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QUOTES :

- If unity could be secured only by the compromise of truth and righteousness, then let there be difference, and even war.
- My growth in my spiritual life is proportional to my growth in intellect.

STOICHIOMETRY

This is a branch of chemistry that deals with relative quantities of reactants and products in a chemical reaction.
Any physical quantity will have significant figures, digits and units.
e.g 32 grams or 32g.

SIGNIFICANT FIGURES

What are significant figures?

These are numbers or digits that are known with some degree of confidenc

RULES GOVERNING SIGNIFICANT FIGURES

RULE 1

Rule 1.1 - All non-zero digits are significant; 1-9 are always significant.
e.g 21234 has 5 sig.fig while 46 has only 2 sig.fig.

Rules concerning Zeros

- Trailing Zeros

Rule 1.2 - Zeros to the right of non-zero digits are only significant if followed by a decimal point or indicat by a bar.

e.g 25.00 has 4 significant figures
100.0 has 3 significant figures
$25\bar{0}0$ has only 3 significant figures

Rule 1.3 – All zeros to the right of non-zero digits are <u>not</u> significant (except if they are followed by a decimal point or indicated with a bar as explained in Rule 1.2).

Therefore, 2500 has only 2 sig.fig
10 has only 1 sig.fig

- Leading Zeros

Rule 1.4 – Leading zeros are <u>not</u> significant
e.g 0.00035 has only 2 sig.fig

- Captive Zeros

Rule 1.5 – All zeros in-between non-zero digits are significant.
e.g 10101 has 5 significant figures.

RULE 2

When multiplying or dividing your answer may only show as many significant figures as the multiplier or divisor with the <u>least</u> number of significant figures.

$$\text{e.g} \quad 4.56 \times \underset{\substack{\downarrow \\ \text{limiting term} \\ \text{has the lowest number} \\ \text{of significant figures}}}{1.4} = 6.38 = \underset{\substack{\searrow \\ \text{final answer}}}{6.4}$$

RULE 3

When adding or subtracting numbers, your answer can have as many decima places as there are in the measurement with the least number of decimal places.

e.g

$$\begin{array}{r} 21.33 \\ -\ 10.0 \\ \hline 11.33 \end{array}$$

therefore the answer is 11.3.

Since 10.0 has the least number of decimals (it only has one decimal plac the final answer should be correct to one decimal place or should only have one decimal.

RULE 4

The number in the conversion factors, molar masses, physical constants are considered to be exact, have more significant figures than shown and include in establishing the number of significant figures during calculations.

RULE 5. (ROUNDING OFF)

If the digit after the figure to be rounded off is less than 5, then the figure be rounded off should stay the same. If the number is 5 or greater than 5, the the number of figure to be rounded off must increase by one (1).

e.g Round off 31.32 to one decimal place or point

31.32 = 31.3

Round off 36.87 to one decimal point

36.87 = 36.9

Basic Quantity	Symbol	Basic Unit	Symbol
Length	L	metre	m
Mass	m	Kilogram	Kg
Time	t	second	s
Thermodynamic	T	Kelvin	K
Electric current	I	ampere	A
Amount of Substance	n	mole	mol
Luminous Intensity	Ir	Candela	Cd

NON - SI UNITS REGARDING PHYSICAL QUANTITIES IN COMMON USE.

Physical Quantity	Symbol	Unit	Symbol	Conversion
Volume	V	Litre	L	$1 L = 10^{-3} m^3$
Length	l	Amstrong	Å	$1 Å = 10^{-10}$ m
Pressure	P	Atmosphere	atm	1 atm = 101325 Pa
		Bar	bar	1 bar = 100 000 Pa
		Torr	Torr	1 Torr = 131.25 Pa
Energy	E	Electric Volt	eV	$1 eV = 1.6 \times 10^{-19}$
Temperature	T	Degree Centigrad	°C	1°C = T − 273.15 K
Concentration	C	Molarity	M	mol / L
Pressure	P	Mercury	mmHg	1 mmHg = 131.25 Pa

PRECISION AND ACCURACY

Precision indicates how close the results are to each other or how repeatable the results are. For example, if you get the following volumes during titration 22.6, 22.5, 22.6, then your results are precise. But if you get 20.1, 16.2, 28.9, then your results are not precise.

Accuracy indicates how close values are to the true value. For example, if on a cold day in June your thermometer reads "100°C", then it is not accurate. For more conversion factors refer to CHE1000 Lab Manual.

In other words, accuracy of an experiment is a measure of how close the result is to the actual or true value, while precision of a measurement is the smallest unit of measurement possible in the experiment.

No measurement in the laboratory will be exact. Hence all measurements made in the laboratory have an experimental uncertainity called an Experimental Error. There are three ways in which to express an experimental error; these are (i) Absolute error (ii) Fractional error (iii) Percentage error

Never be satisfied with only a single measurement of a quantity. Repeated measurements improve the precision of your measurement and can also show up careless mistakes.

Summary on rules governing significant figures.

1. Non-zero digits or integers always count as significant figures.
2. Leading zeros are zeros that precede all the non-zero digits. These do not count as significant figures. In the number 0.0025, the three zeros simply indicate the position of the decimal point. This number has only two significant figures.
3. Captive zeros are zeros between non-zeros digits. These always count as significant figures. The number 1.008 has four significant digits or figures.
4. Trailing zeros are zeros at the right end of a number. They are significant only if the number contains a decimal point. The number 100 has only one significant figure, whereas the number 1.00×10^2 has three significant. The number one hundred written as 100. also has three significant figures.
5. Exact numbers. Many times calculations involve numbers that were not obtained using measuring devices but were determined by counting: 10 experiments, 3 apples, 8 molecules. Such numbers are called exact numbers. They can be assumed to have an infinite number of significant figures. Other examples of exact numbers are the 2 in $2\pi r$ (the circumference of a circle) and 4 and 3 in $\frac{4}{3}\pi r^3$ (the volume of the sphere).

Exact numbers also can arise from definitions. For example, one inch is defined as exactly 2.54 centimetres. Thus, in the statement 1 in = 2.54 cm, neither the 2.54 nor the 1 limits the number of significant figures when used in a calculation.

1. For multiplication or division, the number of significant figures in the result is the same as the number in the least precise measurement used in the calculation. For example, consider the calculation

$$4.56 \times 1.4 = 6.38 \xrightarrow{\text{corrected}} 6.4$$

limiting term has two significant figures.

two significant figures.

The product should only have two significant figures, since 1.4 has two significant figures.

2. For addition or subtraction, the result has the same number of decimal places as the least precise measurement used in the calculation.

$$\begin{array}{r} 12.11 \\ 18.0 \\ +\ 1.013 \\ \hline 31.123 \end{array} \xrightarrow{\text{corrected}} 31.1$$

18.0 ← limiting term has one decimal place

Note that for multiplication and division, significant figures are counted. For addition and subtraction, the decimal places are counted.

8 ELEMENTARY IDEAS OF ATOMS, IONS AND MOLECULES

All substances are made up of atoms, ions or molecules.

Each element is made up of atoms.

Each atom is made up of protons, neutrons and electrons. Electrons are contained in the part of the atom called or known as Shells or Energy-levels.

Protons are positively-charged, electrons are negatively charged and neutrons do not have charge at all (they are neutral).

In an atom, the number of protons equals the number of electrons. Thus, the charge of an atom is zero (0).

Particle	mass in grams	unified mass (u)
Proton	9.1096×10^{-28}	0.0005489
Electron	1.67276×10^{-24}	1.007277
Neutron	1.67492×10^{-24}	1.008665

$$1\,u = 1.6605 \times 10^{-24} \text{ grams}$$

$1\,u = {}^{1}/_{N_A}$, where N_A is the Avogadro's constant.

ISOTOPIC, ATOMIC AND MOLECULAR MASSES

Isotopes have the same number of protons, but different number of neutrons hence the different mass numbers.
An element X can be represented by the following model of representation:

$^{A}_{Z}X$ where a = the atomic number (mass number)
z = the proton number

Protons and neutrons equal the mass of an atom (A); $Z + N = A$.

Isotopic Mass (A_i)

Because of loss of mass to binding energy, isotopic masses are measured using the Mass Spectrometer (MS).

Atomic Mass (Atomic Weight) or Relative Atomic Weight

The atomic mass is the average mass of one element. The units for atomic mass of elements are based on Carbon-12. The mass spectrometer (MS) is caliberated to read carbon-12 at the peak of 12.0000 g.
The atomic mass (A) of an element is calculated as:

$$A = \sum_{i=1} A_i f_i$$, where A_i is the isotopic mass and F_i is the percentage abundance/100

Example: Calculate the atomic mass of carbon given that 98.89% of carbon atoms weigh 12u while 11.1% of them weigh 13u.

Answer:

$$\frac{A_i F_i}{100} + \frac{A_i F_i}{100} = \frac{12u \times 98.89\%}{100} + \frac{13 \times 1.10\%}{100}$$

$$= 11.8998 + 0.1443$$

$$= \underline{12.01 \text{ units}}$$

NOTE: $F_1 + F_2$ should equal 100.

AVOGADRO'S CONSTANT

It is defined as the number of atoms of molecules in one mole, that is the number of carbon in 12.0000 g of carbon 12.

$$N_A = 6.022 \times 10^{23} / \text{mol}$$

It is almost like a collective noun e.g 1 pair of shoes = 2 shoes
1 mole of shoes = 6.022×10^{23} shoes

Formular For Calculating Mass of One Atom of an Element in Grams

$$\text{Mass of one atom} = A \times 1.6605 \times 10^{-24}\ \text{g}$$

Remember the conversion factor: $1\ u = 1.6605 \times 10^{-24}$ g

A in u = mass of atom in grams (unified mass)

$$\text{Mass of atom in grams} = \frac{A_u \times 1.6605 \times 10^{-24}\ \text{g}}{1u}$$

$$= A \times 1.6605 \times 10^{-24}\ \text{g}$$

Example: Calculate the mass of 2 ~~grams~~ atoms of oxygen.

Answer: Mass of atom $= A_u \times 1.6605 \times 10^{-24}$

$= (16 \times 2) \times 1.6605 \times 10^{-24}$

$= 32 \times 1.6605 \times 10^{-24}$

$= 5.3136 \times 10^{-23}$ grams

Formular for Calculating Mass of One Mole of Atoms

$$\text{Mass of 1 mol of atoms} = A \times 1.6605 \times 10^{-24}\ g \times 6.022 \times 10^{23}$$

1 mole of atoms = A g, which is the same as A g/mol.

On the periodic table no units are shown. Thus the units will depend on what you are looking for. For example, 12.01 for carbon on the periodic table ca taken as 12 u as the weight of 1 atom or 12g as the weight of 1 mol of

Example 2 : Calculate the number of mols present in 54g of aluminium.

Answer : On the periodic table, one mole of Aluminium weighs 27grams.

$$\frac{54\ \cancel{g}}{27\ g/mol} = 2 \text{ moles.}$$

Therefore, there are two moles of Aluminium in 54g of Aluminiu

OR

$$\text{1 mole of Aluminium} = 27g$$

$$x \text{ moles} = 54g$$

$$x \text{ moles} = \frac{54g \times 1 \text{ mol of Aluminium}}{27g}$$

$$x = 2 \text{ moles of Aluminium.}$$

THE MOLE AND MOLE CONCEPT

The number of moles in a substance can be calculated in several ways. The number of moles is denoted by the n.

