it. In fact, any substance can reduce any other substance placed below it in the series. The reducing power of the substances decreases in going down the series.
- The substance placed at the bottom of the series (F) possesses the highest value of standard reduction potential i.e. it has the strongest tendency to get reduced. Consequently, it acts as the strongest oxidizing agent. The oxidizing power of the substances decreases in going from bottom to the top of the series.

Some important conclusions from the electrochemical series:

- i) The reactivity of metals decreases on moving down the series.
- ii) Any metal placed above hydrogen in the series can displace hydrogen from a dilute acid
- iii) The electropositive character of metals decreases on moving down the series.
- iv) A metal can displace any other metal placed below it in the series from its salt solution.
- v) The stability of the oxides of metals decreases on moving down the series.
- vi) A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidized.

Table 3.1 The standard electrode potentials at 298 K

Ions are present as aqueous species and H₂O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne ⁻	→ Reduced form)	E° /V
F ₂ (g) + 2e ⁻	→ 2F ⁻	2.87
Co ³⁺ + e ⁻	→ Co ²⁺	1.81
H ₂ O ₂ + 2H ⁺ + 2e ⁻	→ 2H ₂ O	1.78
MnO ₄ ⁻ + 8H ⁺ + 5e ⁻	→ Mn ²⁺ + 4H ₂ O	1.51
Au ³⁺ + 3e ⁻	→ Au(s)	1.40
Cl ₂ (g) + 2e ⁻	→ 2Cl ⁻	1.36
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻	→ 2Cr ³⁺ + 7H ₂ O	1.33
O ₂ (g) + 4H ⁺ + 4e ⁻	→ 2H ₂ O	1.23
MnO ₂ (s) + 4H ⁺ + 2e ⁻	→ Mn ²⁺ + 2H ₂ O	1.23
Br ₂ + 2e ⁻	→ 2Br ⁻	1.09
NO ₃ ⁻ + 4H ⁺ + 3e ⁻	→ NO(g) + 2H ₂ O	0.97
2Hg ²⁺ + 2e ⁻	→ Hg ₂ ²⁺	0.92
Ag ⁺ + e ⁻	→ Ag(s)	0.80
Fe ³⁺ + e ⁻	→ Fe ²⁺	0.77
O ₂ (g) + 2H ⁺ + 2e ⁻	→ H ₂ O ₂	0.68
I ₂ + 2e ⁻	→ 2I ⁻	0.54
Cu ⁺ + e ⁻	→ Cu(s)	0.52
Cu ²⁺ + 2e ⁻	→ Cu(s)	0.34
AgCl(s) + e ⁻	→ Ag(s) + Cl ⁻	0.22
AgBr(s) + e ⁻	→ Ag(s) + Br ⁻	0.10
2H ⁺ + 2e ⁻	→ H ₂ (g)	0.00
Pb ²⁺ + 2e ⁻	→ Pb(s)	-0.13
Sn ²⁺ + 2e ⁻	→ Sn(s)	-0.14
Ni ²⁺ + 2e ⁻	→ Ni(s)	-0.25
Fe ²⁺ + 2e ⁻	→ Fe(s)	-0.44
Cr ³⁺ + 3e ⁻	→ Cr(s)	-0.74
Zn ²⁺ + 2e ⁻	→ Zn(s)	-0.76
2H ₂ O + 2e ⁻	→ H ₂ (g) + 2OH ⁻ (aq)	-0.83
Al ³⁺ + 3e ⁻	→ Al(s)	-1.66
Mg ²⁺ + 2e ⁻	→ Mg(s)	-2.36
Na ⁺ + e ⁻	→ Na(s)	-2.71
Ca ²⁺ + 2e ⁻	→ Ca(s)	-2.87
K ⁺ + e ⁻	→ K(s)	-2.93
Li ⁺ + e ⁻	→ Li(s)	-3.05

1. A negative E° means that the redox couple is a stronger reducing agent than the H⁺/H₂ couple.
2. A positive E° means that the redox couple is a weaker reducing agent than the H⁺/H₂ couple.

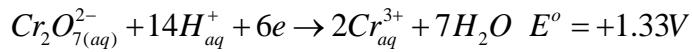
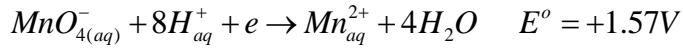
Question 9: Is an acidified permanganate solution more powerful oxidizing agent than an acidified dichromate solution under standard conditions?

Write the chemical equation for spontaneous reaction and determine the standard cell potential

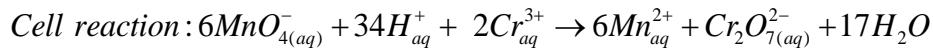
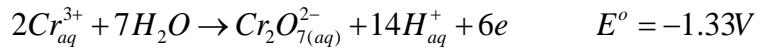
Solution:

MnO_4^- - permanganate ion

$\text{Cr}_2\text{O}_7^{2-}$ - dichromate ion



From the electrode potential values, $\text{MnO}_{4(aq)}^-$ is more positive than $\text{Cr}_2\text{O}_7^{2-}$, hence more powerful oxidizing agent.

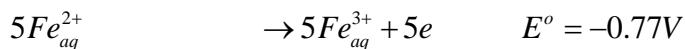
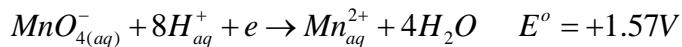


$$E_{cell}^\circ = +1.57\text{V} + (-1.33\text{V})$$

$$= +0.18\text{V}$$

Question 10: Can aqueous KMnO_4 be used to oxidize Iron(II) to iron (III) under standard condition in acidic solution.

Solution: In the question KMnO_4 is the oxidizing agent



$$= +0.74\text{V}$$

Yes KMnO_4 can oxidize Fe^{2+} to Fe^{3+} because the cell potential for the reaction is +ve

Relationship between the standard cell potential and the equilibrium constant, K

From thermochemistry, the free energy change for any chemical reaction in equilibrium can be expressed as

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

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

where K = equilibrium constant

T = temperature in Kelvin

R = gas constant

Also we know that

$$\Delta G^\circ = -nFE_{cell}^\circ$$

Relating the two equations

$$-RT \ln K = -nFE_{cell}^\circ$$

$$E_{cell}^\circ = \frac{RT}{nF} \ln K$$

Or

$$\ln K = \frac{nF}{RT} E_{cell}^\circ$$

$$\therefore E_{cell}^\circ = \frac{RT}{nF} \ln K$$

or

$$\ln K = \frac{nF}{RT} E_{cell}^\circ$$

$$R = 8.314 \text{ J/K mol}$$

$$F = 9.6485 \times 10^4 \text{ C/mol}$$

$$T = 25^\circ\text{C} = 298.15\text{K}$$

All are constant at constant temperature.

$$\frac{RT}{F} = 0.025693 \text{ V}$$

$$\frac{RT}{F} = 0.025693 \text{ V}$$

Therefore

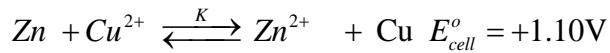
$$E_{cell}^o = \frac{0.025693 V}{n} \ln K$$

$$E_{cell}^o = \frac{0.025693V}{n} \ln K$$

or

$$\ln K = \frac{n}{0.025693V} E_{cell}^o$$

Question 11: Calculate K for equilibrium constant for Daniel cell



Solution

$$\ln K = \frac{nE_{cell}^o}{0.025693V} = \frac{(2)(1.10V)}{0.025693V} = 85.7$$

$$K = 1.5 \times 10^{37} \quad (\text{move more to the products})$$

$$K = \frac{[Zn_{aq}^{2+}]}{[Cu_{aq}^{2+}]} \quad \text{since solid concentration are negligible}$$

Summary

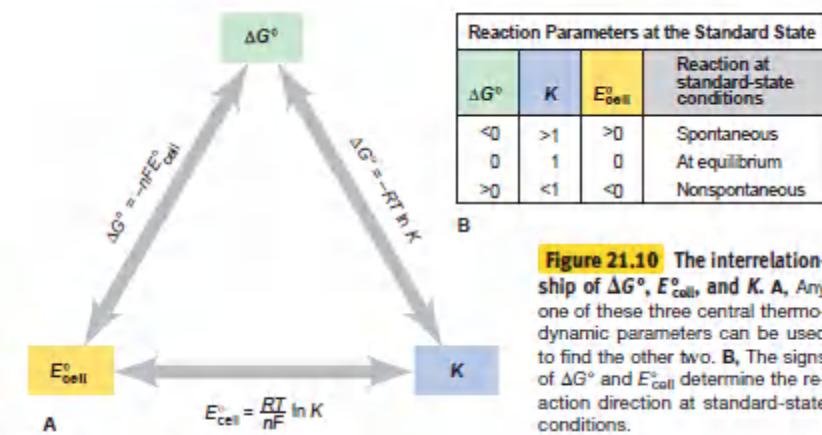


Figure 21.10 The interrelationship of ΔG° , E_{cell}° , and K . **A.** Any one of these three central thermodynamic parameters can be used to find the other two. **B.** The signs of ΔG° and E_{cell}° determine the reaction direction at standard-state conditions.

The Nernst Equation Variations in electrode Potential

Up to this point, we have used only standard electrode potential to determine the direction which a give reaction will proceed.

However, there are many instances in which a concentration less than 1M would be desirable for an ionic redox reaction.

- Hence the potential will be lower.

In any galvanic cell, as the battery is being used up, the battery gets faints (spent)

- In galvanic cell, we start at standard condition e.g. Daniel Cell $E_{\text{cell}}^\circ = 1.10 \text{ V}$
- As the battery works, the concentration of the ions in solution changes in both anode and cathode
- Hence the cell potential changes and the battery becomes weaker.
- As equilibrium is established by the redox reaction, the cell free energy $\Delta G = 0$. Hence the cell potential becomes zero $E_{\text{cell}}^\circ = 0.00 \text{ V}$

The formula for predicting the variation of the cell potential with concentration and pressure is expressed by NERNST EQUATION.

- The change in free energy as a function of concentration of a reaction is given as

$$\Delta G_{\text{reaction}} = \Delta G_{\text{reactant}}^\circ + RT \ln Q$$

Q is not equilibrium constant but reaction.

Where $\Delta G_{\text{reaction}}^\circ$ = Free energy as standard condition.

$$\Delta G_{\text{reaction}}^\circ = -nFE_{\text{cell}}^\circ$$

$$\Delta G_{\text{reaction}} = -nFE_{\text{cell}}$$

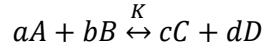
Substitute in above

$$-nFE_{cell} = -nFE_{cell}^o + RT \ln Q$$

Therefore,

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln Q \quad \textbf{Nernst Equation}$$

For a general overall redox reaction



$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

or

$$E_{cell} = E_{cell}^o - \frac{0.025693 V}{n} \ln Q$$

$$\text{Since } \frac{RT}{P} = 0.025693 V$$

or

$$E_{cell} = E_{cell}^o - \frac{2.303RT}{nF} \ln Q$$

At 298K,

$$\frac{2.303RT}{nF} = \frac{2.303 \times 8.314 \times 298}{96500} = 0.059 V$$

$$E_{cell} = E_{cell}^o - \frac{0.059 V}{n} \log Q$$

EXAMPLE

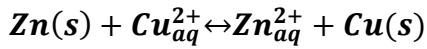
Question 1: Calculate the potential of 25°C of a Daniel cell in which the concentration of $\text{Zn}^{2+}_{\text{aq}}$ ions is 0.10 mol/l and that of the Cu^{2+} ion is 0.0010 mol/l. $E_{\text{cell}}^{\circ} = 1.10 \text{ V}$

Solution

$$[\text{Zn}^{2+}] = 0.10 \text{ M} \quad E_{\text{cell}}^{\circ} = 1.10 \text{ V}$$

$$[\text{Cu}^{2+}] = 0.0010 \text{ M} \quad E_{\text{cell}}^{\circ} = ?$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.059 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^{\circ} - \frac{0.059 \text{ V}}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \end{aligned}$$



$$\begin{aligned} E_{\text{cell}} &= 1.10 \text{ V} - \frac{0.025693 \text{ V}}{2} \log \frac{[0.10 \text{ M}]}{[0.0010 \text{ M}]} \\ &= 1.10 \text{ V} - 0.059 \text{ V} \\ &= +1.04 \text{ V} \end{aligned}$$

The cell potential is lower than standard cell potential of Daniel cell.

Significant of Nernst Equation

When an overall cell potential is zero, the reaction corresponding to this cell is under condition of chemical equilibrium.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log Q$$

when the reaction is at equilibrium

$$E_{\text{cell}} = 0, \quad \text{Therefore } Q = K \text{ (equilibrium constant)}$$

Hence

$$0 = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log K$$

At 298K (25°C),

$$\log K = \frac{nE_{cell}^o}{0.059}$$

CHM 101

ELECTROCHEMISTRY

Prof. O.O.SORIYAN

MODULE 3

MODULE 3

Concentration effects
(Nernst equation) Redox
Reaction.

Oxidation Potentials treated
in terms of free Energy
change.

Objectives of Module 3

At the end of this topic, students will be able to

- Determine the relationship between cell potential and Gibbs free energy
- Examine relationship between the standard cell potential and the equilibrium constant, K
- Apply Nernst equation for calculating the emf of galvanic cell and define standard potential of cell.

Relationship between cell potential and free energy

From thermochemistry, we know for a reaction to be spontaneous, free energy (ΔG) must be negative

$$\Delta G = -\nu e$$

and cell potential for the reaction E_{cell}^o must be positive

$$E_{cell}^o = +\nu e$$

for an electrochemical cell, the energy change for a chemical reaction is given by

$$\Delta G^o = -nFE_{cell}^o$$

n = number of moles of electrons transfer in the reaction as given by the balanced equation.

F = Faraday constant - it is measured by charge per mole of electrons .

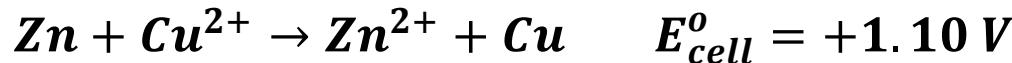
F = 96500 coulomb/mole or 9.6485×10^4 C/mole

From this equation, the following conclusions can be obtained:

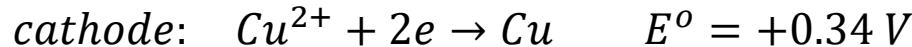
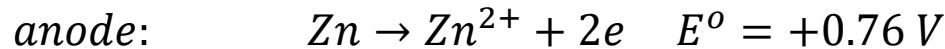
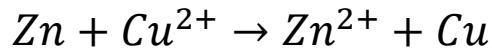
- a) When E_{cell}^o is positive, the cell reaction is feasible
- b) When E_{cell}^o is negative; the cell reaction is not feasible.
- c) When E_{cell}^o is zero, the cell reaction is in equilibrium.

EXAMPLE

Example: Calculate the free energy of Daniel Cell? The cell reaction is



Solution



From the half reaction, the number of mole of electron is

$$n = 2$$

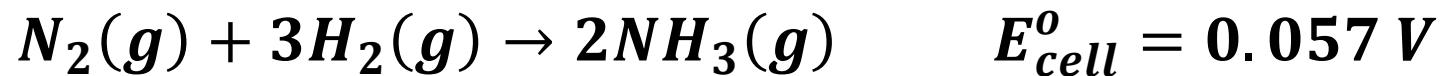
$$\begin{aligned}\Delta G &= -nFE_{\text{cell}}^{\circ} \\ &= -(2)(99.65 \times 10^4 \text{ C/mol})(1.10 \text{ V}) \\ &= -2.10 \times 10^5 \text{ J/mole}\end{aligned}$$

Note : $1 \text{ CV} = 1 \text{ J}$

$$\begin{aligned}\Delta G &= -2.10 \times 10^5 \text{ J/mole} \\ &= -210 \text{ kJ/mole}\end{aligned}$$

Assignment

Assignment 7: Calculate the free energy for the following reaction



Electrochemical series

- ▶ *The electrochemical series is the arrangement of various electrode systems in the increasing order of their standard reduction potentials.*

Table 3.1 The standard electrode potentials at 298 K

Ions are present as aqueous species and H₂O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne ⁻)	→ Reduced form)	E°/V
F ₂ (g) + 2e ⁻	→ 2F ⁻	2.87
Co ³⁺ + e ⁻	→ Co ²⁺	1.81
H ₂ O ₂ + 2H ⁺ + 2e ⁻	→ 2H ₂ O	1.78
MnO ₄ ⁻ + 8H ⁺ + 5e ⁻	→ Mn ²⁺ + 4H ₂ O	1.51
Au ³⁺ + 3e ⁻	→ Au(s)	1.40
Cl ₂ (g) + 2e ⁻	→ 2Cl ⁻	1.36
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻	→ 2Cr ³⁺ + 7H ₂ O	1.33
O ₂ (g) + 4H ⁺ + 4e ⁻	→ 2H ₂ O	1.23
MnO ₂ (s) + 4H ⁺ + 2e ⁻	→ Mn ²⁺ + 2H ₂ O	1.23
Br ₂ + 2e ⁻	→ 2Br ⁻	1.09
NO ₃ ⁻ + 4H ⁺ + 3e ⁻	→ NO(g) + 2H ₂ O	0.97
2Hg ²⁺ + 2e ⁻	→ Hg ₂ ²⁺	0.92
Ag ⁺ + e ⁻	→ Ag(s)	0.80
Fe ³⁺ + e ⁻	→ Fe ²⁺	0.77
O ₂ (g) + 2H ⁺ + 2e ⁻	→ H ₂ O ₂	0.68
I ₂ + 2e ⁻	→ 2I ⁻	0.54
Cu ⁺ + e ⁻	→ Cu(s)	0.52
Cu ²⁺ + 2e ⁻	→ Cu(s)	0.34
AgCl(s) + e ⁻	→ Ag(s) + Cl ⁻	0.22
AgBr(s) + e ⁻	→ Ag(s) + Br ⁻	0.10
2H ⁺ + 2e ⁻	→ H ₂ (g)	0.00
Pb ²⁺ + 2e ⁻	→ Pb(s)	-0.13
Sn ²⁺ + 2e ⁻	→ Sn(s)	-0.14
Ni ²⁺ + 2e ⁻	→ Ni(s)	-0.25
Fe ²⁺ + 2e ⁻	→ Fe(s)	-0.44
Cr ³⁺ + 3e ⁻	→ Cr(s)	-0.74
Zn ²⁺ + 2e ⁻	→ Zn(s)	-0.76
2H ₂ O + 2e ⁻	→ H ₂ (g) + 2OH ⁻ (aq)	-0.83
Al ³⁺ + 3e ⁻	→ Al(s)	-1.66
Mg ²⁺ + 2e ⁻	→ Mg(s)	-2.36
Na ⁺ + e ⁻	→ Na(s)	-2.71
Ca ²⁺ + 2e ⁻	→ Ca(s)	-2.87
K ⁺ + e ⁻	→ K(s)	-2.93
Li ⁺ + e ⁻	→ Li(s)	-3.05

Increasing strength of oxidising agent ↑

↓ Increasing strength of reducing agent

1. A negative E° means that the redox couple is a stronger reducing agent than the H⁺/H₂ couple.
2. A positive E° means that the redox couple is a weaker reducing agent than the H⁺/H₂ couple.