The formulars used to calculate moles of substances are as follows:

1. $n = \frac{\text{mass in grams (given)}}{\text{molar mass in g/mol}} = \frac{m}{Mm}$

2. $n = \text{molarity} \times \text{volume} = \text{mol/L} \times \text{L}$

3. $n = \frac{PV}{RT}$ where P = pressure of a gas
R = the gas constant
T = temperature of a gas
V = volume of a gas

To understand $n = \frac{m}{Mm}$, what is molar mass, or molecular weight?

MORE ON ROUNDING OFF AND SIGNIFICANT FIGURES, ACCURACY AND PRECISION.

- It is incorrect to round off sequentially.
- Intermediate rounding gives a significantly different result ~~than~~ that which can be obtained by rounding only at the end. Therefore, do not round off before the final answer is arrived at. Only round off at the end.
- When measuring quantities, more precise measurements should be taken so that more precise results may be obtained. Remember to measure a series of quantities to the same precision; do not use different precisions.

4. $n = \frac{It}{f}$ where I = current (A)
t = time (s)
f = faraday's constant ($96485\ C\,mol^{-1}$)

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Mole concept provides a simple mole to mole (mole – mole) relationship in the following chemical dimensions :

(i) Species in a molecular formular
(ii) Species in a chemical equation

Example : Balance the following chemical equation.

$$H_2 + O_2 \longrightarrow H_2O$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

This balanced equation shows the relationship of the reactants and product in terms of their respective number of moles.
Hence we can deduce the following important equation :

$$\frac{n_{H_2}}{2} = \frac{n_{O_2}}{1} = \frac{n_{H_2O}}{2}$$

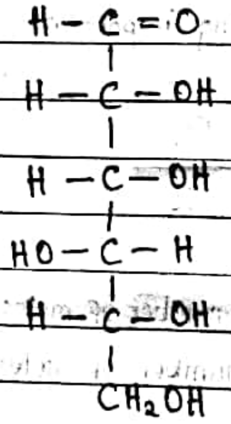
We can now be able to find out the number of moles of any chemical substance in a chemical equation given the number of moles or grams of another.

EMPIRICAL, MOLECULAR AND STRUCTURAL FORMULARS

The Empirical Formular (E.F) of a substance or compound or molecule shows the formular of a compound in its simplest ratio.
For example, the empirical formular (E.F) of glucose is CH_2O.

The Molecular Formular (M.F) of a substance, compound or molecule shows the actual number of atoms in a compound, molecule or substance.
For example, the molecular formular (M.F) is a compound glucose is $C_6H_{12}O$.

The Structural Formular (S.F) shows the actual arrangement of atoms in a compound.
For example, let us consider the compound glucose.



Determination of the Empirical and Molecular Formulars

One method of determining the empirical and molecular formulars of compounds

- The molecular formula for a substance is the real representation of how the atoms are arranged and their number in all.
- The empirical formular for a substance is the simplest representation of the atoms contained in that substance.

16 Example : Determine the E.M.F and M.F of the compound that gives the following percentages on analysis : 71.65% of Cl ; 24.28% of C and 4.07% of H. The molar mass is 98.96 g/mol.

Solution : E.M.F	Cl	C	H
	71.65	24.28	4.07
	$\frac{71.65}{35.5}$	$\frac{24.28}{12.01}$	$\frac{4.07}{1.008}$
	2.021	2.021	4.04
	$\frac{2.021}{2.021}$	$\frac{2.021}{2.021}$	$\frac{4.04}{2.021}$
	1	1	2

Therefore, the empirical formular is $ClCH_2$.

M.F ⇒ Calculate the molar mass of each of the element in the compound, $ClCH_2$.

$H = 1.008 \Rightarrow 1.008 \times 2 = 2.016$ g/mol

$Cl = 35.5 \Rightarrow 35.45 \times 1 = 35.45$ g/mol

$C = 12.01 \Rightarrow 12.01 \times 1 = 12.01$ g/mol

Then add the molar masses and finally divide it into the total molar mass of the compound $ClCH_2$.

$2.016 + 35.45 + 12.01$ = molar mass

49.476 g/mol = molar mass of E.F of $ClCH_2$.

98.96 g/mol / 49.476 g/mol = 2 = n

Therefore, $nClCH_2 \Rightarrow 2ClCH_2 \Rightarrow Cl_2C_2H_4$

Molecular Formular ⇒ $Cl_2C_2H_4$.

Example: Calculate the amount of water produced when 96g of oxygen gas reacts with 10.1g of hydrogen.

Solution:

$$O_{2(g)} + H_{2(g)} \longrightarrow H_2O_{(l)}$$

$$O_{2(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(l)}$$

$$n_{O_2} = \frac{96\,g}{32\,g/mol} = 3\text{ mols}$$

$$n_{H_2} = \frac{10.1\,g}{2.02\,g/mol} = 5\text{ mols}$$

$$\frac{n_{O_2}}{1} \qquad \frac{n_{H_2}}{2}$$

3 mols 2.5 mols

Therefore, hydrogen gas is the limiting reagent.

PERCENTAGE YIELD

Not all reactants will turn into products in a real life lab situation. What you get in the lab is the actual yield. What you calculate on paper is the theoretical yield.

$$\text{Percentage Yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

For example, if you only get 63g of H_2O, then percentage yield $= \frac{63}{90} \times 100$ which will give you 70%.

Que: Methanol (CH_3OH) also called methyl alcohol is the simplest alcohol. It is used as a fuel in race cars and is a potential replacement for gasoline. Methanol can be manufactured by combining gaseous carbon monoxide and hydrogen. Suppose 68.5kg $CO(g)$ is reacted with 8.60 kg $H_2(g)$. Calculate theoretical yield of methanol. If 3.57×10^4 g CH_3OH(methanol) is actually produced, what is the percent yield of methanol?

Ans: (a)

$$CH_3OH(g) \longrightarrow CO(g) + H_2(g)$$

$$CH_3OH(l) \longrightarrow CO(g) + 2H_2(g)$$

First we calculate, the limiting reactants of the two reactants.

$n = m/mm$ $\qquad$ $n_{co} = m/mm$

$n_{H_2} = 8.60 \times 1000/2$ $\qquad$ $n_{co} = 68.5 \times 1000/12+16$

$n_{H_2} = 8600/2$ $\qquad$ $n_{Co} = 68500/28$

$n_{H_2} = \underline{\underline{4300}}$ mol $\qquad$ $n_{Co} = \underline{\underline{2446.43}}$ mol

Mole – mole ratio of CO and H_2 = 1 : 2

$$\frac{1}{2} = \frac{2446.43}{4300} \qquad \frac{H_2}{\frac{4300}{2}} \qquad \frac{CO}{\frac{2446.43}{1}}$$

$$= \underline{\underline{2150}} \qquad \underline{\underline{2446.43}}$$

The limiting reactant was Hydrogen gas.

$$\underset{4g}{\underline{2H_2}} + CO \longrightarrow \underset{32g}{\underline{CH_3OH}}.$$

If $4g(H_2) \longrightarrow 32g$ of CH_3OH, What would $8.60\ kg\ (H_2)$ yield?

$$4g = 32g$$
$$1000 \times 8.60 = x$$
$$4x = 8600 \times 32$$
$$\frac{4x}{4} = \frac{275200}{4}$$
$$x = \underline{68{,}800g} \text{ or } \underline{6.8 \times 10^4 g}$$

(b) $\text{Percent Yield} = \frac{\text{actual}}{\text{theoretical}} \times 100\%$

$$\%\ \text{yield} = \frac{3.57 \times 10^4}{6.8 \times 10^4} \times 100\%$$
$$\%\ \text{yield} = 0.525 \times 100\%$$
$$\%\ \text{yield} = \underline{\underline{52.5\%}}$$

SOLUTION STOICHIOMETRY

Molarity is concentration in mol/L.
Molarity is the number of moles per litre of a solution.
The concentration of a diluted solution can be calculated using:

$$\underbrace{M_{initial} \times V_{initial}}_{n_{initial}} = \underbrace{M_{final} \times V_{final}}_{n_{final}}$$

However, the number of moles does not change when a solution is diluted i.e $n_{initial} = n_{final}$, therefore $M_i \times V_i = M_f \times V_f$

Que: Calculate the volume of 0.2M NaOH needed to make a diluted solution of concentration 0.04M and volume 30L.

Data: $M_1 = 0.2\,M$
$M_2 = 0.04\,M$
$V_2 = 30L$

$M_1 \times V_1 = M_2 \times V_2$
$0.2 \times V_1 = 0.04 \times 30$
$0.2 M V_1 = 0.04\ mol$
$V_1 = 0.04\ mol / 0.2\ mol/L$
$V_1 = 0.04/0.2\ L$
$V_1 = \underline{0.2}\ L \times 30$
$V_1 = \underline{\underline{6L}}$

REACTIONS IN SOLUTION

Acid - Base reactions happen between acid and bases. The definitions of an acid according to different pioneering scientists are as follows:

1. Bronsted - Lowry : An acid is a proton donor and a base is a proton acceptor. (H^+) proton.
2. Lewis : An acid is an electron acceptor, and a base is an electron donor.
3. Arrhenius :

$$\underset{acid}{HA} + \underset{base}{B} \rightleftharpoons A^- + HB^+$$

Rules for assigning oxidation numbers

Compound	Oxidation Number	Exception
1. Pure elements e.g Na(s), Al(s), Fe(s)	0	
2. Diatomic molecules or neutral molecules e.g $H_2(g)$ $O_2(g)$, $N_2(g)$, $CO_2(g)$	0	
3. Compounds e.g NaCl(s) $ZnSO_4(aq)$	0 the oxidation number is 0 for the whole compound.	
4. Monoatomic ions e.g Na^+, Ba^{2+}, Cl^-, Ca^{2+}, Al^{3+}	0 The oxidation number is equal to the charge on the ion. E.g $Na^+ = +1$, $Ba^{2+} = +2$; $Cl^- = -1$	
5. Polyatomic ions	0 The oxidation number is equal to the charge on the entire ion.	
6. F in compounds	-1 e.g HF	
7. Oxygen in compounds	-2	In a peroxide where it is -1 e.g H_2O_2
8. Hydrogen in compounds	+1	In a hydride (H^-) where it is -1 e.g NaH

Compound	Oxidation Number
9. Group One (1)	+1
Group Two (2)	+2
Group Three (3)	+3
10. Transitional Elements	Depends on the compound in which the element is found. Mn, Cr, Zn, Cu, Al;
11. Carbon in compounds	In the range +4 to −4

Balancing Redox - Reactions

There are two methods : 1. Oxidation numbers (Research)

2. Ion - electron method

Using the ion - electron method to balance in acidic media

Example : Balance the reaction below in acidic media.

$$Cr_2O_7^{2-}{}_{(aq)} + CH_3CH_2OH_{(aq)} \longrightarrow Cr^{3+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

NOTE : A Balanced equation for a chemical reaction indicates the substances present at the start of the reaction and those produced as the reaction proceeds. It provides no information, however, about how the reaction occurs. The process by which a reaction occurs is called the Reaction Mechanism.