Some important conclusions from the electrochemical series

- i) The reactivity of metals decreases on moving down the series.
- ii) Any metal placed above hydrogen in the series can displace hydrogen from a dilute acid
- iii) The electropositive character of metals decreases on moving down the series.
- iv) A metal can displace any other metal placed below it in the series from its salt solution.
- v) The stability of the oxides of metals decreases on moving down the series.
- vi) A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidized.

Assignment

Question 7: Is an acidified permanganate solution more powerful oxidizing agent than an acidified dichromate solution under standard conditions? Write the chemical equation for spontaneous reaction and determine the standard cell potential

Question 8: Can aqueous KMnO_4 be used to oxidize Iron(II) to iron (III) under standard condition in acidic solution.

Relationship between the standard cell potential and the equilibrium constant, K

From thermochemistry, the free energy change for any chemical reaction in equilibrium can be expressed as

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

where K = equilibrium constant

T = temperature in Kelvin

R = gas constant

Also we know that

$$\Delta G^o = -nFE_{cell}^o$$

Relating the two equations

$$-RT \ln K = -nFE_{cell}^o$$

$$E_{cell}^o = \frac{RT}{nF} \ln K$$

or

$$\ln K = \frac{nF}{RT} E_{cell}^o$$

$$R = 8.314 \text{ J/K mol}; \quad F = 9.6485 \times 10^4 \text{ C/mol}; \\ T = 25^\circ\text{C} = 298.15 \text{ K}$$

All are constant at constant temperature.

$$\frac{RT}{F} = 0.025693 \text{ V}$$

Therefore

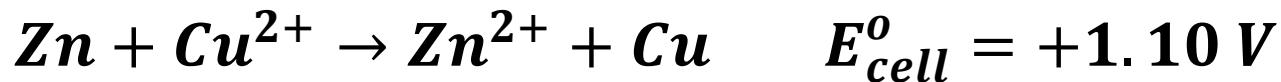
$$E_{cell}^o = \frac{0.025693 \text{ V}}{n} \ln K$$

or

$$\ln K = \frac{n}{0.025693 \text{ V}} E_{cell}^o$$

EXAMPLE

Example : Calculate K for equilibrium constant for Daniel cell



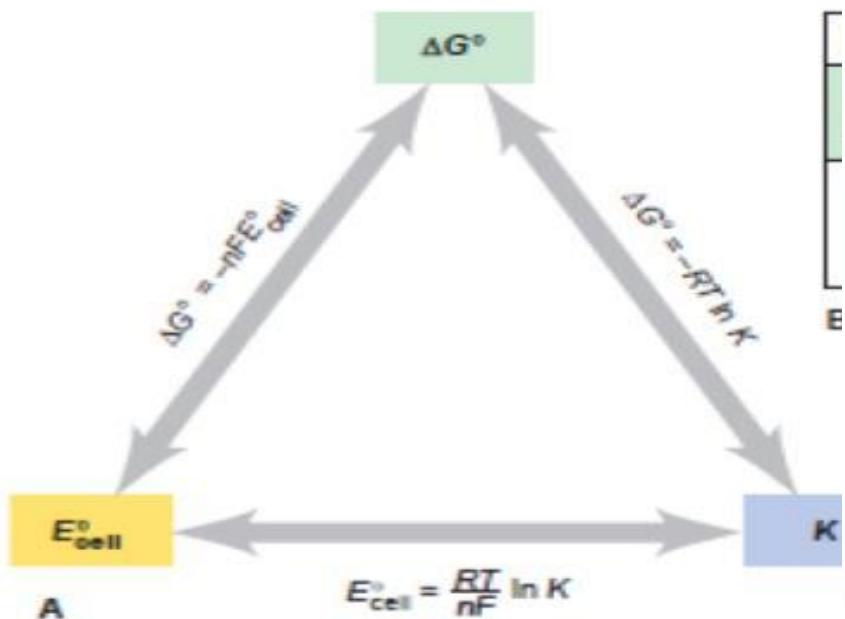
Solution

$$\ln K = \frac{nE_{cell}^o}{0.025693 \text{ V}} = \frac{(2)(1.10 \text{ V})}{0.025693 \text{ V}} = 85.7$$

$$K = 1.5 \times 10^{37} \quad (\text{move to the products})$$

$$K = \frac{[\text{Zn}_{aq}^{2+}]}{[\text{Cu}_{aq}^{2+}]} \quad \text{since solid concentration are negligible}$$

SUMMARY



ΔG°	K	E_{cell}°	Reaction at standard-state conditions
<0	>1	>0	Spontaneous
$=0$	<math=1< math=""></math=1<>	<math=0< math=""></math=0<>	At equilibrium
>0	<1	<0	Nonspontaneous

The Nernst Equation Variations in electrode Potential

Up to this point, we have used only standard electrode potential to determine the direction which a give reaction will proceed.

However, there are many instances in which a concentration less than 1M would be desirable for an ionic redox reaction.

- Hence the potential will be lower.

In any galvanic cell, as the battery is being used up, the battery gets faints (spent)

- In galvanic cell, we start at standard condition e.g. Daniel Cell $E_{cell}^o = 1.10\text{ V}$
- As the battery works, the concentration of the ions in solution changes in both anode and cathode

- Hence the cell potential changes and the battery becomes weaker.
- As equilibrium is established by the redox reaction, the cell free energy $\Delta G = 0$.
- ***Hence the cell potential becomes zero*** $E_{cell}^o = 0.00 V$
 - ▶ The formula for predicting the variation of the cell potential with concentration and pressure is expressed by **NERNST EQUATION**.

The change in free energy as a function of concentration of a reaction is given as

$$\Delta G_{reaction} = \Delta G_{reactant}^o + RT \ln Q$$

Q is not equilibrium constant but reaction.

where $\Delta G_{reaction}^o$ = Free energy as standard condition

$$\Delta G_{reaction}^o = -nFE_{cell}^o$$
$$\Delta G_{reaction} = -nFE_{cell}$$

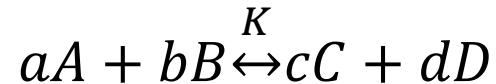
Substitute in above

$$-nFE_{cell} = -nFE_{cell}^o + RT \ln Q$$

Therefore,

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln Q \quad \textbf{\textit{Nernst Equation}}$$

For a general overall redox reaction



$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

or

$$E_{cell} = E_{cell}^o - \frac{0.025693 V}{n} \ln Q$$

$$\text{Since } \frac{RT}{P} = 0.025693 V$$

► or

$$E_{cell} = E_{cell}^o - \frac{2.303RT}{nF} \ln Q$$

At 298K,

$$\frac{2.303RT}{nF} = \frac{2.303 \times 8.314 \times 298}{96500} = 0.059 V$$

$$E_{cell} = E_{cell}^o - \frac{0.059 V}{n} \log Q$$

EXAMPLE

Question 1: Calculate the potential of 25°C of a Daniel cell in which the concentration of $\text{Zn}^{2+}_{\text{aq}}$ ions is 0.10 mol/l and that of the Cu^{2+} ion is 0.0010 mol/l.
 $E_{\text{cell}}^{\circ} = 1.10 \text{ V}$

Solution

$$\begin{aligned} [\text{Zn}^{2+}] &= 0.10 \text{ M} \\ [\text{Cu}^{2+}] &= 0.0010 \text{ M} \end{aligned}$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= 1.10 \text{ V} \\ E_{\text{cell}}^{\circ} &=? \end{aligned}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.059 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^{\circ} - \frac{0.059 \text{ V}}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \end{aligned}$$

$$\begin{aligned} \text{Zn}(s) + \text{Cu}^{2+}_{\text{aq}} &\leftrightarrow \text{Zn}^{2+}_{\text{aq}} + \text{Cu}(s) \\ E_{\text{cell}} &= 1.10 \text{ V} - \frac{0.025693 \text{ V}}{2} \log \frac{[0.10 \text{ M}]}{[0.0010 \text{ M}]} \\ &= 1.10 \text{ V} - 0.059 \text{ V} \\ &= +1.04 \text{ V} \end{aligned}$$

The cell potential is lower than standard cell potential of Daniel cell.

Significant of Nernst Equation

When an overall cell potential is zero, the reaction corresponding to this cell is under condition of chemical equilibrium.

$$E_{cell} = E_{cell}^o - \frac{0.059}{n} \log Q$$

when the reaction is at equilibrium

$E_{cell} = 0$, Therefore $Q = K$ (*equilibrium constant*)

Hence

$$0 = E_{cell}^o - \frac{0.059}{n} \log K$$

At 298K (25°C),

$$\log K = \frac{nE_{cell}^o}{0.059}$$

REACTION KINETICS

MODULE 1

Course outline

Introduction to chemical kinetics, Basic definitions of rates, orders of reaction and molecularity. Calculations involving initial rate, Activation energy and Arrhenius equation.

Objectives

At the end of this topic, students will be able to

- Define the average and instantaneous rate of reaction
- Express the rate of the reaction in term of change in concentration of either of the reactants or product with time
- Describe with the help of graph, reaction rate as function of change of concentration of reactant or product with respect to time
- Examine various methods that are used to monitor the rate of chemical reaction
- Review the factors that affect reaction rate
- Define rate constant
- Express the rate of reaction as a rate law equation
- Distinguish the difference between order and molecularity of reaction
- Explain using the collision theory and potential energy diagrams, how different factors such as temperature and concentration, control

Reaction Kinetics

- Why do we put food in fridge? – to make it last longer
 - But how does this work?
- Why do we have to boil an egg to make it hard?
 - Why not just wait until it does itself?

These questions can be answered by knowing about **Reaction kinetics**.

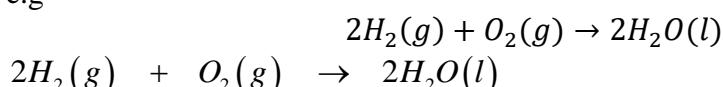
- The boiling of an egg and the way in which food “goes off” is to do with making chemical reactions to go faster or slower.

Two major words are used

- Reaction
- Kinetics
- **A reaction is defined by its reactants and products whose identities must be established by experiment**
 - Once the reactants and products are known, a balance chemical equation for the reaction can be written.

Reactants → Products

e.g



- **Kinetics means motion or movement**

- What has movement got to do with chemical reaction?
- In chemical reaction, kinetics deals with movement of reactants molecules to form the product molecule.

When carrying out a chemical reaction, chemists are concerned with two issues:

- How fast the reactants change to products – i.e the speed at which something happens is called **rate**. The rate at which the reaction proceeds
- The extent to which the reaction is product-favoured – **chemical equilibrium**

Chemical reactions vary enormously in speed

Some reactions are fast:

- Fireworks explode almost immediately to give bright colours due to very fast chemical reaction e.g reaction of H₂ with F₂)
- The precipitation of insoluble salts (virtually instantaneous)

Some reactions are slow:

- The rusting of a bridge is also a chemical reaction but it is very slow (may keep on going for months or even years)
- Fermentation of glucose (can take weeks or month)

Hence, the area of chemistry that concerns reaction rate or speed is called REACTION KINETICS or CHEMICAL KINETICS.

- Another main goal of reaction kinetics is to understand the steps by which a reaction takes place.
 - What is actually happening on the molecular scale?
 - What species must collide to start the reaction?
 - What bonds are broken first?
 - What is the nature of the intermediate
- The series of steps is called the REACTION MECHANISM
 - Understanding the mechanism allows chemists to find ways to facilitate the reaction.

In Conclusion:

Reaction kinetics is a study of the rates of chemical reactions, the factors which affect them and the mechanism by which the chemical reaction occurs.

Rates of Reaction or Reaction Rates

To introduce the concept of rate of reaction, let us consider the decomposition of nitrogen dioxide



Suppose in a particular experiment, we start with a flask of NO₂ at 300°C and we measure the concentrations of NO₂, NO and O₂.

The result is as follows:

Concentration (mol dm ⁻³)			
Time (s)	[NO ₂]	[NO]	[O ₂]
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

From this result:

- Concentration of the reactant (NO₂) decreases with time
- Concentrations of the products (NO and O₂) increases with time.

Reaction kinetics deals with the speed at which these changes occur.

The speed or rate of a process is defined as the change in a quantity over a specific period of time.

- For a chemical reaction, the quantity that changes is the amount or the concentration of reactant or product.

Hence:

Rate of reaction or reaction rate of a chemical reaction is the change in concentration of reactant or product per unit time.

$$\begin{aligned} \text{Rate of reaction} &= \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1} \\ &= \frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1} \\ &= \frac{\Delta[A]}{\Delta t} \end{aligned}$$

- where A = a specific reactant or product
- [] - indicate concentration
- Δ – a change in a given quantity

Let calculate the average rate at which the concentration of NO₂ changes over the first 50 secs of the reaction, using the above data.

$$\begin{aligned} \text{Rate} &= \frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= \frac{\Delta[\text{NO}_2]_{t=50\text{s}} - [\text{NO}_2]_{t=0}}{50(\text{s}) - 0(\text{s})} \end{aligned}$$

$$= \frac{0.0079 \text{ mol} / \text{dm}^3 - 0.010 \text{ mol} / \text{dm}^3}{50(\text{s})}$$

$$= -4.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

- Since the concentration of NO_2 decreases with time

$$\Delta[\text{NO}_2] = -ve \text{ (negative)}$$

It is customary to work with positive reaction in Chemistry. Therefore, we define the rate of this particular reaction as:

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Hence for the above problem,