Step 1 = Split the reaction into 2-half reactions

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

$$2(Cr) + 7(-2) = -2$$
$$2Cr - 14 = -2$$
$$\frac{2Cr}{2} = \frac{12}{2}$$
$$Cr = \underline{\underline{+6}} \Rightarrow \text{Reduction half-reaction}$$

We see here that Cr has been reduced from Cr^{6+} to Cr^{3+}.

$$CH_3CH_2OH \longrightarrow CO_2 + H_2O \Rightarrow \text{Oxidation reaction}$$

Step 2 = Balance all atoms except O and H

$$Cr_2O_{7(aq)}^{2-} \longrightarrow 2Cr^{3+}_{(aq)}$$

$$CH_3CH_2OH_{(aq)} \longrightarrow 2CO_{2(g)} + H_2O_{(l)}$$

Step 3 = Balance oxygen by adding H_2O on side with less O.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Step 4 = Balance H by adding H^+ on side with few H.

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$
$$CH_3CH_2OH + 3H_2O \longrightarrow 2CO_2 + 12H^+$$

Step 5 = Balance charges by adding electrons on the side with higher charge.

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

$$CH_3CH_2OH + 3H_2O \longrightarrow 2CO_2 + 12H^+$$

$$-2 + 14H^+ = 12H^+ + 6e^- \text{ ----- (i)}$$

$$0 = 12H^+$$

28 Balancing in Acidic Media and Basic Media.

Balancing in Basic Media

- Follow all steps as balancing in acidic media.
- Add OH^- equal to number of H^+ on both sides.
- $OH^- + H^+ = H_2O$. Subtract the extra water.

$$CH_3CH_2OH + 2Cr_2O_{7(aq)}^{2-} + 16H^+ + 16OH^- \longrightarrow 2CO_2 + 4Cr^{3+} + 11H_2O.$$

$$+16OH^-$$

$$CH_3CH_2OH + 2Cr_2O_{7(aq)}^{2-} + 16H_2O \longrightarrow 2CO_2 + 4Cr^{3+} + 11H_2O + 16OH^-$$

$$-11H_2O \qquad\qquad -11H_2O$$

$$CH_3CH_2OH + 2Cr_2O_{7(aq)}^{2-} + 5H_2O \longrightarrow 2CO_2 + 4Cr^{3+} + 16OH^-$$

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GAS STOICHIOMETRY

Characterists of gases are as follows:

(i) highly compressible
(ii) thermally expandable
(iii) low viscosity
(iv) have relatively low density
(v) no fixed shape or volume

Measuring Pressure

Gases exert pressure on the walls of the container. Pressure can be measured using a barometer.

The Gas Laws

1. BOYLE'S LAW

Provided that the temperature is kept constant, the volume of a gas is inversely proportional to its pressure.

$$P_1 V_1 = P_2 V_2$$

Question : A gas at 2 atm is compressed from 0.8 L to 0.5 L. Calculate the new pressure (assuming the temperature is kept constant).

Answer : Boyle's Law ; $P_1 = 2\text{atm}$, $V_1 = 0.8\text{L}$, $V_2 = 0.5\text{L}$, $P_2 = ?$

$$P_2 = \frac{P_1 V_1}{V_2} \Rightarrow P_2 = \frac{2\text{atm} \times 0.8\text{L}}{0.5\text{L}}$$

$$P_2 = \frac{1.6\ \text{atm L}}{0.5\ \text{L}} \Rightarrow P_2 = 3.2\ \text{atm.}$$

2. CHARLE'S LAW

At constant pressure, volume of a gas is directly proportional to the temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Example : A gas of volume 3.8 L at 50°C is heated to 80°C. What will be its volume at this temperature?

Solution: $V_1 = 3.8\ L$

$T_1 = 50^\circ C$

$T_2 = 80^\circ C$

$T_1 = 323.15\ K$

$T_2 = 353.15\ K$

$V_2 = ?$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{3.8\ L}{323.15\ K} = \frac{V_2}{353.15\ K}$$

$$V_2 \times 323.15K = 3.8L \times 353.15K$$

$$\frac{V_2\,(\cancel{323.15K})}{\cancel{323.15K}} = \frac{1341.97\ L\cancel{K}}{323.15\cancel{K}}$$

$$V_2 = 4.152777348\ L$$

$$V_2 = 4.2\ L$$

NOTE : The temperature should be converted to the Kelvin scale always.

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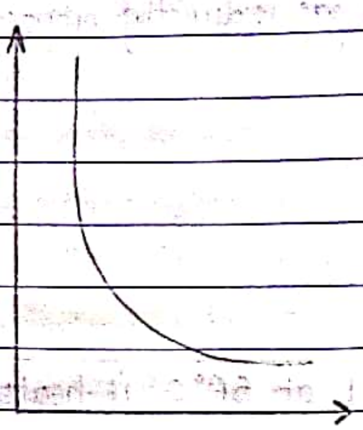
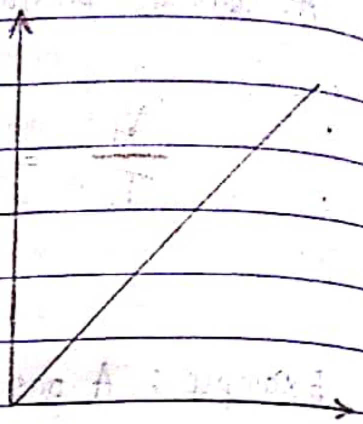
Boyle's Law Graphs





3. GAY - LUSSAC'S LAW

At constant volume, the pressure of a gas is directly proportional to its temperature.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

4. AVOGADRO'S LAW

Equal volumes of gases at the same temperature has equal number of particles (moles).

$V = an$; where V = volume
a = constant
n = number of moles

5. THE IDEAL GAS LAW

An ideal gas is a gas that follows Boyle's Law.
All the four gas laws can be combined to form one law called the Ideal Gas Law.

$PV = nRT$, where P = pressure , R = gas constant
V = volume , T = temperature
n = number of moles

The gas constant is 0.08206 $L \cdot atm \cdot mol^{-1} \cdot K^{-1}$. When the pressure is measured in torr, the gas constant becomes equal to 62.364 $L \cdot torr \cdot mol^{-1} \cdot K^{-1}$.

GAS STOICHIOMETRY

The molar volume of a gas at standard temperature and pressure (s.t.p) can be calculated using the formular : $PV = nRT$. The conditions at s.t.p are 1 atm and 0°C.

Example : Calculate the volume of 1 mol of a gas at s.t.p.

Solution: $PV = nRT$

$$\boxed{K = {}^{\circ}C + 273.15}$$

$$V = nRT / P$$

$$V = \frac{1 \times 0.08206 \times 273.15}{1}$$

$K = 0°C + 273.15$
$K = 273.15$
$\therefore 0°C = 273.15\,K$

$$V = \frac{1\,\cancel{mol} \times 0.08206\,L \cdot \cancel{atm} \cdot \cancel{mol^{-1}} \cdot \cancel{K^{-1}} \times 273.15\,\cancel{K}}{1\,\cancel{atm}}$$

$$V = 0.08206\,L \times 273.15$$

$$V = 22.414689\,L$$

$$V = 22.4\,L$$

Thus, one mole of any gas at standard room temperature and pressure (s.t.p) occupies 22.4 L.

33 Dalton's Law of Partial Pressures

Partial pressure (P.P) refers to the pressure exerted by an individual gas in a mixture of gases, or P.P is the pressure that a gas would exert if it occupied a container alone. Adding up all P.Ps gives the total pressure : P(total) = $P.P_1 + P.P_2 + P.P_3$ + e.t.c

$$P(total) = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \text{e.t.c}$$

$$P(total) = \frac{nRT}{V}$$

$$P.P_1 = \frac{\text{number of mols of gas 1}}{\text{total number of mols of all gases}} \times \text{Total pressure}$$

$P.P_1$ = mole fraction, x total pressure.

Example : 46 L of helium and 12 L of oxygen both at 25°C and 1 atm are pumped into a 5 L container at 25°C. Calculate the partial pressures and the total pressure exerted by the two gases.

Answer : $PV = nRT$

$$P = \frac{nRT}{V}$$

$$n = \frac{PV}{RT}$$

$$n = \frac{1\,\text{atm} \times 46\,\cancel{L}}{0.08206\,\cancel{L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\cancel{K^{-1}} \times 298\,\cancel{K}}$$

Collecting a gas over water

Dalton's law of P.P is useful when a gas is collected by displacement of water. Since the gas is bubbled through water, the total pressure of the wet gas is the sum of P.P of the gas and the vapour pressure (P.P of water vapour).

Example : A sample of solid potassium chlorate ($KClO_3$) was heated in a test-tube and decomposed as follows

$$2KClO_3 \qquad 2KCl + 3O_2$$

The oxygen was collected by displacement of water at 22°C and the total pressure of 754 torr. Calculate the P.P of oxygen gas and mass of potassium chlorate, given that the total volume of gas was 0.650L and vapour pressure of water at 22°C is 21 torr.

Solution : Total pressure = 754 torr at 22°C
Vapour pressure = 21 torr at 22°C

Total Pressure of wet gas = P.P of O_2 + P.P of H_2O (water) (vapour pressure)

$$\text{P.P of } O_2 = 754 \text{ torr} - 21 \text{ torr}$$
$$= 733 \text{ torr}$$

Molar Mass of Gases

The molar mass of a gas can be measured in the lab.

The procedure is as follows:
A flask is weighed, liquid is added to it and then it is heated in a water bath. The liquid soon fills the volume of the flask and the pressure is determined. Finally, the flask is cooled and measured again.

$$n = \text{mass} / \text{molar mass} = PV/RT$$

$$\text{mass}/\text{molar mass} = PV/RT$$

$$\text{molar mass} = \text{mass} \times RT / PV$$

$$\text{molar mass} = \frac{\text{mass} \times RT}{P \times V}$$

$$\text{molar mass} = \frac{\text{mass} \times RT}{V \times P}$$

$$\text{molar mass} = \text{density} \times \frac{RT}{P}$$

$$\boxed{\text{molar mass} = \frac{\text{density}\, RT}{P}}$$

Kinetic Molecular Theory of Gases

(i) Gases are made of particles called molecules.

(ii) These molecules are in constant motion.

(iii) Molecules collide with each other and with the walls of the container.

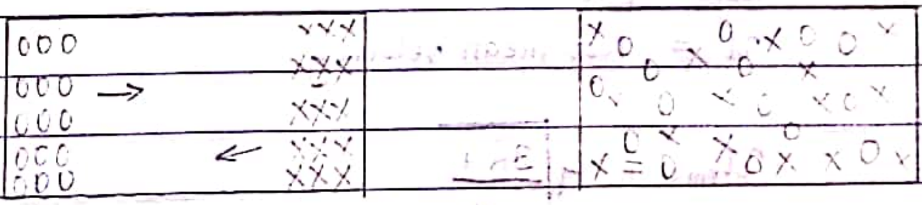
(iv) Molecules do not attract each other.

(v) Average kinetic energy is directly proportional to temperature.

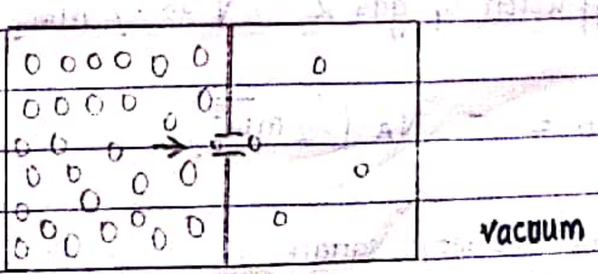
Diffusion and Effusion

Diffusion describes the movement of molecules from a place of high concentration to low concentration.