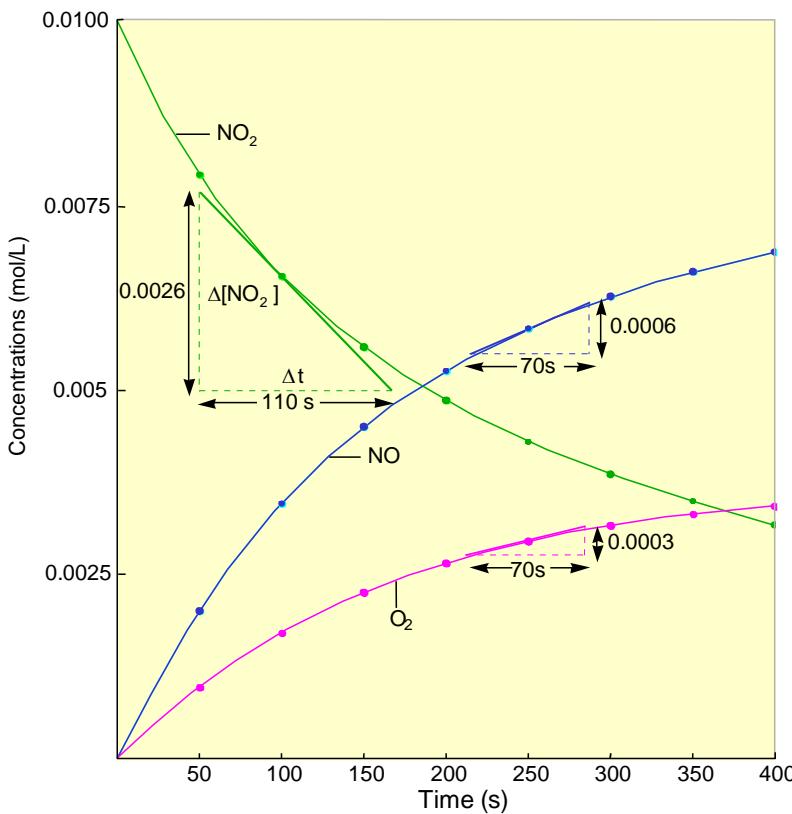
$$\text{Rate} = -(-4.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1})$$

$$= 4.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

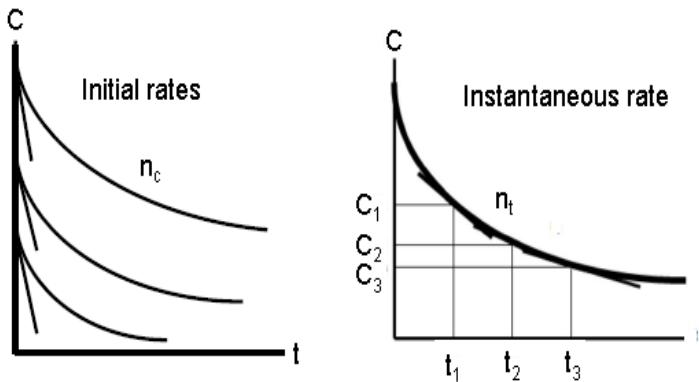
Units of rate of reaction = concentration/unit time = $\text{mol dm}^{-3} \text{ s}^{-1}$

The average rate for this reaction during several other time intervals are as follows:

$-\frac{\Delta[\text{NO}_2]}{\Delta t}$	time period(s)
4.2×10^{-5}	0 - 50
2.8×10^{-5}	50 - 100
2.0×10^{-5}	100 - 150
1.4×10^{-5}	150 - 200
1.0×10^{-5}	200 - 250



- The rate of reaction is the change in number of molecules of reactants or product per unit time.
- These are called AVERAGE RATES over 50s intervals.
 - The **average rate** of the reaction over each interval is the change in concentration divided by the change in time:
- Reactions are fastest at the start and get slower as the reactants concentration drops.**
- Reactants Concentration decreases with time
- Product Concentration increases with time
- The steeper the curve the faster the rate of the reaction
- The value of the rate at a particular time can be obtained by computing the slope of a line tangent to the curve at the point. This is known as INSTANTANEOUS RATE.



- The rate of reaction decreases as the reaction proceeds and the reactant is gradually used up.
- One can only state the rate of reaction at a certain time.

The rate at the start of the reaction when an infinitesimally small amount of the reactant has been used up is called the INITIAL RATE of the reaction.

The rate can also be defined in terms of products.

- In doing this, we must take into account the coefficients in the balanced equation for the reaction
- This is because the stoichiometry determines the relative rates of the consumption of the reactants and the generation of the products

e.g



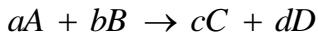
- Both NO_2 and NO have a coefficient of 2
- Therefore, NO is produced at the same rate as NO_2 is consumed.
- Looking at the curve (graph), The curve for NO and NO_2 are the same except that it is inverted
 - This shows that at any interval of time the slope of the tangent of NO must be negative of the slope of NO_2 .
 - Verify this by your graph at home.
- In contrast, O_2 has a coefficient of 1 which means it is produced half as fast as NO , which has a coefficient of 2.
 - Therefore, the rate of NO production is twice the rate of O_2 produced
 - *Slope of NO_2 = Slope of O_2*

Rate after 250 s:

$$8.6 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} \text{ for } \text{NO}$$

$$4.3 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} \text{ for } \text{O}_2$$

In general,



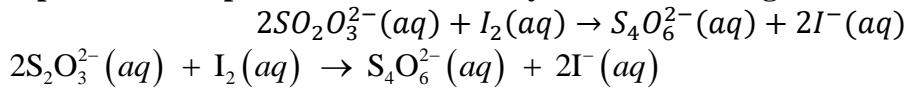
$$Rate = -\frac{1}{a} \frac{\Delta A}{\Delta t} = -\frac{1}{b} \frac{\Delta B}{\Delta t} = \frac{1}{c} \frac{\Delta C}{\Delta t} = \frac{1}{d} \frac{\Delta D}{\Delta t}$$

For a reaction,



$$Rate = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} \text{ and so on.}$$

Example 1: Thiosulphate ion is oxidized by iodine according to the following reaction:



If **0.0080 mole of S₂O₃²⁻** is consumed in **1.0 liter of solution per sec**, what is the rate of consumption of I₂? At what rate are S₄O₆²⁻ and I⁻ produced?

Solution:

Rate of consumption of S₂O₃²⁻ = 0.008 mol l⁻¹s⁻¹.

From the stoichiometry:

$$Rate = \frac{1}{2} \frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} = \frac{1}{1} \frac{\Delta[\text{I}_2]}{\Delta t} = \frac{\Delta[\text{S}_4\text{O}_6^{2-}]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{I}^-]}{\Delta t}$$

$$\frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} = 2 \left(\frac{\Delta[\text{I}_2]}{\Delta t} \right)$$

or

$$\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \left(\frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} \right)$$

$$= \frac{1}{2} [0.008 \text{ mol l}^{-1}\text{s}^{-1}] = 0.004 \text{ mol l}^{-1}\text{s}^{-1}$$

$$\frac{\Delta[\text{S}_4\text{O}_6^{2-}]}{\Delta t} = 0.004 \text{ mol l}^{-1}\text{s}^{-1}$$

$$\frac{\Delta[\text{I}^-]}{\Delta t} = 0.008 \text{ mol l}^{-1}\text{s}^{-1}$$

CHM 101

REACTION KINETICS



Prof. O.O.SORIYAN

MODULE 1

COURSE OUTLINE

Module 1: Introduction to Reaction
or chemical kinetics

- ▶ Module 2: Factors affecting rate of reaction,
Various methods that are used to monitor
the rate of chemical reaction
 - Basic definitions of rates, orders of reaction
and molecularity
 - Calculations involving initial rate

Module 3: The Collision Theory

- Activation energy
- Arrhenius equation.

Module 1

Introduction to Reaction
or
chemical kinetics

Objectives Of Module 1

At the end of Module 1, students will be able to

- Define basic terms in chemical kinetics
- Define the average and instantaneous rate of reaction
- Express the rate of the reaction in term of change in concentration of either of the reactants or product with time



INTRODUCTION

- Why do we put food in fridge? – to make it last longer
 - But how does this work?
- Why do we have to boil an egg to make it hard?
 - Why not just wait until it does itself?
- ▶ These questions can be answered by knowing about **Reaction kinetics**.
- The boiling of an egg and the way in which food “goes off” is to do with making chemical reactions to go faster or slower.

Reaction Kinetics

- ▶ Two major words are used
 - Reaction
 - Kinetics

1. REACTION

A reaction is defined by its reactants and products whose identities must be established by experiment

- Once the reactants and products are known, a balance chemical equation for the reaction can be written.

Reactants → Products

e.g



2. KINETICS

Kinetics means motion or movement

- In chemical reaction, kinetics deals with movement of reactants molecules to form the product molecule.

In chemical reaction, chemists are concerned with two issues:

- ❖ How fast the reactants change to products
- ❖ the speed at which something happens is called **rate**.



- ❖ The extent to which the reaction is product-favoured

Reaction Rate

Chemical equilibrium

Chemical reactions vary enormously in speed

- Some reactions are fast:
 - Fireworks explode almost immediately to give bright colours due to very fast chemical reaction e.g reaction of H₂ with F₂)
 - The precipitation of insoluble salts (virtually instantaneous)
- Some reactions are slow:
 - The rusting of a bridge is also a chemical reaction but it is very slow (may keep on going for months or even years)
 - Fermentation of glucose (can take weeks or month)

Introduction

- ▶ The area of chemistry that concerns reaction rate or speed is called REACTION KINETICS or CHEMICAL KINETICS.

Another goal of Reaction Kinetics

- ▶ To understand the steps by which a reaction takes place.
 - What is actually happening on the molecular scale?
 - What species must collide to start the reaction?
 - What bonds are broken first?
 - What is the nature of the intermediate
- ▶ The series of steps is called the REACTION MECHANISM

CONCLUSION

- ▶ Reaction kinetics is a study of
 - the rates of chemical reactions,
 - the factors which affect them and
 - the mechanism by which the chemical reaction occurs.

Rates of Reaction

To introduce the concept of rate of reaction, let us consider the decomposition of nitrogen dioxide



Suppose in a particular experiment, we start with a flask of NO_2 at $300^\circ C$ and we measure the concentrations of NO_2 , NO and O_2 .

The result is as follows:

EXPERIMENTAL DATA

Time (s)	Concentration (mol dm ⁻³)		
	[NO ₂]	[NO]	[O ₂]
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
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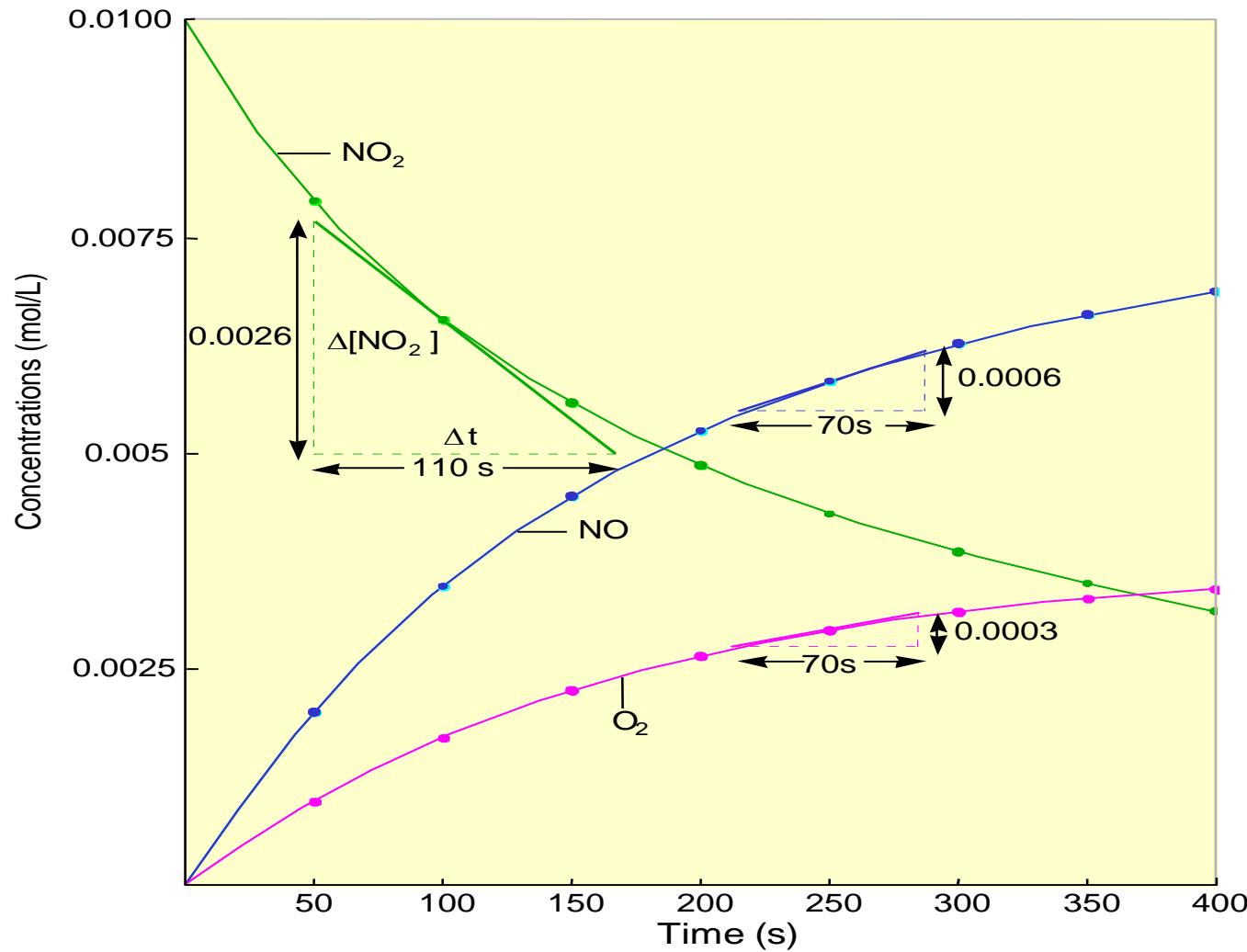
From this result:

- Concentration of the reactant (NO_2) decreases with time
- Concentrations of the products (NO and O_2) increases with time.

Reaction kinetics deals with the speed at which these changes occur.

- **The speed or rate of a process is defined as the change in a quantity over a specific period of time.**

Concentration versus time plot



Rate of reaction or reaction rate

- ▶ Rate of reaction or reaction rate of a chemical reaction is the change in concentration of reactant or product per unit time.

Rate of Reaction

$$= \frac{\text{Concentration of } A \text{ at } t_2 - \text{Concentration of } A \text{ at } t_1}{t_2 - t_1}$$

$$= \frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1} = \frac{\Delta[A]}{\Delta[t]}$$

Let calculate the average rate at which the concentration of NO_2 changes over the first 50 secs of the reaction, using the above data.

$$\begin{aligned} \text{Rate} &= \frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= \frac{\Delta[\text{NO}_2]_{t=50s} - [\text{NO}_2]_{t=0}}{50(s) - 0(s)} \\ &= \frac{0.0079\text{mol dm}^{-3} - 0.010\text{mol dm}^{-3}}{50s} \\ &= -4.2 \times 10^5 \text{mol dm}^{-3}\text{s}^{-1} \end{aligned}$$

Since the concentration of NO_2 decreases with time

$$\Delta[\text{NO}_2] = -ve \text{ (negative)}$$

It is customary to work with positive reaction in Chemistry. Therefore, we define the rate of this particular reaction as:

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Hence for the above problem,

$$\begin{aligned}\text{Rate} &= -(-4.2 \times 10^{-5} \text{ mol dm}^{-3}\text{s}^{-1}) \\ &= 4.2 \times 10^{-5} \text{ mol dm}^{-3}\text{s}^{-1}\end{aligned}$$

Units of rate of reaction = concentration/unit time = mol dm⁻³s⁻¹

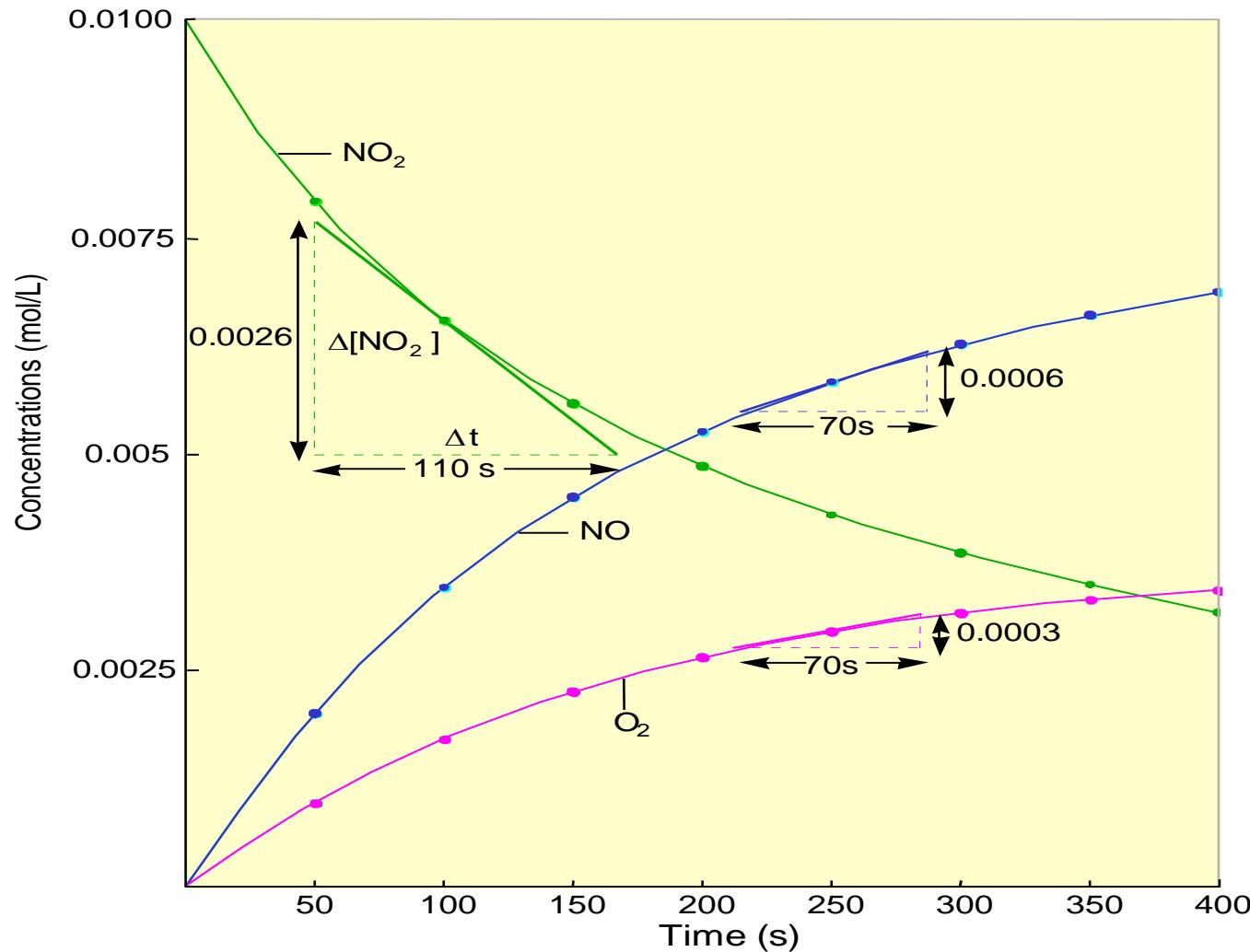
Average Rate

- ▶ The **average rate** of the reaction over each interval is the change in concentration divided by the change in time.
- ▶ AVERAGE RATES over 50s intervals of the experimental result are in the next slide.

Average Rate

$-\frac{\Delta [NO_2]}{\Delta t}$	<i>time period (s)</i>
$4.2 \times 10 - 5$	0 – 50
$2.8 \times 10 - 5$	50 – 100
$2.0 \times 10 - 5$	100 – 150
$1.4 \times 10 - 5$	150 – 200
$1.0 \times 10 - 5$	200 – 250

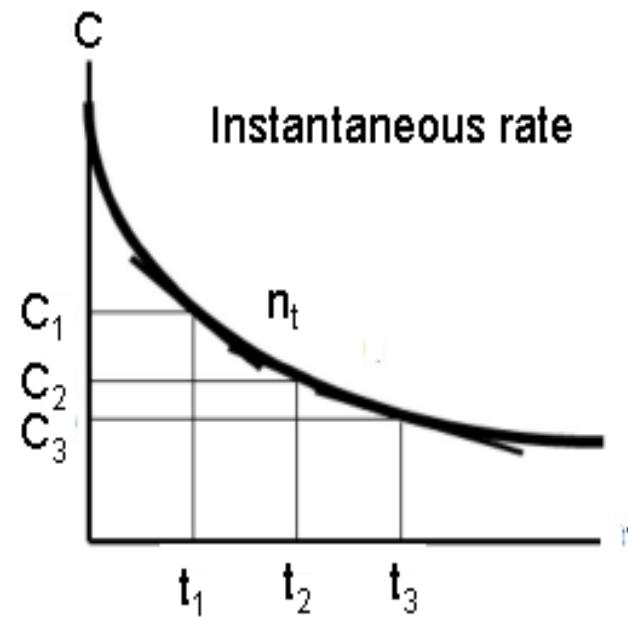
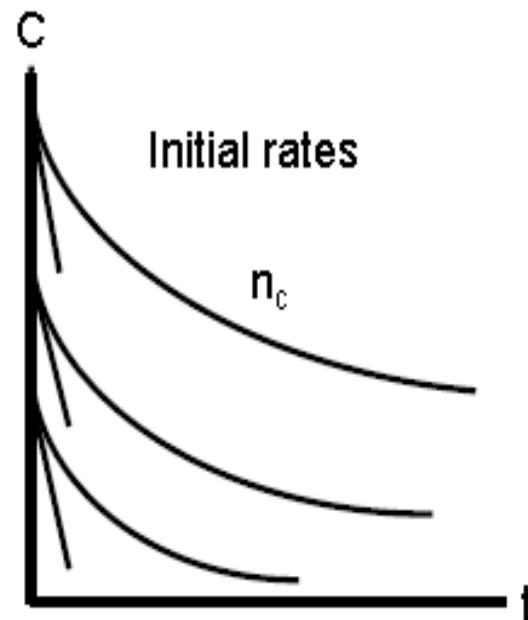
Concentration versus time plot



- The rate of reaction is the change in number of molecules of reactants or product per unit time.
- These are called AVERAGE RATES over 50s intervals.
 - The **average rate** of the reaction over each interval is the change in concentration divided by the change in time:
- **Reactions are fastest at the start and get slower as the reactants concentration drops.**
- Reactants Concentration decreases with time
- Product Concentration increases with time
- The steeper the curve the faster the rate of the reaction
- The value of the rate at a particular time can be obtained by computing the slope of a line tangent to the curve at the point. This is known as **INSTANTANEOUS RATE**.

The value of the rate at a particular time is known as INSTANTANEOUS RATE.

The rate at the start of the reaction when an infinitesimally small amount of the reactant has been used up is called the INITIAL RATE of the reaction.



- ▶ The rate can also be defined in terms of products.
- In doing this, we must take into account the coefficients in the balanced equation for the reaction
- This is because the stoichiometry determines the relative rates of the consumption of the reactants and the generation of the products

e.g



- Both NO_2 and NO have a coefficient of 2
- Therefore, NO is produced at the same rate as NO_2 is consumed.

- Looking at the curve (graph), The curve for NO and NO₂ are the same except that it is inverted
 - This shows that at any interval of time the slope of the tangent of NO must be negative of the slope of NO₂.
 - Verify this by your graph at home.

In contrast, O₂ has a coefficient of 1 which means it is produced half as fast as NO, which has a coefficient of 2.

Therefore, the rate of NO produce is twice the rate of O₂ produced

- $\text{Slope of } \text{NO}_2 = \text{Slope of } \text{O}_2$

Rate after 250 s:

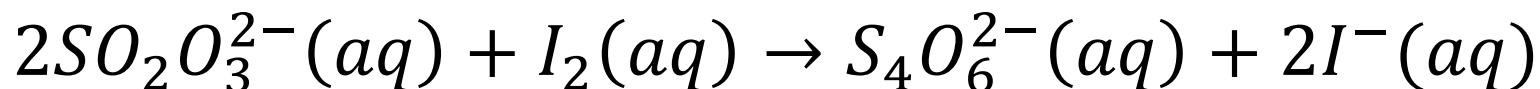
- $8.6 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ for NO
- $4.3 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ for O₂

Rate in terms of Products formation

- ▶ In general,
 - $aA + bB \rightarrow cC + dD$
 - $Rate = -\frac{1}{a} \frac{\Delta A}{\Delta t} = -\frac{1}{b} \frac{\Delta B}{\Delta t} = \frac{1}{c} \frac{\Delta C}{\Delta t} = \frac{1}{d} \frac{\Delta D}{\Delta t}$
- ▶ For a reaction,
 - $BrO_3^- (aq) + 5Br^- (aq) + 6H^+ (aq) \rightarrow 3Br_2 (aq) + 3H_2O (l)$
 - $Rate = -\frac{\Delta [BrO_3^-]}{\Delta t} = -\frac{1}{5} \frac{\Delta [Br^-]}{\Delta t} = -\frac{1}{c} \frac{\Delta [H^+]}{\Delta t} = \frac{1}{3} \frac{\Delta [Br_2]}{\Delta t} = \frac{1}{3} \frac{\Delta [H_2O]}{\Delta t}$

EXAMPLE

Example 1: Thiosulphate ion is oxidized by iodine according to the following reaction:



If **0.0080** mole of $S_2O_3^{2-}$ is consumed in 1.0 liter of solution per sec, what is the rate of consumption of I_2 ? At what rate are $S_4O_6^{2-}$ and I^- produced?

Solution:

Rate of consumption of $\text{S}_2\text{O}_3^{2-} = 0.008 \text{ mol l}^{-1}\text{s}^{-1}$.

From the stoichiometry:

$$\text{Rate} = \frac{1}{2} \frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} = \frac{1}{1} \frac{\Delta[\text{I}_2]}{\Delta t} = \frac{\Delta[\text{S}_4\text{O}_6^{2-}]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{I}^-]}{\Delta t}$$
$$\frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} = 2 \left(\frac{\Delta[\text{I}_2]}{\Delta t} \right)$$

or

$$\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \left(\frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} \right)$$
$$= \frac{1}{2} [0.008 \text{ mol l}^{-1}\text{s}^{-1}] = 0.004 \text{ mol l}^{-1}\text{s}^{-1}$$

$$\frac{\Delta[\text{S}_4\text{O}_6^{2-}]}{\Delta t} = 0.004 \text{ mol l}^{-1}\text{s}^{-1}$$

$$\frac{\Delta[\text{I}^-]}{\Delta t} = 0.008 \text{ mol l}^{-1}\text{s}^{-1}$$

REACTION KINETICS

MODULE 2

- Factors affecting rate of reaction
- Various methods that are used to monitor the rate of chemical reaction
- Basic definitions of rates, orders of reaction and molecularity
- Calculations involving initial rate

Objectives of Module 2

At the end of module 2, students will be able to

- The factors affecting reaction rate
- Express the rate of the reaction in term of change in concentration of either of the reactants or product with time
- Describe with the help of a graph, reaction rate as a function of change of concentration of reactant or product with respect to time
- Examine various methods that are used to monitor the rate of chemical reaction
- Define rate constant
- Express the rate of reaction as a rate law equation
- Distinguish the difference between order and molecularity of a reaction

FACTORS AFFECTING THE RATE OF REACTION

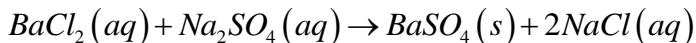
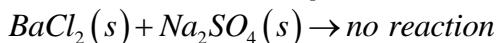
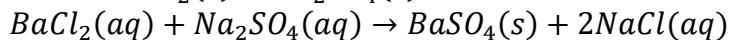
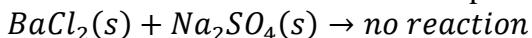
A number of factors can be changed to alter the steep of a chemical reaction.

These are:

- i. Physical State of reactants
 - ii. Concentration of reactants
 - iii. Temperature of reaction
 - iv. Surface area and size of reactants
 - v. The presence of a catalyst
 - vi. The pressure of gaseous reactants
 - vii. The presence of light
- } This are for selected reactions

A. Physical State of reactant

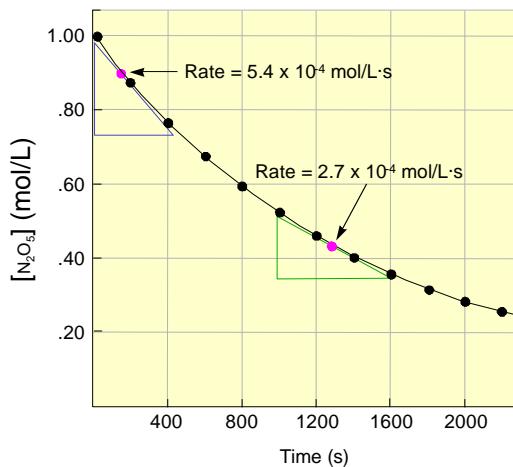
Consider the reaction between barium chloride and sodium sulphate



- When barium chloride and sodium sulphate are in solid state, they do not react (i.e the rate of reaction is zero)
 - This is because the ions of the reactants are held in fixed positions in their ionic lattices.
 - Hence, no effective collisions can occur between the ions of the reactants
 - **However** in aqueous state, the ions are mobile and collide with each other effectively, given rise to a chemical reaction.

B. Concentration of reactants

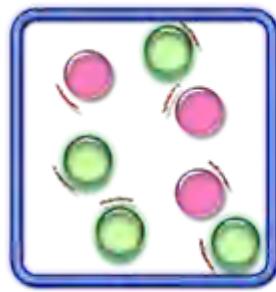
- A chemical reaction will occur only if particles of reacting substances are allowed to come into contact
- The rate would therefore depend on the frequency with which the particles collide
- This will also depend on their density i.e on their concentration
 - The more “crowded” the particles are the more often we should expect them to bump into one another.
- The characteristic concentration – time curve shows that the larger the concentration of the reactant, the greater is the rate



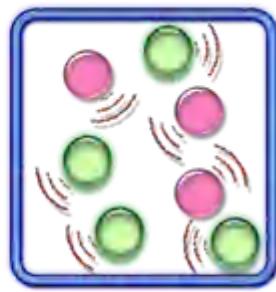
- The slope gets flatter as the reaction time increases
e.g $-\frac{\Delta[N_2O_5]}{\Delta t}$ is larger at time $t = 0$
and $-\frac{\Delta[N_2O_5]}{\Delta t}$ tends to 0 as t tends to infinity
- Hence, an increase in the concentration of reactants produces increase in reaction rate.

C. Temperature of the reaction

- When studying the effect of concentration, the temperature is kept constant.
- If the reaction is at constant concentration while varying the temperature.
- The rate increases as the temperature increases
 - When the temperature increases, the molecules of the reactant move faster as a result of gaining more energy
 - Hence the particles move faster and collide with one another more frequently
 - Therefore, the reaction becomes faster
 - The rate can be double for every 10°C rise in temperature.



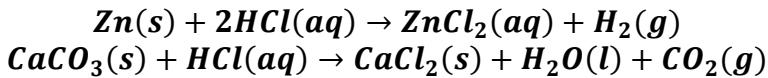
Particles have less energy, less frequent and successful collision



Particles have high energy, more frequent and successful collision

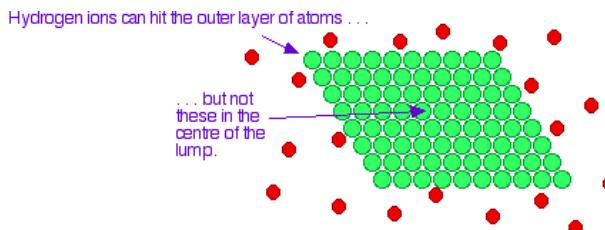
D. Surface area and size of the reactants

- **Homogeneous reactions** are reaction in which all the reactants are present in the same phase. e.g in solution, gas phase or solid phase.
- **Heterogeneous reactions** are reaction in which all the reactants are not in the same phase
e.g

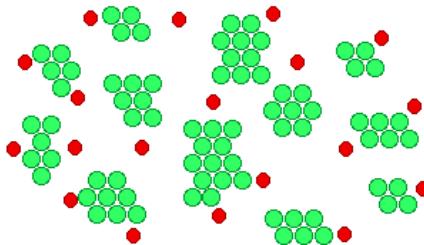


When the reaction is heterogenous, the particle size influences the rate of reaction.

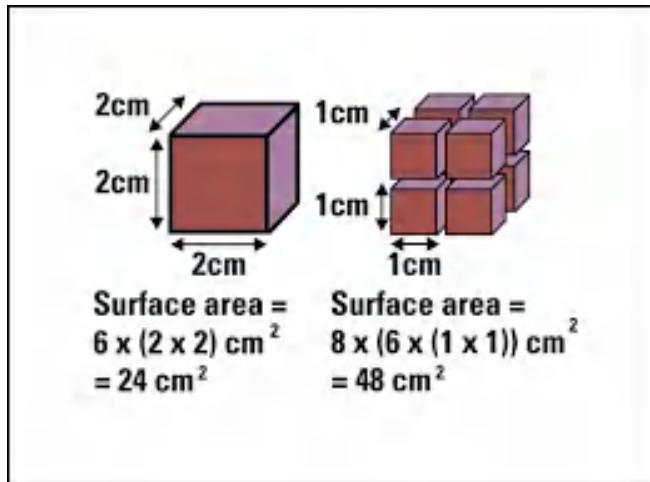
- If chips of calcium carbonate (marble) and powdered calcium carbonate are used, the reaction is faster in powdered marble
- This is because the powder has larger surface area than the marble chips



With the same number of atoms now split into lots of smaller bits, there are hardly any magnesium atoms which the hydrogen ions can't get at:



- The more finely the solid reactant is, the greater the surface area exposed to the surrounding.



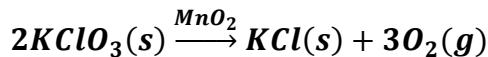
- The reaction rate increases when the surface area of the reactants is increased.

E. The presence of Catalyst

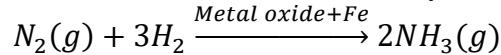
A catalyst is a substance which alters the rate of chemical reaction but remains chemically unchanged at the end of the reaction

- Catalysts tends to be specific in their action e.g a substance may catalyse one reaction and not another.
- A catalyst which increases the rate of a reaction is called **POSITIVE CATALYST**
 - A catalyst may change its physical nature during the reaction but it is chemically unchanged at the end of the reaction. e.g Coarsely powder MnO₂ becomes fine powder at the end of the reaction.
 - A catalyst will function even though it is present in only minute proportion

Example



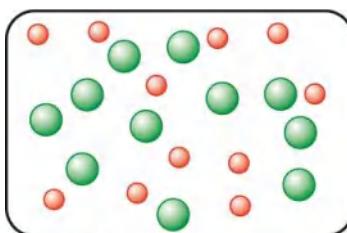
- An inhibitor decreases the rate of chemical reaction (used to suppresses an unwanted reaction)
- They are known as **NEGATIVE CATALYST**
- The biological catalyst is called **ENZYMES**. They are biochemical catalyst
 - They are usually protein.
- There are certain substances which are not catalyst themselves, but when added increases the effect the catalyst has on the rate of reaction. Such substances are called **PROMOTERS**
 - e.g. addition of metal oxide to the Iron used as catalyst in Haber process



F. The pressure of gaseous reactants

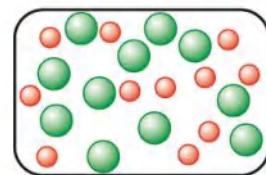
This can ONLY occur in reactants that are gases.