When two or more gases diffuse, they mix without forming a new compound



Effusion describes the passage (passing) of gas molecules through a tiny opening and into a vaccum.



* When gas molecules collide with each other, they do not lose energy.

The rate of effusion is the speed at which the gas travels through the hole to the vaccum.

Graham's Law of Effusion

The rate of effusion is inversely proportional to the square root of the mass of the particle (or density or molar mass).

$$\frac{\text{Rate of effusion of gas 1}}{\text{Rate of effusion of gas 2}} \quad \frac{\sqrt{M_{m_2}}}{\sqrt{M_{m_1}}} \quad \frac{t_2}{t_1}$$

Rate of effusion is also inversely proportional to time.

$$K.E = \frac{1}{2}mv^2$$

$$K.E = \frac{1}{2}mu^2$$, where u = mean velocity

$$u = \sqrt{u^2}$$

u = root mean velocity

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

$$\frac{\text{Rate of effusion of gas 1}}{\text{Rate of effusion of gas 2}} \quad \frac{\sqrt{3RT/M_{m_1}}}{\sqrt{3RT/M_{m_2}}}$$

$$\text{Average } K.E = N_A\left(\frac{1}{2}m\overline{u^2}\right)$$

Que: Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C.

40 $T = 25°C + 273.15 = 298.15\ K$

$R = 8.3145\ J/K \cdot mol$

$n = mass/mm$

$mass = n \times mm$

$mass = 1 \times 4$

mass = 4 grams of He in 1 mole, or 0.004 kg in 1 mole of He.

$mass = 4.00 \times 10^{-3}\ kg/mol$

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

$u_{rms} = \sqrt{(3 \times 8.3145 \times 298.15)/4.00 \times 10^{-3}}$

$u_{rms} = 1.36 \times 10^{3}\ m/s.$

NOTE: Here, $R = 8.3145\ J/K \cdot mol$, <u>not</u> $0.08206\ atm \cdot L \cdot mol^{-1} \cdot K^{-1}$.

QUANTUM MECHANICS

41 ATOMIC STRUCTURE AND PERIODICITY

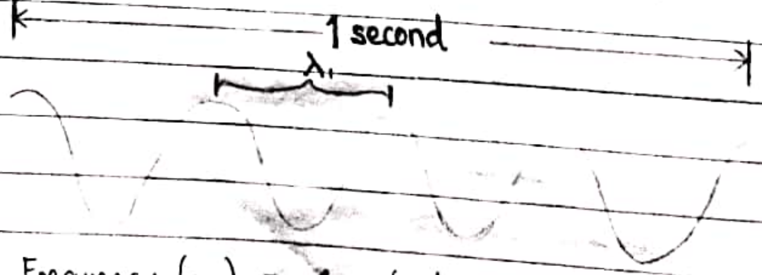
ELECTROMAGNETIC RADIATION

One of the ways that energy travels through space is by electromagnetic radiation. The light from the sun, the energy used to cook food in a microwave oven, the x-rays used by the dentists, and the radiant hea from a fireplace are all examples of electromagnetic radiation. Althou these forms of radiant energy seem quite different, they all exhibit the same type of wavelike behaviour and travel at the speed of light in a vacaum.

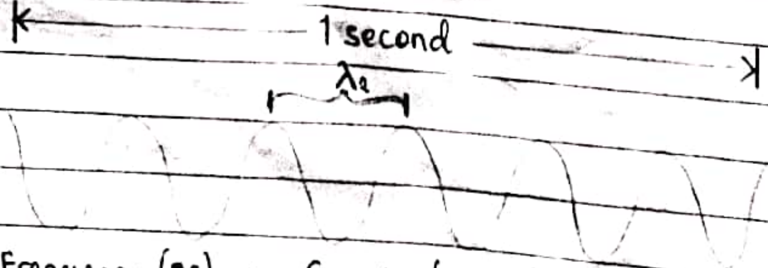
Waves have three primary characteristies: wavelength, frequency, and speed.

- Wavelength is the distance between two consecutive peaks or troughs in a wave. It is symbolized by the greek letter lambda (λ).
- Frequency is defined as the number of waves or cycles per second that pass a given point in space. It is symbolized by another greek letter nu (ν)

Since all types of electromagnetic radiation travel at the speed of light, short wavelength radiation must have a high frequency.



Frequency (ν) = 4 cycles/second = 4 Hertz



Frequency (ν) = 6 cycles/seconds = 6 Hertz

The wave with the shortest wavelength (λ_2) has the highest frequency and the wave with the longest wavelength (λ_1) has the lowest frequency. This implies an inverse relationship between wavelength and frequency that is : $\lambda \propto 1/\nu$.

Or $\lambda \propto 1/\nu \Rightarrow \lambda\nu = c$ where λ is the wavelength in meters (m)
ν is the frequency in cycles per second
and c is the speed of light.

- The speed of light (c) is 2.9979×10^{8} m/s.

The energy from the sun reaches the earth mainly in the form of visible and ultraviolet radiation, whereas the glowing coals of a fireplace transmits heat energy by infrared radiation.
In a microwave oven the water molecules absorb microwave radiation in the food, which increases their motions. This energy is then transferred to other types of molecules via collisions, causing an increase in the food's temperature.

NOTE • Electromagnetic radiation does not need or use a medium as opposed to the other forms of heat or energy transfer that require a medium, e.g conduction and convection.

Example : The brilliant red colours seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as $Sr(NO_3)_2$ and $SrCO_3$ are heated. Calculate the frequency of red light of wavelength 6.50×10^{2} nm.

Solution : We can convert wavelength to frequency using the equation :

$\lambda\nu = c$

$\nu = c/\lambda$

$\nu = 2.9979 \times 10^{8} / 6.50 \times 10^{2}$ nm

$\nu = 2.9979 \times 10^{8} / 6.50 \times 10^{2}\ \cancel{nm} \times 10^{-}$[illegible]m/1[illegible]$\cancel{nm}$

$\nu = 4.612153846 \times 10^{14}$ sec

$\nu = 4.61 \times 10^{14}$ Hz

Max Plank (1858 – 1947) when studying the radiation profiles emitted solid bodies heated to incandescence found that the results could not be explained in terms of the physics of his day which held that matter could absorb or emit any quantity of energy.
Planck accounted for these observations only by postulating that energy c be gained or lost only in whole-number multiples of the quantity $h\nu$, where h is a constant called Planck's constant.

Planck's Constant = 6.626×10^{-34} J.S.

Therefore, the change in energy for a system (ΔE) can be represented by the following equation: $\Delta E = nh\nu$ where n is an integer (1,2,3,...
h is Planck's constant and
ν is the frequency of the electromagnetic radiation that is absorbed or emitted.

- Energy of matter only occurs in discrete units of size $h\nu$, and each of these small packets of energy is called a Quantum.
  Any system can transfer energy only in whole quanta, and hence it is clear that energy can and is in fact quantized. Thus energy has particulate properties.

The energy of a Photon: The blue colour of fireworks is often achieved by heating copper(I) chloride ($CuCl$) to about 1200°C. Then the compound emitts blue light having a wavelength of 450nm. What is the increment of energy (quantum) that is emitted at 4.50×10^2 nm by $CuCl$?

Solution : The quantum energy can be calculated from the equation :

$\Delta E = nh\nu$ $\qquad$ $h = 6.626 \times 10^{-34}$ J·s

$\Delta E = h\nu$ $\qquad$ $\nu = c/\lambda$

$\nu = 2.9979 \times 10^{8} / 4.50 \times 10^{2} \times 1/10^{9}$

$\Delta E = h\nu$ $\qquad$ $\nu = 2.9979 \times 10^{8} / 4.5 \times 10^{7}$

$\Delta E = 6.626 \times 10^{-34} \times 6.662 \times 10^{14}$ $\qquad$ $\nu = 6.662 \times 10^{14}$ Hertz.

$\Delta E = 4.4142412 \times 10^{-19}$ J

A sample of CuCl emitting light at 450nm can lose energy only in increaments of $4.4142412 \times 10^{-19}$ J, the size of the quantum in this case.

- Electromagnetic radiation can be viewed as a stream of "particles" called Photons. The energy of each photon is given by the expression

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

, where ν is the frequency of radiation,
h is Planck's constant
λ is the wavelength

- In other words, electromagnetic radiation is a stream of photons or particles of light or small chunks of energy.
- The energy of a photon of electromagnetic radiation is directly proportional to the radiation's frequency.

$$E = h\nu$$

NOTE • The equation of the above statement has the left-hand side that deals with properties of energy whilst the right-hand side deals with wave properties.

THE PHOTOELECTRIC EFFECT

The photoelectric effect refers to the phenomenon in which electrons are emitted from a surface of a metal when light strikes it. The following observations characterize the photoelectric effect:

1. Studies in which the frequency of the light is varied show that no electrons are emitted by a given metal below a specific threshold frequen ν_0.

2. For light with frequency lower than the threshold frequency, no electr are emitted regardless of the intensity of the light.

3. For light with frequency greater than the threshold frequency, the number of electrons emitted increases with the intensity of the light.

4. For light with frequency greater than the threshold frequency, the kinetic energy of the emitted electrons increases linearly with the frequency of the light.

- The threshold frequency is the minimum energy required to remove the electron from the metal surface.
- Therefore, minimum energy required to remove an electron $= E_0 = h\nu_0$.
- Electrons that are emitted are known as Photoelectrons.

Electromagnetic radiation is quantized (consists of photons). Because a photon with energy less than E_0 ($\nu < \nu_0$) cannot remove an electron, light with a frequency less than the threshold frequency produces no electrons.

- The energy in excess of that required to remove the electron is given to the electron as kinetic energy (KE):

$$KE_{electron} = \frac{1}{2}\underset{\substack{\uparrow\\\text{mass of}\\\text{electron}}}{m_e}\underset{\substack{\uparrow\\\text{velocity}\\\text{of electron}}}{v}^2 = \underset{\substack{\uparrow\\\text{energy of}\\\text{incident proton}}}{h\nu} - \underset{\substack{\uparrow\\\text{Energy required}\\\text{to remove electron}\\\text{from metal surface}}}{h\nu_0}$$

QUANTUM MECHANICAL MODEL OF ATOM

- Schrodinger worked on the wave nature of electrons (wave equation).
- The wave equation describes the wave pattern of an electron.

Ψ = si

$$H\Psi = E\Psi$$

H = set of mathematical operations
Ψ = wave function (orbital)
E = total energy

- Ψ^2 (square of the wave function) is the probability density of electrons that is, if an electron cannot be found Ψ^2 is used to locate or find it.
- An orbital is a region of space where there is a higher possibility of finding an electron.
- Ψ depends on x, y and z coordinates because it is three-dimensional.
- The radial part is the distance of the electron's position from the nucleus.
- The angular part is also necessary and very important, as well as two other components.
- In order to solve the Schrodinger equation, we need three integers, which are also called quantum numbers, namely, n, ℓ and m_ℓ.

$$\Psi_{(x,y,z)} = \Psi(\gamma)_{n,\ell} \quad \Psi_{\ell,m_\ell}(\sigma, \phi)$$

- $\Psi^2 \quad (\Psi_{n,\ell}(\gamma))^2 \; 4\pi r^2 dr$ = RDF (Radial Distributive Function).

NOTE: KE = eV ; where e = charge of electron
V = voltage given

NOTE: The photoelectric effect is only seen if the photon energy (E) exceeds the binding energy of the electron in the metal.