- An increase in pressure decreases the volume and increases the concentration of the gas
- This leads to an increase in rate of reaction.



Here we have a number of gaseous molecules. The molecules have space to move around and there is little chance of a collision.

Increase pressure



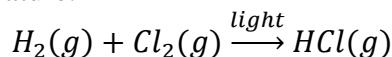
Increasing the pressure decreases the volume and increases the concentration. The molecules have less space to move in and are more likely to collide.

G. The presence of light

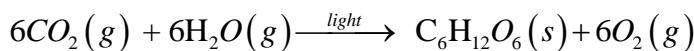
- Light is a source of energy, it can influence the rate of some chemical reaction by energizing some of the molecules involved.

Examples

- A mixture of hydrogen and chlorine gases explodes when exposed to bright sunlight at room temperature.



- Light is vital to the photosynthesis production of starch by plant from carbon dioxide and water



- A precipitate of silver bromide or silver chloride darkens when light is shone on it.

- This is basis of photography

The reactions like these are speeded up by light and are called PHOTOCHEMICAL REACTION

Experimental Determination of Rate

To measure the rate of chemical reaction, we must choose some property of the reaction which will indicate how far the reaction has changed and then observed the way in which the magnitude of the property varies with time.

- Choose some property of the reaction
- Observed the magnitude of the property variation with time

Methods of finding the rate of Chemical Reactions

There are two methods

- Chemical Methods
- Physical Methods

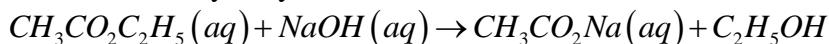
a. Chemical Methods

In this case, the progress of a reaction can be followed by chemical analysis.

1. Titration Method

Titrimetric methods can be used to follow the change in concentration of the reactants or the product

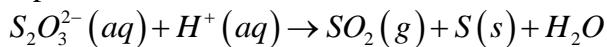
- The alkaline hydrolysis of an ester



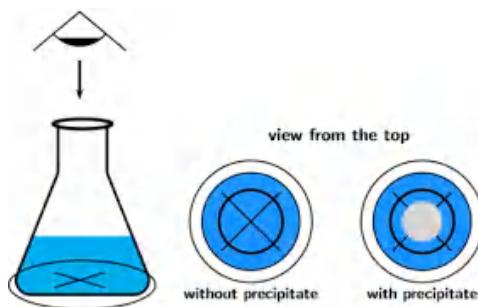
- The concentration of solutions of ester and alkali are known
- The course of an alkaline hydrolysis of an ester is followed by measuring the concentration of alkali at various times after the start of the reaction
- It is the alkaline that remains that is titrated against standard acid using phenolphthalein as indicator
- This titration is repeated at various times interval after the start of the reaction.

2. Precipitation Method

- A reaction in which one of the products is insoluble (form precipitates).
- These precipitate is like a cloudy suspension
e.g A reaction of dilute acid with sodium thiosulphate solution is a good example.



- One of the products is Sulphur which is slowly precipitate as a colloidal suspension.
- The rate of a particular reaction is measured by the length of time it takes for sufficient Sulphur to produce so that the X mark can no longer be seen through this reaction beaker.



- The larger the value of t, the slower is the rate of the reaction.

b. Physical Methods

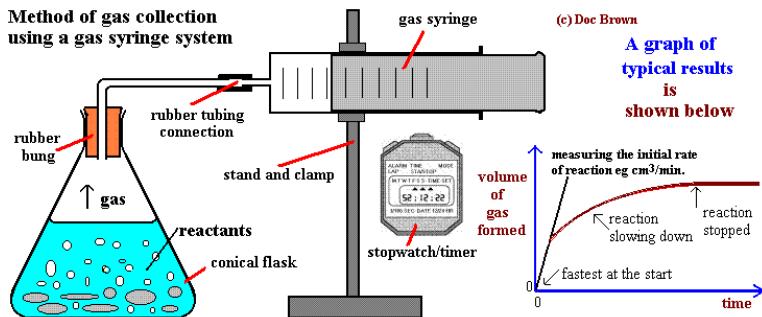
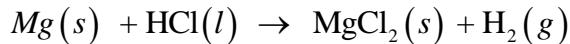
In this case, the progress of the reaction is followed by one physical property of the reactant or product.

1. Colour Change

- A reaction in which a colourless substance is changed to colour substance
- The intensity of the colour will increase as the reaction progress
- We monitor the intensity with time
- The modern equipment which can detect intensity of colour change is called COLORIMETER

2. Gas Production

- A reaction in which a gas is liberated from solution
- The volume of gas or pressure of the gas can be measured with time.



- The gas pushes its way out into the syringe
- The plunge of the syringe is forced back and hence the volume can be read at time interval

Also, an increase or decrease in gaseous pressure can be used to follow many gaseous reaction



- If the reaction takes place at constant volume, the resulting increase in pressure can be followed.

3. Change in electrical properties

A change in the conductance of a solution will occur if ions are used up or created during a reaction.

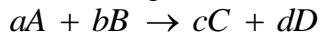
- A change in conductance indicates a change in concentration of ions

RATE EQUATION (LAW), RATE CONSTANT AND ORDER OF REACTION

(a) Rate Equation or Law

The rate equation or law is an experimentally determined equation that shows how the rate of reaction is dependent on the concentration of the reactants raised to appropriate powers.

Let consider the general reaction:



- The rate depends on concentrations of A and B

The relationship is as follows:

$$\text{Reaction Rate} \propto [A]^m [B]^n$$

If the proportionality constant is k.

Therefore,

$$\text{Reaction Rate} = k [A]^m [B]^n$$

This equation is known as the rate law or rate equation.

- $[A]$ and $[B]$ represent the molar concentration of the reactants A and B.
- The letter m and n represent the exponents of $[A]$ and $[B]$ in the rate law.

- It is the power to which each concentration must be raised to give the correct dependence of the rate on concentration.
- These exponents must be determined by actual experiment – they CANNOT be found by theory.
- There is no connection between these exponents and the coefficients of A and B in the balanced equation for the overall reaction.
- The exponents are usually simple whole number such as 0, 1 or 2 but they can be a fraction.
- k is the proportionality constant.

(b) Rate Constant (k)

The **rate constant, k**, is the **proportionality constant in the rate equation** which relates the rate of the reaction to the concentration of the reactants.

The rate constant, k

- is experimentally determined and has no fixed unit.
- is dependent on the particular reaction, temperature and the pressure of a catalyst (if any).
- k increases with temperature and catalyst
- determines how fast the reaction can proceed.

In general, the larger the k value, the faster the reaction.

Since, $\text{Rate} = k[A]^m[B]^n$

Note that, when the reactants are present at unit concentration

$$\text{Rate} = k$$

The rate constant is the rate of reaction when concentrations of the reactants are unity.

The rate constant for any reaction can be determined.

- (i) either by measuring the rate at unit concentration of reactants
- (ii) by knowing the rate at any concentration of reactant using the relation.

$$\text{Rate constant, } k = \frac{\text{Rate}}{[A]^m[B]^n}$$

$$\text{Unit of Rate constant} = \frac{\text{mole dm}^{-3} \text{ sec}^{-1}}{(\text{moles dm}^{-3})^z}$$

$$\text{where } z = a + b$$

Note: Time may also be minutes, hours or years

(c) Order of Reaction

The **order of a reaction** is the **sum of the powers to which the concentration of the reactants is raised to in the rate equation**.

- The **overall order of reaction** is the **sum of the powers to which the concentration of the reactants is raised in the rate equation**.

Consider the rate equation:

$$\text{Reaction Rate} = k[A]^m[B]^n$$

- The reaction is of order m with respect to A and of order n with respect to B
- The **overall order** of the above reaction is **m + n**

- If the exponent $m = 1$, the reaction is **first order** in reactant A
 - If the exponent $m = 2$, the reaction is **second order** in reactant A
 - If the exponent $m = 3$, the reaction is **third order** in reactant A
- It is possible for exponent $m = 0$, i.e. that the rate of the reaction is independent of the concentration of the component A
 - Hence it **zero order** in A
- If the rate law of a particular reaction is

$$\text{Reaction Rate} = k[A][B]^2$$
 - The reaction is first order in A and second order in B
 - The overall order of the reaction = $1 + 2 = 3$: **Third order**.
- The **order** of reaction can ONLY be determined experimentally and they usually zero, positive whole number or fractions ((0,1,2)

Importance of Studying Order of Reaction

1. It predicts the effect of a change of concentration of a reactant on the reaction rate. e.g $\text{Rate} = k[A][B]^2$, it will be more effective to increase [B] for greater increase in reaction rate
2. It can be used to predict the reaction mechanism (not in the syllabus)

Example 1: For a reaction: $A + B \rightarrow \text{product}$, the rate equation is

$$\text{Reaction Rate} = k[A]^m[B]^n$$

$$\text{Reaction Rate} = k[A]^m[B]^n$$

If $m = 1$ and $n = 2$.

- i. If [A] doubles while keeping [B] constant, what will happen to the rate of the reaction?
- ii. How will the rate of reaction change, if [B] increases by 3 times while keeping [A]?
- iii. If [B] is halved while keeping [A] constant, how will the rate change?

Solution:

- i. If [A] doubles while keeping [B] constant i.e $\text{Rate} \propto [A]$, the rate will be doubled
- ii. If [B] increases by 3 times while keeping [A] constant i.e $\text{Rate} \propto [B]^2$, the rate of the reaction will increase 9 times
- iii. If [B] is halved while keeping [A] constant, the rate will decrease 4 times.

MOLECULARITY OF A REACTION

Molecularity is the sum of stoichiometric coefficients of reactants involved in the stoichiometric equation of the reaction.



Stoichiometric coefficient of A and B are 2 and 3

Molecularity = $2 + 3 = 5$

There is no simple relationship between order and molecularity.

NOTE

(i) Molecularity will always be a whole integer while order may be integer, fraction or even a negative number.

(ii) Molecularity is a theoretical concept whereas order is empirical.

- The order of reaction provides the basis for classifying reactions.

The order of reaction can be between zero and 3

- Reaction having order 3 and above are rare.

Rate of reaction is proportional to number of collisions taken place in between reacting molecules.

∴ ***The chance of simultaneous collision of reacting molecules will decrease with increasing no of molecules.***

- Hence reaction having order 4 or more are practically impossible.

Differences between Order and Molecularity

Order of Reaction		Molecularity of a Reaction
1	It is the sum of power of the concentration terms in the rate equation	It is the number of the reacting species undergoing simultaneous collision in the elementary or simple reaction
2	It is an experimentally determined value	It is a theoretical concept
3	It can have fractional value	It is always a whole number
4	It can assume zero value	It cannot have zero value
5	Order of a reaction can change with the conditions such as pressure, temperature, concentration	Molecularity is invariant for a chemical equation

CHM 101

REACTION KINETICS

Prof. O.O.SORIYAN

MODULE 2

MODULE 2

- ▶ Factors affecting rate of reaction
- ▶ Various methods that are used to monitor the rate of chemical reaction
- ▶ Basic definitions of rates, orders of reaction and molecularity
- ▶ Calculations involving initial rate

Objectives of Module 2

At the end of module 2, students will be able to

- The factors affecting reaction rate
- Express the rate of the reaction in term of change in concentration of either of the reactants or product with time
- Describe with the help of a graph, reaction rate as a function of change of concentration of reactant or product with respect to time
- Examine various methods that are used to monitor the rate of chemical reaction
- Define rate constant
- Express the rate of reaction as a rate law equation
- Distinguish the difference between order and molecularity of a reaction

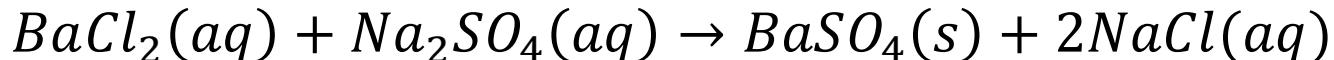
FACTORS AFFECTING THE RATE OF REACTION

These are:

1. Physical State of reactants
2. Concentration of reactants
3. Temperature of reaction
4. Surface area and size of reactants
5. The presence of a catalyst

Physical State of reactant

Consider the reaction between barium chloride and sodium sulphate

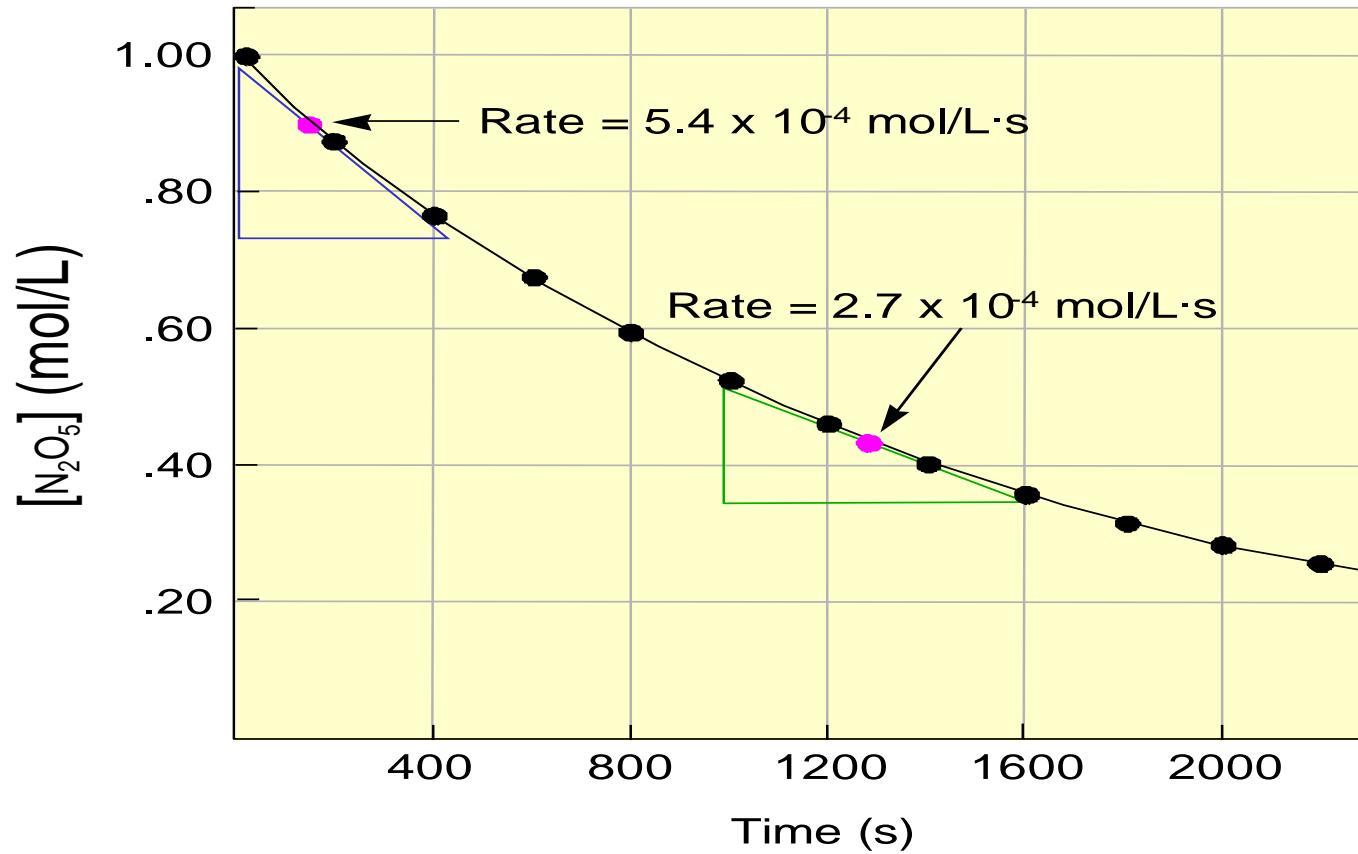


- When barium chloride and sodium sulphate are in solid state, they do not react (i.e the rate of reaction is zero)
 - This is because the ions of the reactants are held in fixed positions in their ionic lattices.
 - Hence, no effective collisions can occur between the ions of the reactants
 - However** in aqueous state, the ions are mobile and collide with each other effectively, given rise to a chemical reaction.

B. Concentration of reactants

- A chemical reaction will occur only if particles of reacting substances are allowed to come into contact
- The rate would therefore depend on the frequency with which the particles collide
- This will also depend on their density i.e on their concentration
 - The more “**crowded**” the particles are the more often we should expect them to bump into one another.
- The characteristic concentration – time curve shows that the larger the concentration of the reactant, the greater is the rate

Concentration of reactants



- Hence, an increase in the concentration of reactants produces increase in reaction rate.

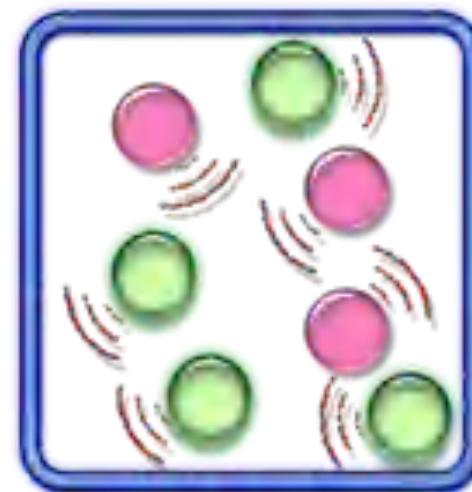
C. Temperature of the reaction

- When studying the effect of concentration, the temperature is kept constant.
- If the reaction is at constant concentration while varying the temperature.
- The rate increases as the temperature increases
 - When the temperature increases, the molecules of the reactant move faster as a result of gaining more energy
 - Hence the particles move faster and collide with one another more frequently
 - Therefore, the reaction becomes faster
 - The rate can be double for every 10°C rise in temperature.

Temperature of the reaction



Particles have less energy, less frequent and successful collision

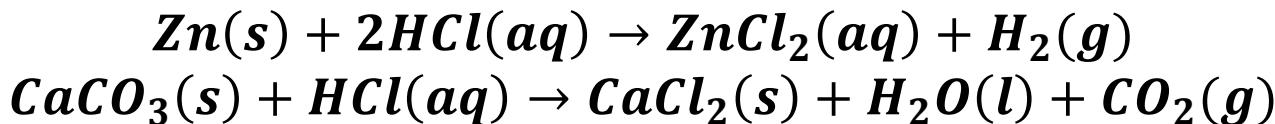


Particles have high energy, more frequent and successful collision

D. Surface area and size of the reactants

- **Homogeneous reactions** are reaction in which all the reactants are present in the same phase. e.g in solution, gas phase or solid phase.
- **Heterogeneous reactions** are reaction in which all the reactants are not in the same phase

e.g



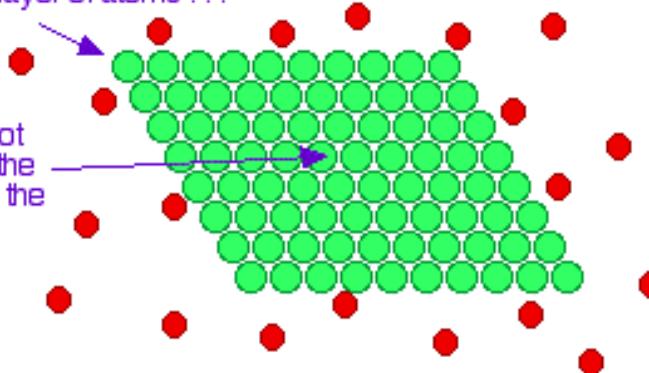
When the reaction is heterogenous, the particle size influences the rate of reaction.

- If chips of calcium carbonate (marble) and powdered calcium carbonate are used, the reaction is faster in powdered marble
- This is because the powder has larger surface area than the marble chips

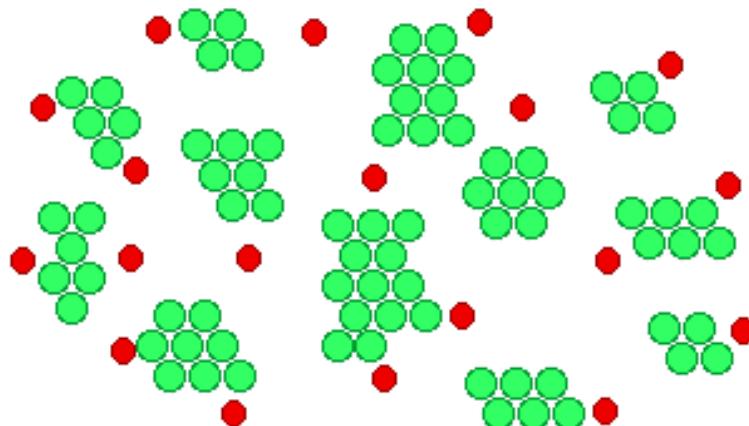
Surface area and size of the reactants

Hydrogen ions can hit the outer layer of atoms ...

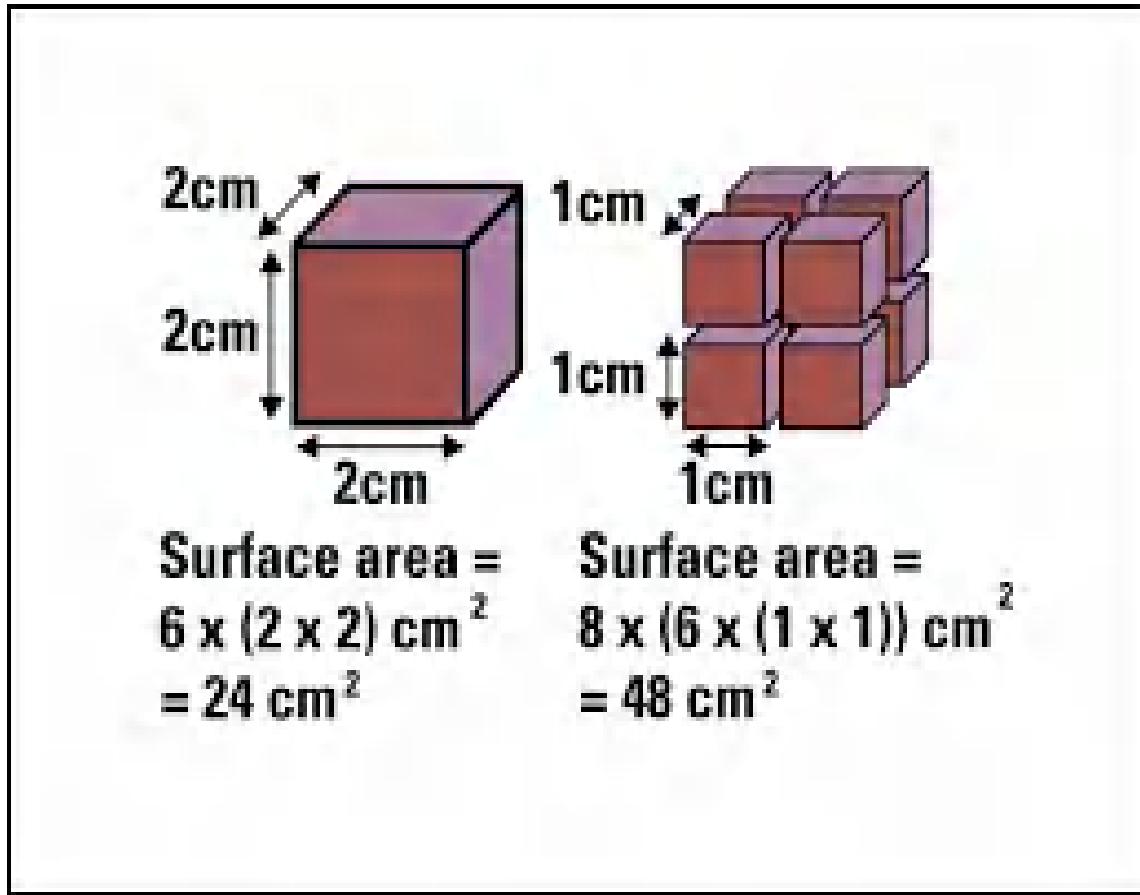
... but not
these in the
centre of the
lump.



With the same number of atoms now split into lots of smaller bits, there are hardly any magnesium atoms which the hydrogen ions can't get at.



The more finely the solid reactant is, the greater the surface area exposed to the surrounding.

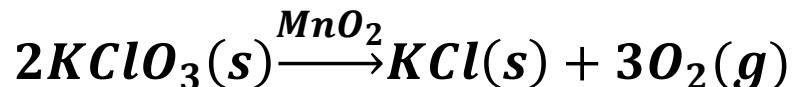


The reaction rate increases when the surface area of the reactants is increased.

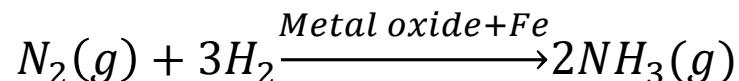
The presence of Catalyst

- ▶ A catalyst is a substance which alters the rate of chemical reaction but remains chemically unchanged at the end of the reaction
- ▶ Catalysts tends to be specific in their action e.g a substance may catalyze one reaction and not another.
- ▶ A catalyst which increases the rate of a reaction is called **POSITIVE CATALYST**
 - A catalyst may change its physical nature during the reaction but it is chemically unchanged at the end of the reaction.
 - e.g Coarsely powder MnO₂ becomes fine powder at the end of the reaction.
 - A catalyst will function even though it is present in only minute proportion

Example



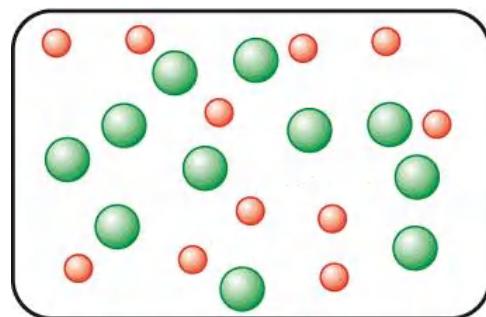
- An inhibitor decreases the rate of chemical reaction (used to suppresses an unwanted reaction)
- They are known as NEGATIVE CATALYST
- The biological catalyst is called ENZYMES. They are biochemical catalyst
 - They are usually protein.
- There are certain substances which are not catalyst themselves, but when added increases the effect the catalyst has on the rate of reaction. Such substances are called PROMOTERS
 - e.g. addition of metal oxide to the Iron used as catalyst in Haber process



F. The pressure of gaseous reactants

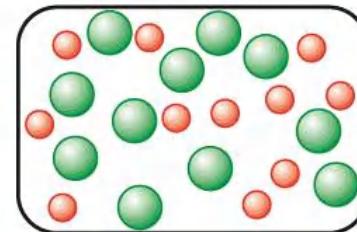
This can ONLY occur in reactants that are gases.

- An increase in pressure decreases the volume and increases the concentration of the gas
- This leads to an increase in rate of reaction.



Here we have a number of gaseous molecules.
The molecules have space to move around
and there is little chance of a collision.

Increase pressure

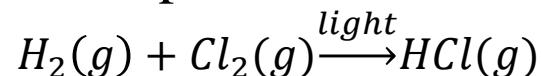


Increasing the pressure decreases the
volume and increases the concentration.
The molecules have less space to move in
and are more likely to collide.

G. The presence of light

- Light is a source of energy, it can influence the rate of some chemical reaction by energizing some of the molecules involved.

- Examples
 - i. A mixture of hydrogen and chlorine gases explodes when exposed to bright sunlight at room temperature.



- i. A precipitate of silver bromide or silver chloride darkens when light is shone on it.

- This is basis of photography
- The reactions like these are speeded up by light and are called PHOTOCHEMICAL REACTION

Experimental Determination of Rate

- To measure the rate of chemical reaction, we must choose some property of the reaction which will indicate how far the reaction has changed and then observed the way in which the magnitude of the property varies with time.
 - Choose some property of the reaction
 - Observed the magnitude of the property variation with time

Methods of finding the rate of Chemical Reactions

There are two methods

1. Chemical Methods
2. Physical Methods

a. Chemical Methods

In this case, the progress of a reaction can be followed by chemical analysis.

1. Titration Method

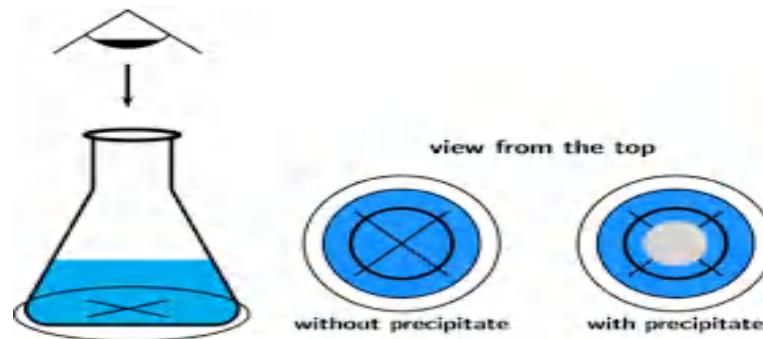
- ▶ Titrimetric methods can be used to follow the change in concentration of the reactants or the product
- The alkaline hydrolysis of an ester
 - ▶ $CH_3CO_2C_2H_5(aq) + NaOH(aq) \rightarrow CH_3CO_2Na(aq) + C_2H_5$

The concentration of solutions of ester and alkali are known

- The course of an alkaline hydrolysis of an ester is followed by measuring the concentration of alkali at various times after the start of the reaction
- It is the alkaline that remains that is titrated against standard acid using phenolphthalein as indicator
- This titration is repeated at various times interval after the start of the reaction.

2. Precipitation Method

- A reaction in which one of the products is insoluble (form precipitates).
- These precipitate is like a cloudy suspension
 - ▶ e.g A reaction of dilute acid with sodium thiosulphate solution is a good example.
 - ▶ $S_2O_3^{2-}(aq) + H^+(aq) \rightarrow SO_2(g) + S(s) + H_2$
 - ▶ One of the products is Sulphur which is slowly precipitate as a colloidal suspension.
- The rate of a particular reaction is measured by the length of time it takes for sufficient Sulphur to produce so that the X mark can no longer be seen through this reaction beaker.



- The larger the value of t , the slower is the rate of the reaction.

B. Physical Methods

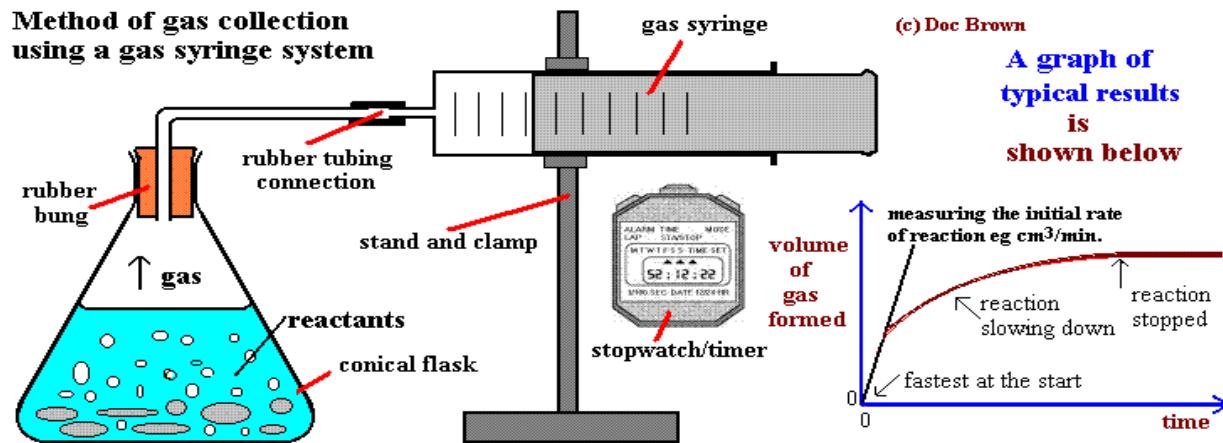
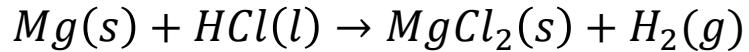
In this case, the progress of the reaction is followed by one physical property of the reactant or product.

1. Colour Change

- A reaction in which a colourless substance is changed to colour substance
- The intensity of the colour will increase as the reaction progress
- We monitor the intensity with time
- The modern equipment which can detect intensity of colour change is called COLORIMETER

2. Gas Production

- A reaction in which a gas is liberated from solution
- The volume of gas or pressure of the gas can be measured with time.

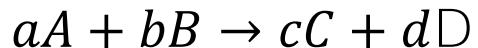


- The gas pushes its way out into the syringe
- The plunge of the syringe is forced back and hence the volume can be read at time interval

Rate Equation or Law

- The rate equation or law is an experimentally determined equation that shows how the rate of reaction is dependent on the concentration of the reactants raised to appropriate powers.

Let consider the general reaction:



$$\text{Reaction Rate} \propto [A]^m[B]^n$$

$$\text{Reaction Rate} = k[A]^m[B]^n$$

This equation is known as the **rate law** or **rate equation**.

- [A] and [B] represent the molar concentration of the reactants A and B.
- The letter m and n represent the exponents of [A] and [B] in the rate law.
 - **It is the power to which each concentration must be raised to give the correct dependence of the rate on concentration.**
 - **These exponents must be determined by actual experiment – they CANNOT be found by theory.**
 - There is no connection between these exponents and the coefficients of A and B in the balanced equation for the overall reaction.
 - The exponents are usually simple whole number such as 0, 1 or 2 but they can be a fraction.
- k is the proportionality constant.