47 Relation Between Quantum Numbers And Atomic Orbitals.

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Design
1	0	0	1	1s
2	0	0	1	2s
	1	-1, 0, 1	3	$2p_x, 2p_y, 2p$
3	0	0	1	3s
	1	-1, 0, 1	3	$3p_x, 3p_y, 3p$
	2	-2, -1, 0, 1, 2	5	$3d_{xz}, 3d_{xy}, 3_{z^2}, 3_x$

Note: An 's' subshell has only 1 orbital, a 'p' subshell has three (3 orbitals and a 'd' subshell has five (5) orbitals.

- Electrons can only gain energy equal to the difference between high and lower orbitals, and therefore move to the higher orbital, which known as Arbsorption.
- When an electron falls from higher state to lower state, energy is emitted, which is known as Emission.
- Bohr came up with an equation that describes the energy of an elect in the atom:

$$E = -\frac{b}{n^2}, \text{ where } b = \text{a constant } 2.18 \times 10^{-18}\,J$$

$$E = -2.18 \times 10^{-18}\,J \left(\frac{Z^2}{n^2}\right)$$

The negative sign indicates that the energy of an electron bound to th nucleus is lower than that of an electron at infinite distance. Energy of an electron in any orbital is negative relative to this state.

$$E = -2.18 \times 10^{-18}\,J \frac{1}{\infty^2} = 0 \quad (\text{for a hydrogen atom})$$

NOTE • $E = -b\left(\frac{Z^2}{n^2}\right)$, where Z = atomic number of the element and n the energy-level occupied by the electron of that elem

SHELLS AND SUBSHELLS

- Electrons in the atoms of all other elements occupy energy levels.
- The energy level nearest to the nucleus is the lowest in energy.
- Each successive level out from the nucleus is higher in energy and has a progressively higher capacity for electrons.
- Each principal energy level, also known as a shell, has one or more subshells.
- The subshells found in the known elements are labelled in order of increasing energy.

$$s < p < d < f$$

increasing energy

- For each shell, the number of subshells is equal to the value of its quantum number, n. Thus, the first shell ($n = 1$) has an 's' subshell. The second shell ($n = 2$) has two subshells, an 's' and a 'p'. The third shell ($n = 3$) has three subshells, an 's', 'p' and a 'd', and the fourth shell ($n = 4$) has four subshells, an 's', 'p', 'd' and an 'f'.
- Each type of subshell has a different electron capacity.

The table below shows how the total electron capacity of the first four shells is distributed among the subshells.

Shell	1	2		3			4			
Subshell	s	s	p	s	p	d	s	p	d	f
Subshell capacity	2	2	6	2	6	10	2	6	10	14
Shell capacity	2	8		18			32			

- The subshell defines the shape of a particular orbital.
- The shell defines the distance from the nucleus of the highest electron probability.

ORBITALS

- A subshell is composed of one or more orbitals. An orbital is the region of space where there is the highest probability of finding a particular elec
- Each orbital can hold two electrons.
- An 's' subshell is composed of one orbital. Thus, being composed of one orbital, an 's' subshell has a capacity of two electrons.
- A 'p' subshell is composed of three orbitals. So it has a capacity of six electrons, two per obital.
- A 'd' subshell is composed of five orbitals. So it has a capacity of ten electrons, two per orbital.
- An 'f' subshell is composed of seven orbitals.

- Consider the third shell (n = 3). It is composed of three subshells (s, p and d). The 18-electron capacity is distributed as follows: two in the one 's' orbital, six in the three 'p' orbitals, and ten in the five 'd' orbitals.

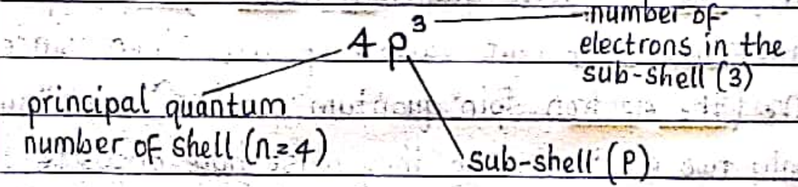
* - The energy of an electron is determined only by the shell and subshell, under normal conditions, therefore the following point follows:

* All of the three different orbitals in a given 'p' subshell (e.g the 3p) have the same energy.

- Each type of orbital (s, p, d, or f) has a particular shape.
- The 'shape' refers to the dimensions of the region of highest probability of finding the particular electron or electrons.
- The electron does not orbit the nucleus in some designated path within the orbital. It just exists within that region.
- For the hydrogen atom, the energy of a particular orbital is determined by its value of n. Thus all orbitals with the same value of n have the same energy — they are said to be degenerate.
- Hydrogen's single electron can occupy any of its atomic orbitals.
- For each successive subshell, there is an increment of two (2) more orbitals. In other words, the 's' subshell has only one orbital, whereas the 'p' subshell has three orbitals and the 'd' subshell has five orbitals and so on

ELECTRON CONFIGURATION

- All electrons in an atom can be assigned to a specific shell and a specific subshell.
- Electron configuration is the designation of all of the electrons in an atom into specific shells and subshells.
- The Aufbau Principle states that electrons will go into the shells and subshells of the lowest energy.
- A shell is designated by the principal quantum number (n), the sub-shell by the appropriate letter, and the number of electrons in that sub-shell by the appropriate superscript number.
- The existence of three electrons in the 'p' subshell of the fourth shell (n = 4) is shown as :



* - We always begin with the ground state of the one electron in the simplest and first element, hydrogen.

The electron is in the n = 1 shell, which has an s subshell. The electron configuration for Hydrogen (H) is then : $1s^1$

Next comes Helium which has two electrons. The 1s subshell has a capacity of two electrons, so Helium (He) has the configuration : $1s^2$.

Next comes Lithium with three electrons. The first two fill the first shell, but the third is assigned to the second shell (n = 2). The second shell has two subshells, the 'S' and 'p', but the lower in energy is the 'S' subshell, so it fills first (Aufbau's principle). The next element is Be. Its four electrons are also assigned to the 1s and 2s subshells. The electron configurations of Li and Be are :

Li $1s^2 2s^1$ and Be $1s^2 2s^2$

- De Broglie's equation allows us to calculate the wavelength for a particle.

$\lambda = h/mv$, where h = Planck's constant (6.626×10^{-34})
m = mass
v = velocity
λ = wavelength.

ELECTRON SPIN AND THE PAULI PRINCIPLE

- The Pauli Principle states that : In a given atom no two electro can have the same set of four quantum numbers $(n, l, m_l$, and m It is also called the Pauli Exclusion Principle.
- Since electrons in the same orbital have the same values of n (the principal quantum number), L (the angular momentum quantum number) and m_l (the magnetic quantum number), this postulate says that they must have different values of m_s. Then, since only two values of m_s (the electron spin quantum number) are allowed, an orbital can hold only two electrons, and they must have opposite spins.
- Polyelectronic atoms are atoms with more than one electron.
- The difficulty of dealing with repulsions between electrons in polyelectronic atoms since the electron pathways are unknown is called the electronic correlation problem, or simply the electron correlation proble
- The electron correlation problem occurs with all polyelectronic atoms.

- For example, consider the sodium atom, which has 11 electrons. Now let's single out the outermost electron and consider the forces this elect feels. The electron is clearly attracted to the highly charged nucleus. However, the electron also feels the repulsions caused by the other 10 elec The net, or overall, effect is that the electron is not bound nearly as tightly to the nucleus as it would be if the other electrons were not prese

Important! We say that the electron is screened or shielded from the nuclear charg by the repulsions of the other electrons.

Important! • The region between the nucleus and the outermost shell's electron, or simply the outermost electron, is called the Core.

- The difference between the sizes and energies of orbitals of polyelectronic atoms is because of the interplay between nuclear attractions and the electronic repulsions.
- For hydrogen, all orbitals in a given principal quantum level have the same energy and are therefore said to be degenerate.
- However, for polyelectronic atoms, for a given principal quantum level, the orbitals vary in energy as follows:

$$E_{ns} < E_{np} < E_{nd} < E_{nf} < E_{ng} < E_{nh}$$

In other words, when electrons are placed in a particular quantum level, they prefer the orbitals in the order s, p, d and then f.

- The Penetration Effect is the tendency of an orbital electron, e.g an electron in the 2s orbital, to spend a small but very significant time amount very near the nucleus than other electrons in the other orbitals, e.g electrons in a 2p orbital.

In other words, the penetration effect causes an electron to be attracted to the nucleus more strongly than an electron in a different higher energy orbital.

Important!
- And, in general, the more effectively an orbital allows its electron to penetrate the shielding electrons to be closer to the nuclear charge, the lower is the energy of that orbital.

For example, the relative energies of the orbitals for $n = 3$ are as follows:

$$E_{3s} < E_{3p} < E_{3d}$$

NOTE: Another statement of the Pauli Exclusion Principle says that no two electrons can have the same spin in the same orbital.

ORBITAL DIAGRAMS

- The orbital diagram of an element represents the orbitals in a subshel as boxes and its electrons as arrows. The spin of an electron is indica by the direction of the arrow pointing either up or down.
- Two electrons with opposite spins in the same orbital are said to be paired. Thus a doubly occupied orbital is represented as follows:

$\boxed{\uparrow\downarrow}$

- We can expand on the electron configuration of the first five elements by including their orbital diagrams.

	1s	2s	2p
H	↑		
He	↑↓		
Li	↑↓	↑	
Be	↑↓	↑↓	
B	↑↓	↑↓	↑

- However, we need to consider the placement of the sixth electron in carbo There are three possibilities. Does it pair with the first 2p electron in the same orbital, have opposite spin in a different orbital, or go into a different orbital with the same spin?
- We have one more rule to guide us. Hund's rule states that electr occupy separate orbitals in the same subshell with parallel spins. Since electrons have the same charge, they will repel each other to differe regions of space. Electrons "want their space" so they prefer separate orbitals rather than pairing in the same orbital.
- Pairing only occurs when separate empty orbitals in the same subshell are not available.
- With Hund's rule, the orbital diagrams for C, N, O, F and Ne ca be written.

	1s	2s	2p		
C	↑↓	↑↓	↑	↑	
N	↑↓	↑↓	↑	↑	↑
O	↑↓	↑↓	↑↓	↑	↑
F	↑↓	↑↓	↑↓	↑↓	↑
Ne	↑↓	↑↓	↑↓	↑↓	↑↓

- A similar phenomenon occurs with elements that have electrons occupying d or f orbitals. For example, Mn (#25) has the following electron configuration and orbital diagram.

$Mn = [Ar]\ 4s^2 3d^5$ $\qquad$ [Ar] 4s: [↑↓] $\quad$ 3d: [↑] [↑] [↑] [↑] [↑]

- Orbital diagrams are also relevant to the types of bonds that a particular element forms.

ELECTRON CONFIGURATION AND THE PERIODIC TABLE

- Electrons beyond the last noble gas are the ones commonly involved in the formation of chemical bonds.

- General configuration : $[NG]\ ns^1$

Special configuration for potassium (K) : $[Ar]\ 4s^1$

Representative Elements : $[NG]\ ns^x np^y$

1. $[NG]\ ns^1$: Except for hydrogen, these are the alkali metals. All have one electron beyond a noble gas configuration.

2. $[NG]\ ns^2$: These are Alkaline Earth metals. All have two electrons beyond a noble gas.