Rate Constant (k)

- ▶ The rate constant, k, is the proportionality constant in the rate equation which relates the rate of the reaction to the concentration of the reactants.
- ▶ **The rate constant, k**
 - is experimentally determined and has no fixed unit.
 - is dependent on the particular reaction, temperature and the pressure of a catalyst (if any).
 - k increases with temperature and catalyst
 - determines how fast the reaction can proceed.

Rate Constant (k) contd

- ▶ In general, the larger the k value, the faster the reaction.

- $\text{Reaction Rate} = k[A]^m[B]^n$
 - Note that, when the reactants are present at unit concentration
 - $\text{Reaction Rate} = k$
 - *The rate constant is the rate of reaction when concentrations of the reactants are unity.*

Unit of rate constant

$$\text{Rate Constant, } k = \frac{\text{Rate}}{[A]^m[B]^n}$$

$$\text{Unit of rate constant} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\{\text{mol dm}^{-3}\}^z}$$

where, $z = m + z$

Note: Time may also be minutes, hours or years

Order of Reaction

- ▶ The order of a reaction is the sum of the powers to which the concentration of the reactants is raised to in the rate equation.
 - The overall order of reaction is the sum of the powers to which the concentration of the reactants is raised in the rate equation.

$$\text{Reaction Rate} = k[A]^m[B]^n$$

The overall order of the above reaction is $m + n$

- If the exponent $m = 1$, the reaction is first order in reactant A
- If the exponent $m = 2$, the reaction is second order in reactant A
- If the exponent $m = 3$, the reaction is third order in reactant A
- ▶ It is possible for exponent $m = 0$, it is zero order in A

- If the rate law of a particular reaction is
 - ▶ $\text{Reaction Rate} = k[A][B]^2$
 - ▶ The reaction is first order in A and second order in B
- The overall order of the reaction = $1 + 2 = 3$: **Third order.**
- The **order** of reaction can ONLY be determined experimentally and they usually zero, positive whole number or fractions ((0,1,2)

Importance of Studying Order of Reaction

1. It predicts the effect of a change of concentration of a reactant on the reaction rate.

e.g

$$\text{Reaction Rate} = k[A][B]^2$$

it will be more effective to increase [B] for greater increase in reaction rate.

2. It can be used to predict the reaction mechanism (not in the syllabus)

Assignments

Assignment 1: For a reaction: $A + B \rightarrow$ product, the rate equation is

$$\textit{Reaction Rate} = k[A]^m[B]^n$$

If $m = 1$ and $n = 2$.

- i. If $[A]$ doubles while keeping $[B]$ constant, what will happen to the rate of the reaction?
- ii. How will the rate of reaction change, if $[B]$ increases by 3 times while keeping $[A]$?
- iii. If $[B]$ is halved while keeping $[A]$ constant, how will the rate change?

Assignment 2: A reactant solution of concentration 0.20 mol dm^{-3} undergoes a first order reaction at initial rate of $3.0 \times 10^{-4} \text{ mol dm}^{-3}\text{s}^{-1}$. Calculate the rate constant?

Assignment 3: A second-order reaction takes place between the reactant A and B, which are both initially present at concentration 0.20 mol dm^{-3} . If the initial rate of reaction is $1.6 \times 10^{-4} \text{ mol dm}^{-3}$, what is the rate constant?

Assignments

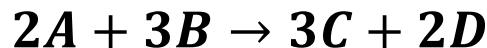
Assignment 4: The following results were obtained for a reaction between A and B.

	Mol dm ⁻³	Mol dm ⁻³	Mol dm ⁻³ s ⁻¹
Run	[A]	[B]	Rate
1	0.50	1.0	2.0
2	0.50	2.0	8.0 •?
3	0.50	3.0	15.0
4	1.0	3.0	36.0
5	2.0	3.0	72.0

- i. What is the rate law for the reaction?
- ii. What is the order of reaction with respect to A and with respect to B

MOLECULARITY OF A REACTION

Molecularity is the sum of stoichiometric coefficients of reactants involved in the stoichiometric equation of the reaction.



Stoichiometric coefficient of A and B are 2 and 3

$$\text{Molecularity} = 2 + 3 = 5$$

There is no simple relationship between order and molecularity.

NOTE

- (i) Molecularity will always be a whole integer while order may be integer, fraction or even a negative number.
 - (ii) Molecularity is a theoretical concept whereas order is empirical.
-
- The order of reaction provides the basis for classifying reactions.
 - The order of reaction can be between zero and 3
 - Reaction having order 3 and above are rare.

- ▶ Rate of reaction is proportional to number of collisions taken place in between reacting molecules.
- ▶ *The chance of simultaneous collision of reacting molecules will decrease with increasing no of molecules.*
- ▶ - Hence reaction having order 4 or more are practically impossible

Differences between Order and Molecularity

	Order of Reaction	Molecularity of a Reaction
1	It is the sum of power of the concentration terms in the rate equation	It is the number of the reacting species undergoing simultaneous collision in the elementary or simple reaction
2	It is an experimentally determined value	It is a theoretical concept
3	It can have fractional value	It is always a whole number
4	It can assume zero value	It cannot have zero value
5	Order of a reaction can change with the conditions such as pressure, temperature, concentration	Molecularity is invariant for a chemical equation

CHEMICAL KINETICS

MODULE 3

The collision Theory

- Activation energy
- Arrhenius equation.

Objectives of Modules 3

At the end of Modules 3, students will be able to

- Explain using the collision theory and potential energy diagrams, how different factors such as temperature and concentration, control the rate of reaction.
- Understand the Arrhenius equation and be able to do calculations on the equation.

The Collision Model

Overall reaction rates can be increased by:

- Increasing the concentration of reactants
- Increasing the temperature
- ***The underlying physical interpretation for these two observations is the Collision Model of chemical kinetics***

The main point of the Collision Model is that

1. ***molecules must physically collide in order to react***
 2. ***The more collisions that occur over a given period of time, the faster the reaction rate***
- ***Increasing concentration*** (i.e. the number of molecules in a given volume) will increase the number of collisions and result in a faster reaction rate

What about increasing temperature?

- Increasing temperature results in an increase in the velocity of molecules
- As molecules move faster, there are ***more collisions per unit of time***
- Not only are there
 1. more collisions, but
 2. the collisions are harder (i.e. the impacts involve greater energy levels)

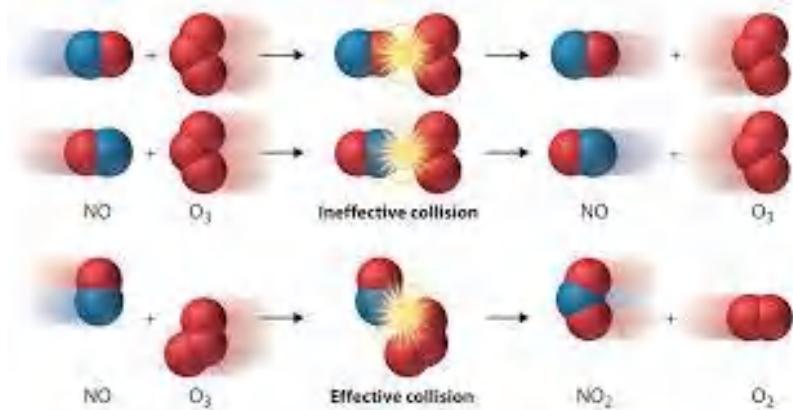
Does every collision result in a reaction?

- Only a small fraction of collisions ($\sim 1 \text{ in every } 10^{13} \text{ collisions!}$) results in a reaction.

Why doesn't every molecular collision result in a reaction?

- i. ***They must come together in proper orientation.***

For a reaction: $NO + O_3 \rightarrow NO_2 + O_2$



- a. The colliding particle must have sufficient energy to initiate a reaction.
i.e. energy to break relevant bonds

ii. Activation Energy

1888 Swedish chemist Svante Arrhenius proposed:

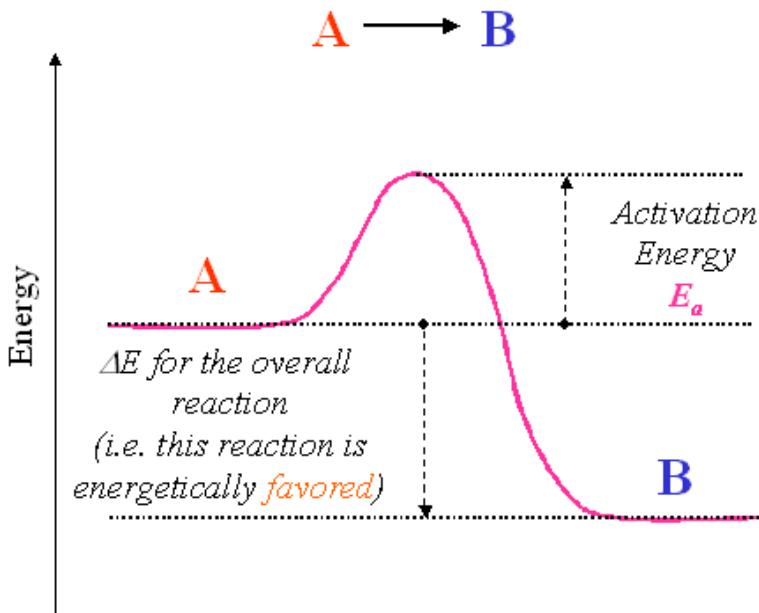
Molecules must possess a certain minimum amount of energy in order to react

- The available energy is related to the kinetic energy of the molecular collision
- The kinetic energy of impact can be used to stretch, bend and break covalent bonds, resulting in chemical reactions (recall that in a typical chemical reaction some bond is broken and a new bond is formed)
- If molecules are moving too slowly, they collide with insufficient energy, and just *bounce off each other instead of reacting*

The minimum energy needed to cause a particular chemical reaction is called

the **ACTIVATION ENERGY**

- Activation Energy is symbolized by E_a
- The value of E_a is dependent upon the particular reaction in question (it is a different value for different reactions)
- Although a reaction may be energetically favorable (i.e. $-\Delta H_{rxn}$) **the rate of reaction depends upon the magnitude of the activation energy**; the higher the activation energy, the slower the reaction



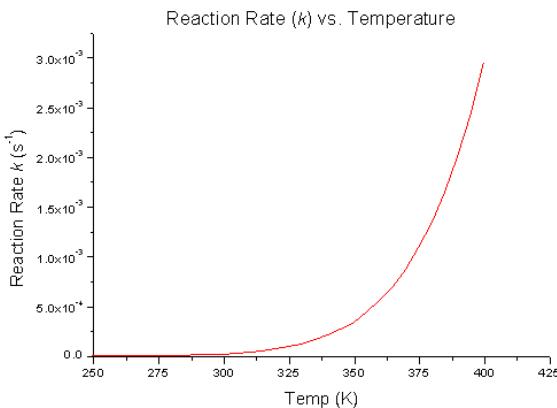
In the above energy diagram for the reaction $\text{A} \rightarrow \text{B}$ we have the following features:

1. Overall, the reaction is **energetically favorable**. In other words, the product, **B**, is at a lower energy level than the reactant, **A**. Energetically, **the reaction will proceed with a net release of energy (i.e. goes downhill energetically as it goes from $\text{A} \rightarrow \text{B}$)**
2. However, for the reaction to proceed, there is an **activation energy barrier** that molecule **A** will have to overcome

Molecules of A will have to acquire enough energy to overcome E_a in order for the reaction to proceed. This energy will come from the kinetic energy associated with molecular collisions

The Arrhenius Equation

Arrhenius studied the relationship between the increase in reaction rate and increasing temperature:



- The increase in reaction rate (k) is **not** linear with temperature
- The relationship between the reaction rate and temperature was found by Arrhenius to be:

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

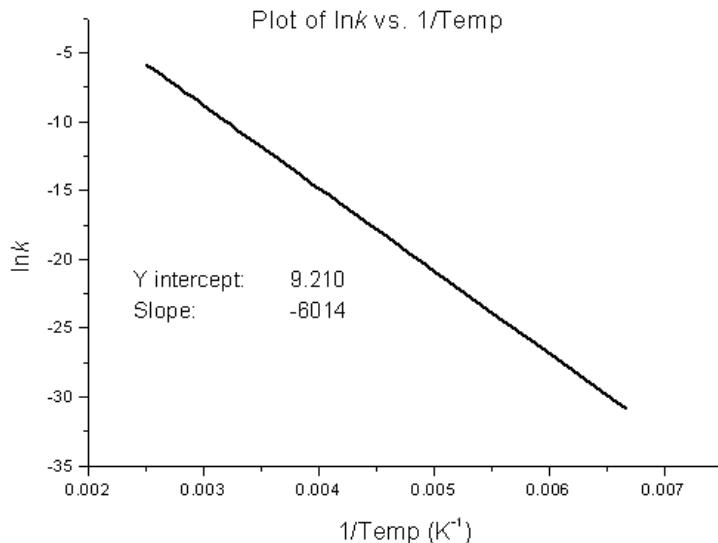
- k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/mol K), and T is the temperature (Kelvin)
- The term A is the **frequency factor**.
 - It is related to the frequency of collisions and the probability that the collisions are productive (i.e. correctly oriented)
 - It is specific for the particular reaction

Plotting the Arrhenius Equation

- If we take the natural log of both sides of the Arrhenius equation we get:

$$\begin{aligned}\ln k &= -\frac{E_a}{RT} + \ln A \\ \ln k &\left(-\frac{E_a}{R} \right) \frac{1}{T} + \ln A \\ y &= mx + b\end{aligned}$$

- Thus, this will have the form of a linear equation if we plot $\ln k$ vs. $1/T$. The slope of this line will be equal to $(-E_a/R)$ and the y intercept will be $\ln A$



- Thus, for this data, $-E_a/R = -6014$, and E_a therefore equals 50,000 J/mol. $\ln A = 9.210$, therefore, $A = 10,000 \text{ s}^{-1}$

Another form of the Arrhenius Equation

If we know the reaction rate at two different temperatures, T_1 and T_2 we can calculate the activation energy, E_a , without knowing the value for the frequency factor, A

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

and

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtracting the equation for $\ln k_2$ from $\ln k_1$ gives:

$$\begin{aligned}\ln k_1 - \ln k_2 &= \left(-\frac{E_a}{RT_1} + \ln A \right) - \left(-\frac{E_a}{RT_2} + \ln A \right) \\ \ln \frac{k_1}{k_2} &= \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)\end{aligned}$$

This relationship allows us to determine the rate constant, k_1 , at some temperature, T_1 , when we know the activation energy, E_a , and the rate constant, k_2 , at some other temperature, T_2

Effect of Catalysis

A catalyst is a substance that changes the speed of a chemical reaction (i.e. increasing the reaction rate) without undergoing a permanent chemical change itself during the process

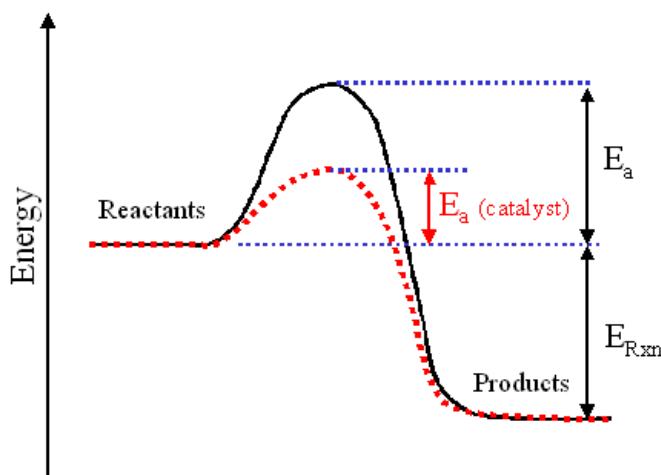
- A chemical reaction may be **energetically favorable** (i.e. may be exothermic), *but if the activation barrier is high (i.e. the activation energy is high) the reaction rate may be extremely slow*
- A lot of research is performed to identify new catalysts for chemical reactions of commercial interest (time is money, after all)
- Also, a lot of research is performed to develop methods to inhibit the action of certain catalysts, so that some reactions will **not** occur (e.g. certain biochemical reactions that rely upon the action of catalytic molecules)
- The **Arrhenius equation** states that the rate constant, k , of a reaction is **directly** proportional to the frequency factor (A), **inversely** proportional to the activation energy E_a , and directly proportional to the temperature:

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

- If a catalyst is to increase the reaction rate, k , it would appear to be able to do so by one of two ways:

1. Increase the frequency factor, A (i.e. in some way increase the rate of successful molecular collisions)
2. Decrease the activation energy, E_a

Generally speaking, a catalyst typically increases reaction rates by lowering the activation energy, E_a . This is related to the energy required to stretch and break a bond, thus, catalysts must facilitate this process in some way.



- Also, a catalyst often lowers the overall activation energy for a reaction by providing a completely different reaction mechanism for the reaction. In other words, a different set of underlying elementary reaction steps.