3. $[NG]\ ns^2 np^1$: The p subshell begins at 2p for B through Ne, and each p subshell is numbered consecutively down the table.

E.g. $In = [Kr]\ 5s^2 4d^{10} 5p^1$

The fourth and fifth period elements Ga (#31) and In (#49) also have filled d subshells beyond the noble gas configuration. In the sixth period, Tl (#81) has a filled 6d and 4f beyond the noble gas

4. $[NG]\ ns^2np^2$

5. $[NG]\ ns^2np^3$

6. $[NG]\ ns^2np^4$: These elements are known as the Chalcogens. They are all nonmetals except for Polonium (Po).

7. $[NG]\ ns^2np^5$: These elements are known as the Halogens. The halogens are all nonmetals and one electron short of having a noble gas configuration.

8. Noble Gases $[NG]\ ns^2np^6$: The noble gas elements are significant because they rarely form chemical bonds. These elements have full outer s and p sub-shells except for He, which has a full S subshell.

Transition Metals : $[NG]\ ns^2(n-1)d^x$, also called the D-block. Group IIIB begins the filling of a d subshell. There are some exceptions to the normal order of filling in this group. Group VIB has the configuration $[NG]\ ns^1(n-1)d^5$, and group IB has the configuration $[NG]\ ns^1(n-1)d^{10}$. It is assumed that Unq (#104) through the last element (#109) have filled 5f subshells, although little experimental information confirms this at present. The first element, Sc, begins the filling of the 3d subshell. Each d subshell is numbered consequetively beginning with 3 at the top. Hf (#42) through Hg (#80) also have filled 4f subshell.

Inner Transition Metals : $[NG]\ ns^2(n-1)d^1(n-2)f^x$

These are two series of inner transition elements : the Lanthanides, which have the general configuration $[Xe]\ 6s^2 5d^1 4f^x$; and the Actinides, which have the general configuration $[Rn]\ 7s^2 6d^1 5f^x$.

Either Lanthanum or Lutetium and Actinium or Lawrencium belong to the "d-block" and has n = 5, not n = 4 as for the "f-block," and n = 6, not n = 5 as for the "f-block", respectively.

QUANTUM NUMBERS

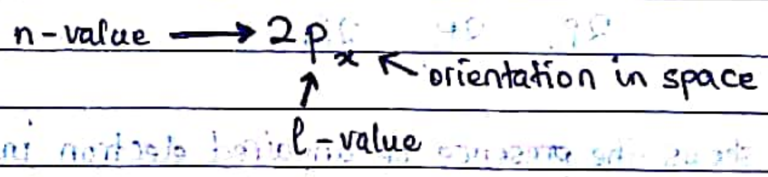
Quantum numbers describe the various properties of an orbital.

NOTE: The principal quantum number (n) has integral values: 1, 2, 3 and is related to the size and energy of the orbital.

NOTE: The angular momentum quantum number (l) has integral values from 0 to n-1 for each value of n, and it is related to the shape of atomic orbitals. The value of l for a particular orbital is commonly assigned a letter: $l = 0$ and is called 'S', $l = 1$ is 'p', $l = 2$ is called 'd' and $l = 3$ is called 'f'.

NOTE: The magnetic quantum number (m_l) has integral values of between l and $-l$, including 0 (zero). The value of m_l is related to the orientation of the orbital in space relative to other orbitals in the atom.

NOTE: A set of orbitals is sometimes called a subshell, and is designated by giving a value of n and the letter for l. Thus an orbital where $n = 2$ and $l = 1$ is symbolised as 2p. There are 3 (three) 2p orbitals, which have different orientations in space.



Que: For principal quantum level $n = 5$, determine the number of allowed subshells (different values of l), and give the designation of each.

Solution: For $n = 5$, the allowed values of l are 0, 1, 2, 3, 4 because $n-1 \Rightarrow 5-1 = 4$. Thus the subshells and their designations are:

$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
5s	5p	5d	5f	5g

NOTE: The 'p' orbitals are not spherical like 'S' orbitals but have two lobes separated by a node at the nucleus. The p orbitals are labelled according to the axis of the xyz coordinate system along which the lobes lie. For example, the 2p orbital with lobes centered along the x-axis is called the $2p_x$ orbital.

PARAMAGNETISM AND DIAMAGNETISM

The number of unpaired electrons in an atom, ion or molecule determine th magnetic properties of the substance. The substances that contain unpair electrons are called Paramagnetic and substances that contain all paired electrons are called Diamagnetic. In a lithium (Li) atom one unpaired electron is present in 2s orbital and it is therefore paramagnetic. The electron configuration of Beryllium ($z = 4$) is $1s^2 2s^2$ and its orbital diagram is $\boxed{\uparrow\downarrow}(1s^2)$, $\boxed{\uparrow\downarrow}(2s^2)$.

In Beryllium, all four electrons are paired and therefore, it is diamagnetic.

The element boron ($z = 5$) has five electrons. Two electrons with opposite spins occupy the 1s orbital, another pair of electrons occupy the 2s orbital and the fifth electron is present in a 2p orbital. The 2p subshell consists of three orbitals. The electronic configuration of boron is as follows :- $1s^2 2s^2 2p^1$, and the orbital diagram is also as follows:

↑↓	↑↓	↑		
$1s^2$	$2s^2$	$2p_x$	$2p_y$	$2p_z$

The diagram above shows the presence of unpaired electron in Boron and it is therefore paramagnetic.

The electron configuration of carbon ($z = 6$) can be followed from Boron by an indication of an additional electron.

NOTE:- Hund's Rule states that the most stable configuration or arrangement of electrons in a subshell is one with the maximum number of parallel spins or altenatively electrons must occupy all the orbitals of a given subshell singlely before pairing starts.

PERIODIC TRENDS

- The layout of the periodic table gives valuable information about the elements : chemical and physical e.t.c
- The vertical columns are known as groups. Elements in the same group have the same configuration in the valence shell (outermost shell) : Group I $[X]ns^1$, Group II $[X]ns^2$.
- The horizontal rows are called periods. There are seven periods each representing quantum numbers $n = 1 \longrightarrow n = 7$.
- Each period is filled more or less sequentially. The period an element is in tells the highest shell occupied.

Valence Electrons

- The electrons in the most outer shell or principal quantum level of an atom are called Valence electrons.
  $1s^2 2s^2 2p^6$ (valence electrons = 8)
- The elements in the same group have the same valence electron configuration.

- $H = 1s^1$ we see here that what changes is the principal
  $Li = 2s^1$ quantum number (n) : 1 for H and 2 for Li.

Effective Nuclear Charge

Properties of elements are affected by the amount of positive charge experienced by the outer electrons.

The positive charge is always less than the ~~nucl~~ full nuclear charge (except for hydrogen)

The negative charge of the inner electrons partially offset (neutralise) the positive charge of the nucleus.

The effective nuclear charge is determined by the difference between the charge of the nucleus and the charge of the core.

Example of the effective nuclear charge

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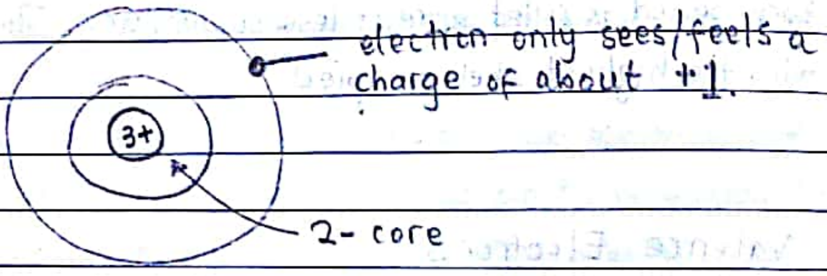
- Li $1s^2 2s^1$
- ($1s^2$) core lies below the valence electron
- Are tightly packed around the nucleus, for most time lie between the nucleus and the outer electron.
- The core has a charge of 2− and the nucleus charge is 3+.
  The effective charge 'felt' by the outer electron is 1+.



- As you go down the group, there is absolutely no change in the effective nuclear charge.
- As you go across the table (periodic table) from the left to the right, the effective nuclear charge increases

- Down the group, effective nuclear charge remains nearly constant whilst the principal quantum number of the valence shell increases.
- Two important factors to consider : (i) increasing principal number and (ii) the effective nuclear charge.

ELECTRONEGATIVITY

- This is the measure of the attraction of an atom for the electrons in a chemical bond.
- The higher the electronegativity of an atom, the greater its attraction for bonding electrons.
- Electronegativity is related to ionization energy. Elements with low ionization energies have low electronegativities.

- n increases as one descends the group.
- The orbital containing the valence electrons become bigger hence atom grows larger.
- As the period, left to right, the nuclear charge increases, and the outer shells become more populated but the inner core remains the same.
- E.g Li to F nuclear charge changes 3+ to 9+ whilest core($1s^2$) remains the same.

Ionic Sizes

- When an atom gains an electron (anion), the size increases i.e sizes of ion is greater than neutral atom. Generally: $X^{3-} > X^{2-} > X^{-1} > X$
- When electrons are added the mutual repulsion between electrons increases. and electrons push each other.
- When electrons are removed (cation) the size of the atom decreases i.e cation size is smaller than the neutral atom. Generally: $A^{3+} < A^{2+} < A^{+} < A$
- Electron – electron repulsion decreases when electrons are removed, allowing the remaining electrons to be drawn closer around the nucleus.

Ionisation Energy

- The energy required to remove an electron from an isolated, gaseous atom or ion in its ground state.

$$X(g) \longrightarrow X^{+}(g) + e^{-}$$

- Measures amount of work needed to pull out an electron and it gives an idea of how tightly bound the electron is to the nucleus.
- Requires energy input – the tightly bound, the more energy is required to remove the electron.
- Successive ionisation energies become increasingly larger.

$Li(g) \longrightarrow Li^{+}(g) + e^{-}$ $IE_1 = 520\ kJ$

$Li^{+}(g) \longrightarrow Li^{2+}(g) + e^{-}$ $IE_2 = 7297\ kJ$

$Li(g) \longrightarrow Li^{2+}(g) + 2e^{-}$ $IE_{total} = 7817\ kJ$

$IE_1 < IE_2 < IE_3 \ldots$

- The ionisation energy decreases as you go down the group but increases as you go across the period.

Electron Affinity

- This is the opposite of ionisation energy.
- Electron affinity reflects the ability of an atom to accept an electron. It is the energy ehange that occurs when an electron is added to a gaseous atom.

Example: $F(g) + e^- \rightarrow F^-(g)$ EA $= -328$ kJ mol^{-1}

Note that

Why gain an electron?

For a free electron approaching an atom there is opposition of attractive effects the nucleus and repulsive forces in the outer electrons.

- If attractive forces exceed the repulsive, an electron is gained and energy is given off.
- By gaining an electron, F^-, a fluorine atom acquires the very stable a noble gas configuration of Ne.

$$F(1s^2 2s^2 2p^5) + e^- \longrightarrow F^- (1s^2 2s^2 2p^6)$$

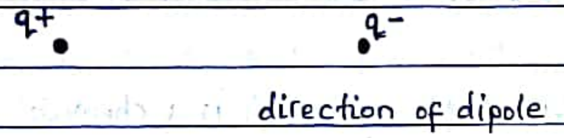
Positive Electron Affinity

- Gain of a second electron by a non-metal gives positive electron affinities
- Electron approaches an electron-dense space
- Energy is required to perform the change
- A typical example - is the second electron affinity of oxygen

- Elements with high ionisation energies have high electronegativities (a pull that is exerted on electrons by the nucleus).