ASSIGNMENT

Assignment 3: A reaction is found to have an activation energy of 50 kJ mole^{-1} at 25°C . On addition of a catalyst, the rate speeds up by a factor of 10^6 . What is the activation energy with the catalysis?

CHM 101

REACTION KINETICS

Prof. O.O.SORIYAN

MODULE 3

MODULE 3

The collision Theory

- ▶ Activation energy
- ▶ Arrhenius equation.

Objectives Of Modules 3

At the end of Modules 3, students will be able to

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The Collision Model

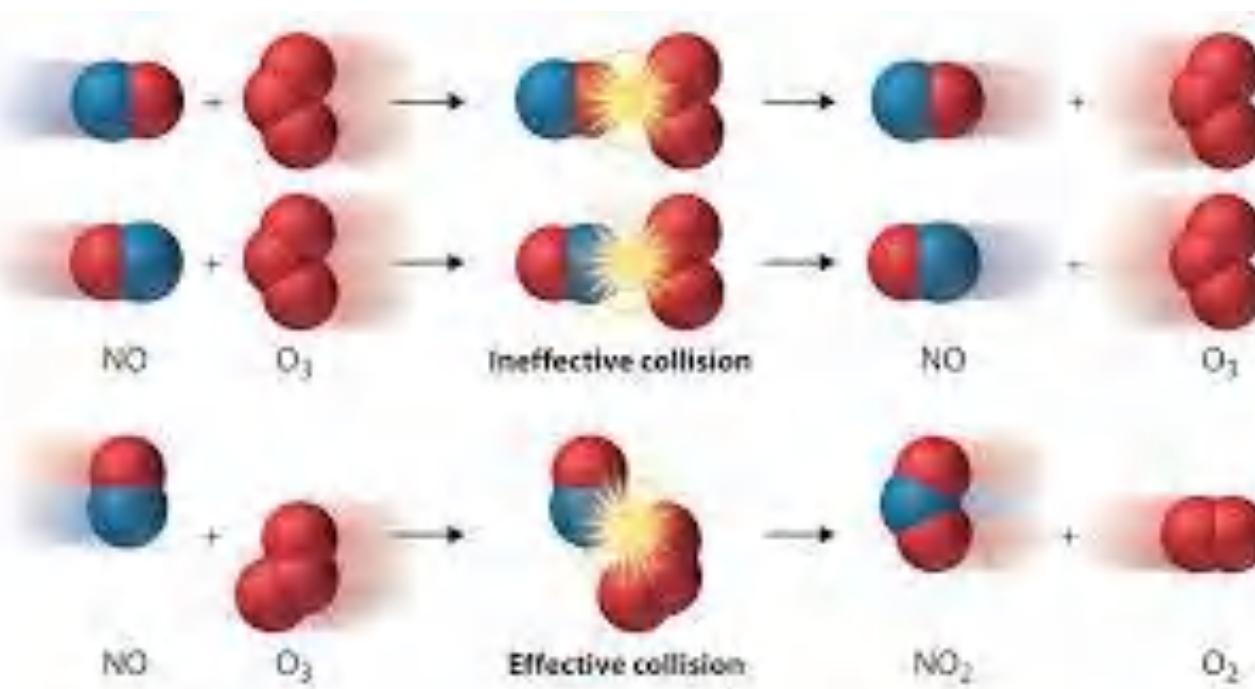
- ▶ The main point of the Collision Model is that:
 - *molecules must physically collide in order to react*
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What about increasing temperature?

- Increasing temperature results in an increase in the velocity of molecules
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 1. more collisions, but
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- ▶ Does every collision result in a reaction?
- Only a small fraction of collisions (*~1 in every 10^{13} collisions!*) results in a reaction.
- ▶ *Why doesn't every molecular collision result in a reaction?*

Molecular collision result in a reaction

1. They must come together in proper orientation.



Molecular collision result in a reaction

2. The colliding particle must have sufficient energy to initiate a reaction. (i.e energy to break relevant bonds)

Activation Energy

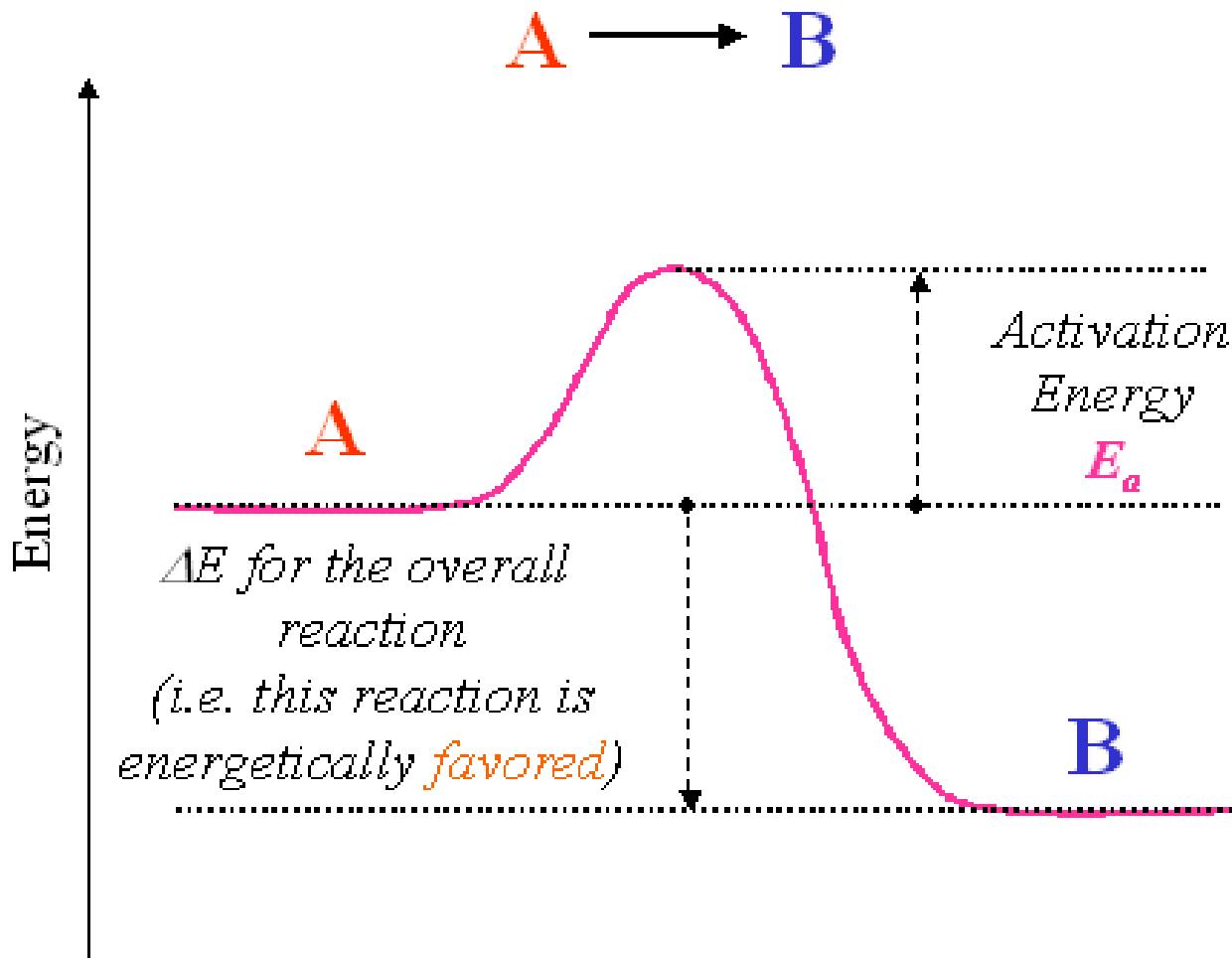
- ▶ 1888 Swedish chemist Svante Arrhenius proposed:
 - *Molecules must possess a certain minimum amount of energy in order to react*
- ▶ The minimum energy needed to cause a particular chemical reaction is called the **ACTIVATION ENERGY (E_a)**

- The available energy is related to the kinetic energy of the molecular collision
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The minimum energy needed to cause a particular chemical reaction is called the ***ACTIVATION ENERGY***

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ACTIVATION ENERGY (E_a)

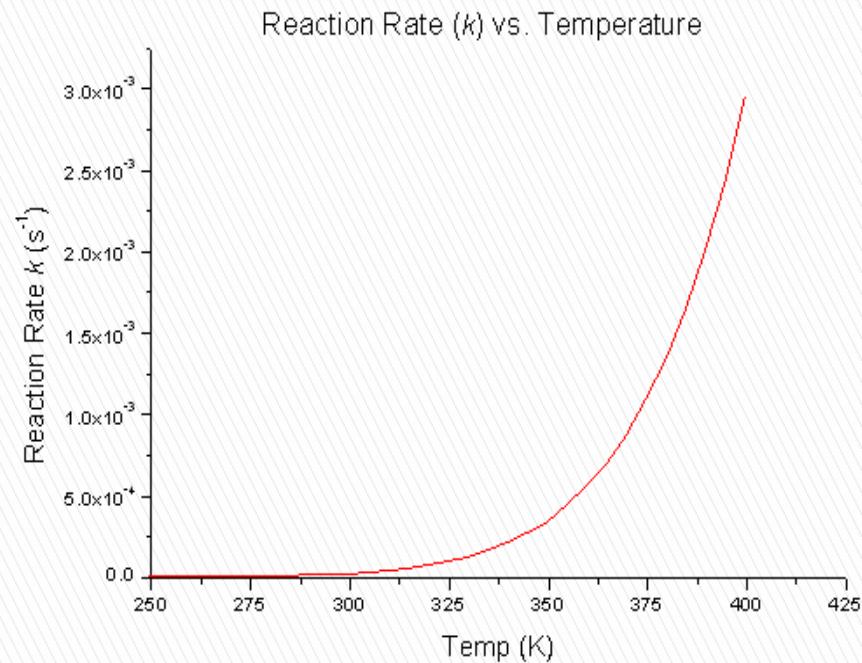


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$$▶ k = A e^{-(\frac{E_a}{RT})}$$



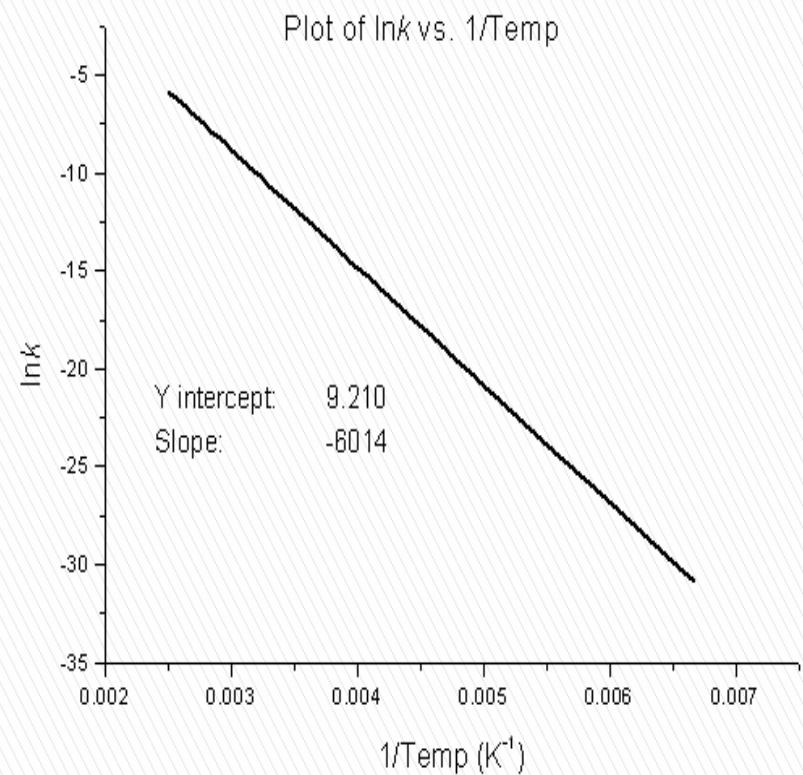
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$$\ln k = \left(-\frac{E_a}{R}\right)\frac{1}{T} + \ln A$$

$$y = mx + b$$



Plot of $\ln k$ vs $1/T$

Another form of the Arrhenius Equation

- If we know the reaction rate at two different temperatures, T_1 and T_2 we can calculate the activation energy, E_a , without knowing the value for the frequency factor, A

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtracting the equation for $\ln k_2$ from $\ln k_1$ gives:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

ASSIGNMENT

Assignment 1: A reaction has $E_a = 84\text{ kJ mol}^{-1}$. What is the effect on the rate (other things equal) of raising the temperature from 20°C to 30°C ?

Assignment 2: At what temperature will the rate of a reaction be three times that found at 20°C , other things being equal? ($E_a = 51.2\text{ kJ mol}^{-1}$)

Effect of Catalysis

*A **catalyst** is a substance that changes the speed of a chemical reaction (i.e. increasing the reaction rate) **without** undergoing a permanent chemical change itself during the process*

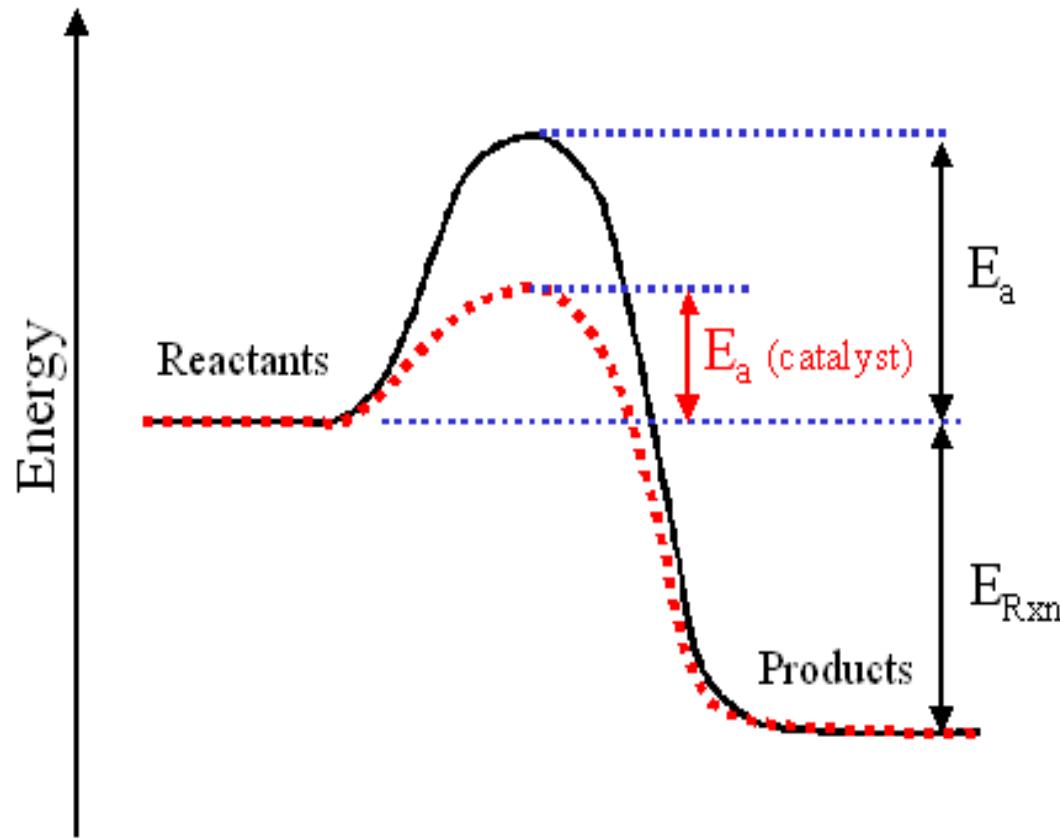
- A chemical reaction may be **energetically favorable** (i.e. may be exothermic), *but if the activation barrier is high (i.e. the activation energy is high) the reaction rate may be extremely slow*
- A lot of research is performed to identify new catalysts for chemical reactions of commercial interest (time is money, after all)

- Also, a lot of research is performed to develop methods to inhibit the action of certain catalysts, so that some reactions will **not** occur (e.g. certain biochemical reactions that rely upon the action of catalytic molecules)
- The *Arrhenius equation* states that the rate constant, k , of a reaction is *directly* proportional to the frequency factor (A), *inversely* proportional to the activation energy E_a , and directly proportional to the temperature:

$$k = Ae^{-E_a/RT}$$

If a catalyst is to increase the reaction rate, k , it would appear to be able to do so by one of two ways:

1. Increase the frequency factor, A (i.e. in some way increase the rate of successful molecular collisions)
 2. Decrease the activation energy, E
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- ▶ *Generally speaking, a catalysts typically increases reaction rates by lowering the activation energy, E_a . This is related to the energy required to stretch and break a bond, thus, catalysts must facilitate this process in some way.*



Also, a catalyst often lowers the overall activation energy for a reaction by providing a completely different reaction mechanism for the reaction.

In other words, a different set of underlying elementary reaction steps.