- The difference in electronegativity between two atoms gives a measure of the polarity between two atoms.

Suppose a positive and negative charge are separated from one another.



Dipole moment = distance × charge

$\mu = q \times d$

Note: q is Coulomb and d is distance in metres(m).

CHEMICAL BONDING

The properties of substances are (in part) determined by chemical bonds. Strong attractive forces hold atoms and ions together ~~bA~~ in compounds and molecules.

An ionic bond involves transfer of one or more electrons from the valence shell. A positive and negative ion forms, giving rise to electrostatic forces between atoms forming the bond.

- Ionic bonding occurs between elements with low ionization energy and high electron affinity.

K [.[Ar] $4s^1$.]

- In a covalent bond, one or more electrons are shared between two atoms.

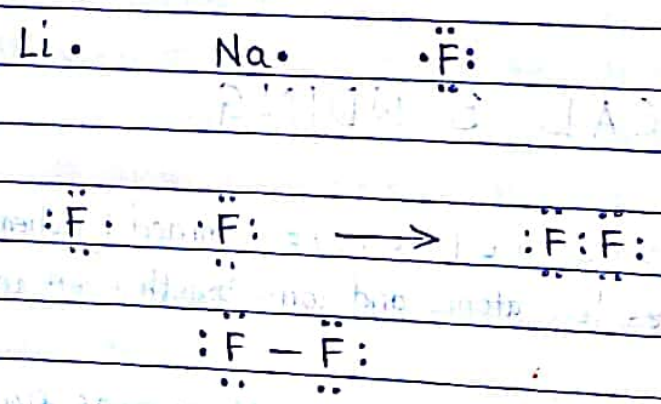
Important!

- In coordinate covalent bonds, the shared electron comes from the lone pair of one of the atoms in the molecule.
- Transfer of electrons results in a more stable configuration in the ions. The tendency to form this stable configuration is known as Octet rule, e.g i the He (helium) configuration.

LEWIS SYMBOLS AND LEWIS STRUCTURE

A Lewis structure (or Lewis dot symbols) is a chemical symbol of an elemen surrounded by dots, each representing one of the s and/or p valence electron of the atom.

Lewis symbol is used to represent the distribution of valence electrons in an atom or molecule.



- In other words, Lewis dot symbols of these elements represent valence electr as dots around the symbol of the element.
- Since the elements in each group have the same number of valence electrons (same subshells but different shells), each element in a group has the same number of dots representing electrons.

The dot symbols are usually shown first with one electron on each side of th element and then with paired electrons on each side. Note that the Roma numeral of the group number also represents the number of valence electron dots, for a neutral atom.

- A Lewis structure for a molecule shows the order and arrangement of atoms in a molecule (the structural formula) as well as all of the valence electrons for the atoms involved.
- A pair of electrons is sometimes shown as a pair of dots (:) or as a dash (—).
- In many texts, a pair of dots is used to represent unshared pairs (also called lone pairs) of electrons on an atom, and a dash to represent a pair of electrons that are shared between atoms. In this way, shared and unshared electrons can be distinguished.

NOTE : Hydrogen is written second in binary compounds with Groups IVA and VA (four and five) elements but is written first with Group VIA and VIIA (six and seven) elements.

NOTE : In most cases, the first atom in a formula is the central atom, and other atoms are bound to it.

FORMULAR FOR CALCULATING FORMAL CHARGE

$FC = V - \left(N + \frac{B}{2}\right)$ where V = Number of valence electrons

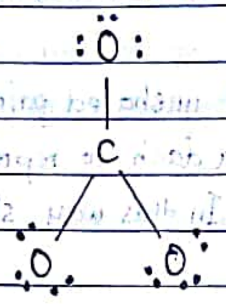
N = Number of non-bonded valence electrons on the atom in a molecule

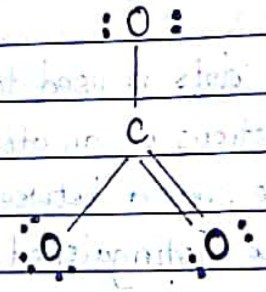
B = Total number of electrons shared in a covalent bond with other atoms in a molecule.

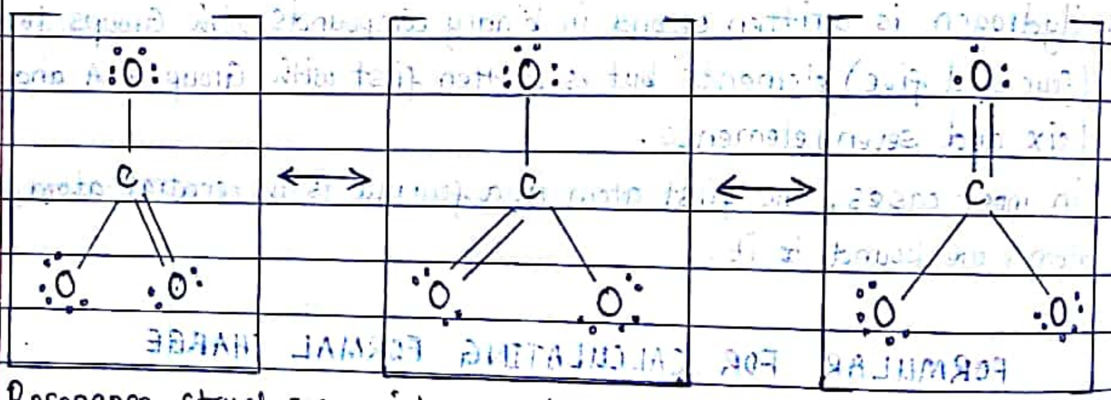
- The sum of the formal charges of the atoms in the Lewis structure must equal to zero for a neutral atom or equal to the ionic charge for a polyatomic ion.
- The formal charge must be as small as possible.
- Negative charges usually appear on the most electronegative atoms, and positive on the least electronegative atoms.

RESONANCE STRUCTURES

- The actual structure of the molecule can be viewed as a resonance hybrid of the three structures shown below:







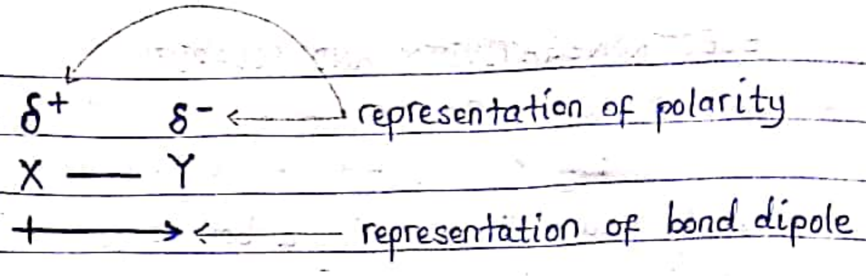
- Resonance structures exist for molecules when equally correct Lewis structu can be written without changing the basic skeletal geometry or the positi of any atoms.

ELECTRONEGATIVITY AND POLARITY OF BONDS

- You are probably aware that sharing a box of popcorn at a movie rarely means equal sharing. The hungrier, faster popcorn eater usually gets the lion's share. Likewise, in a chemical bond between two different atoms, the pair of electrons is not shared equally, and one atom gets the lion's share of the electrons.
- The ability of an atom of an element to attract electrons to itself in a covalent bond is known as the element's electronegativity.
- The most electronegative element is Fluorine, which is assigned an electronegativity value of 4.0. Notice that nonmetals tend to have higher values of electronegativity than metals.
- The values of negativity-electro (electronegativity) were first calculated by Linus Pauling who won two Nobel Prizes and a proponent of vitamin C.

- Electrons carry a negative charge. In a covalent bond between two atoms of different electronegativity, the more electronegative atom attracts the electrons in the bond partially away from the other atom and thus acquires a partial negative charge (symbolised by δ^-). This leaves the less electronegative atom with a partial positive charge (symbolised by δ^+).

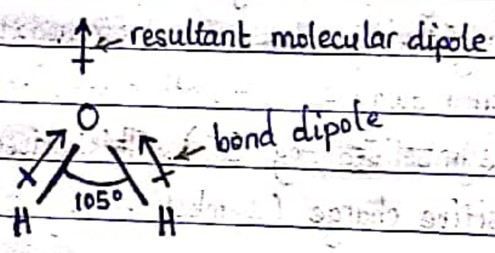
- A Covalent bond that has a partial separation of charge due to the unequal sharing of electrons is known as a Polar-Covalent Bond (or simply, polar bond).
- A polar bond has a negative end and a positive end and is said to contain a Dipole (two poles).
- A polar bond is something like Earth itself which contains a magnetic dipole with a north and south magnetic pole. (The poles in a bond dipole are electrostatic rather than magnetic).
- The dipole of a bond is represented by an arrow pointing from the positive to the negative end ($+\!\!\!\longrightarrow$).



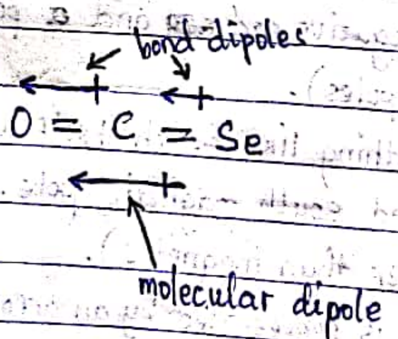
- When electrons are shared between atoms of the same element, they are obviously shared equally.
- If electrons are shared equally, the bond is known as (Unpolar) Nonpolar bond. On the other hand, the greater the difference in electronegativity between two atoms, the more polar the bond.

mportant! In fact, if the difference is 1.9 or greater, it may indicate that one atom has gained complete control of the pair of electrons. In other words, the bond is ionic.

- Consider the case of water. The two O–H bond dipoles are equal, but they are not at an angle of 180°, so they do not cancel.



- Consider, for example again, the molecule COSe, which is linear like CO_2 but has bond dipoles that are not equal. There is a net or resultant dipole and the molecule is polar. The combined effect of the bond dipoles is the molecular dipole.



- Since the covalent bonds in most molecules are polar, does that mean the molecule itself is polar? Surprisingly, the answer is "not necessarily".

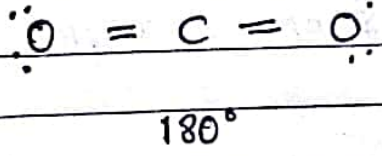
Important! The polarity of a molecule depends on its geometry.

- Lewis structures can tell us about the geometry of some simple molecules.
- The approximate geometry of the atoms around a central atom can be predicted by the valence shell electron pair repulsion (VSEPR) theory. This theory tells us that electron pairs, either unshared pairs or electrons localised in a bond, repel each other to the maximum extent. In other words, the negatively charged electron pairs get as far away from each other as possible.

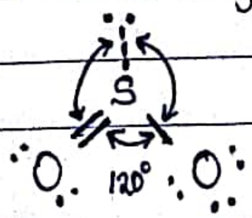
REMEMBER: Double and triple bonds are all considered as one group~~s~~ of electrons, so they are treated the same as a single bond in this theory.

- The molecular geometry of a molecule is the geometry described by the bonded atoms and does not include the unshared pairs of electrons.

- In the CO_2 molecule, for the four electrons in each C – O bond to be as far apart as possible, they will lie on opposite sides of the ~~beryllium~~ carbon atom at an angle of 180°. The geometry of the molecule is then described to be linear.

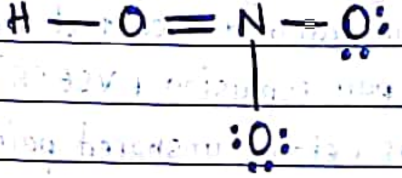


- Considering the SO_2 molecule which has three electron groups, the three electron groups can get away as far as possible from each other by assuming the geometry of an equilateral triangle with an O – S – O angle of 120°. The geometry of this molecule is described as trigonal planar. The ~~C~~central atom is bonded ~~by~~ to two other atoms, and it has one unshared pair of electrons. Thus we describe the molecular geometry of the three atoms in SO_2 as V-shaped

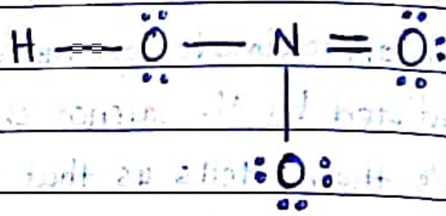


Question : Using the concept of formal charges determine which of the following is more plausible for nitric acid, HNO_3 ;

(a)



(b)



Answer :

HYBRIDIZATION THEORY

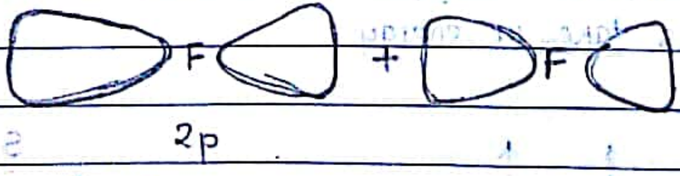
- Used to explain some of the shapes of molecules in VSEPR theory.
- Hydridization Theory says that atoms bonded in molecules will undergo structural changes in their valence level atomic orbitals.
- New sets of orbitals are formed called Hybrid orbitals.
- Hydridization explains the geometry of the compound.
- Hybrid orbitals have some characteristics of the original atomic orbitals but differ in shape.
- A Hybrid is something made by combining different elements.
- Allotropes are different forms of the same element, e.g diamond and graphite are both carbon atomic compounds.

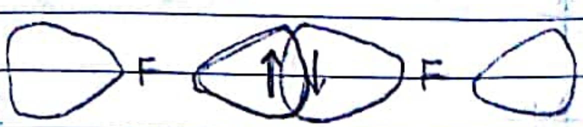
HOW DO BONDS ACTUALLY FORM?

Bonds are formed when atoms share (or transfer) an electron(s).

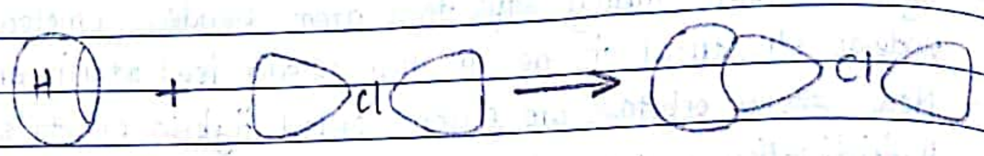
- The space electrons occupy — orbitals.
- Does our view of atomic orbitals mesh with VSEPR?

- S orbitals ..... no problem. p-orbitals? Recall, dumbbell shape — oriented 90° along x, y, and z axes. What about F_2?



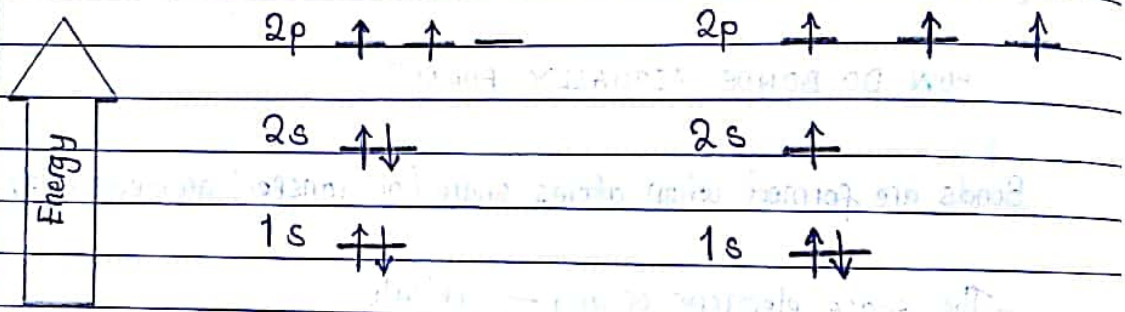


What about HCl ?



HYBRIDIZATION — THAT'S HOW ?

- Energy gap between s and p orbitals is low.
  - An electron arbsobs energy and is promoted to (2p).

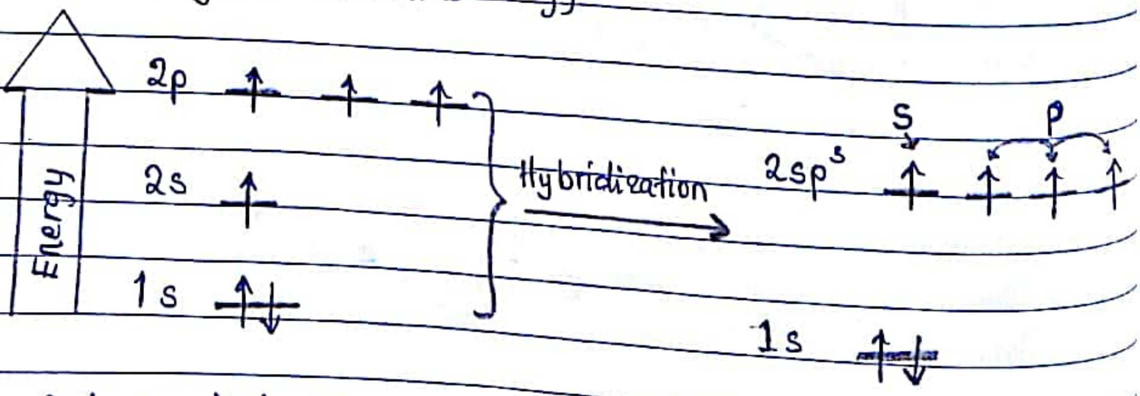


Carbon: ground state electron configuration.

Carbon: excited state electron configuration.

Promotion — followed by Hybridization

- Remember that promotion is energy intesive, takes energy. But not as much energy saved when you can form additional bonds.
  - Making bonds releases energy
  - Breaking bonds takes in energy

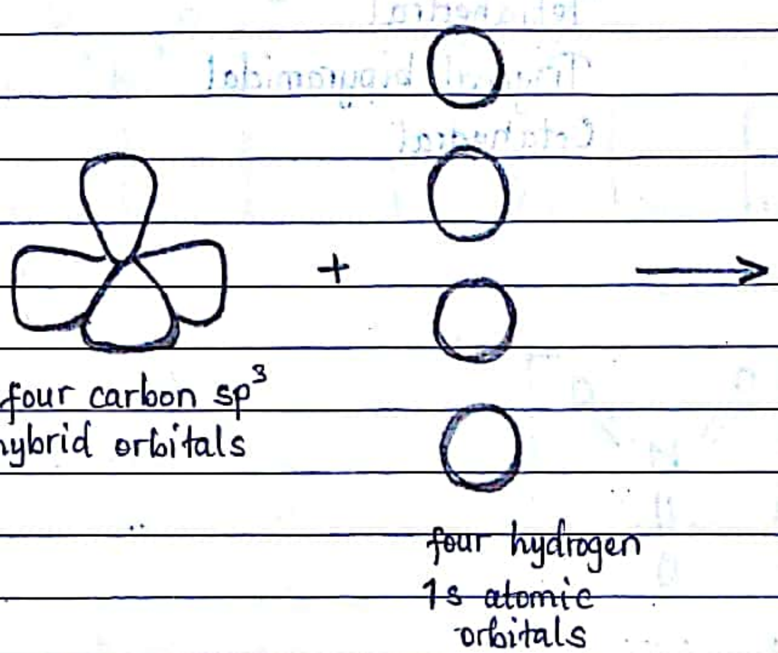


Carbon: excited state electron configuration

Carbon: sp^3 hybridized configuration

72 This helps explain Methane

- Also important to remember is the fact that the number of atomic orbitals into a hybrid scheme must equal the number of hybrid orbitals out of that scheme.
  - sp^3 orbital (one s and three p orbitals).



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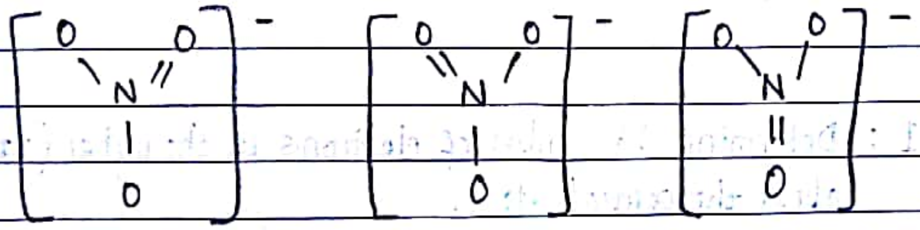
Hybrid Orbitals and their Geometric Orientation

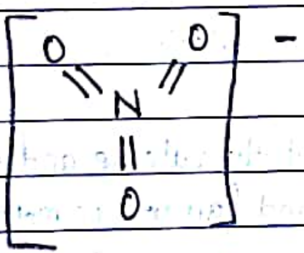
Hybrid Orbitals	Geometric Orientation	Example
sp	Linear	$BeCl_2$
sp^2	Trigonal planar	BF_3
sp^3	Tetrahedral	CH_4
sp^3d	Trigonal bipyramidal	PCl_5
sp^3d^2	Octahedral	SF_6

Sometimes a single structure fails to explain experimental measurements bond lengths and energies.

The concept of resonance is used to indicate a composite or 'average' structure, where two or more structures are possible.



These is no true double bond



bond order $\frac{4}{3}$

VSEPR – the technique :

Valence – Shell – Electron – Pair – Repulsion Theory (VSEPR Theory)

- Shapes of molecules are determined by experiment or quantum mechanical calculations.
- VSEPR theory uses Lewis- structures to predict the molecular geometry of covalently bonded molecules.
- The VSEPR theory focuses on pairs of electrons in the valence shell, because electrons repel each other.
- It states that the 3-dimensional arrangement of atoms surrounding a central atom is determined by the following:

① Repulsions between the bonding and the non-bonding electron pairs in the valence shell of the central atom.

② Electrons arrange themselves as far apart as possible, minimizing repulsions.

③ Double bonds and triple bonds can be treated as single bonds bet the neighbouring atoms.

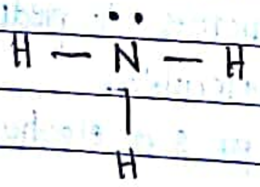
Only six steps are required to generate the molecular geometry e.g CH $[NH_4]^+$, NH_3, or NH^{2-}.

Step 1 : Determine the number of electrons in the outer (valence) she about the central atom.

Element : C , N , H
Nº of valence electrons :: 4 , 5 , 1

Step 2 : Find the valence and number of electrons associated with the ligand (an ion or molecule attached to a metal atom by coordinate bonding) X, e.g the valence is 1, no of electron for H is 1 only.

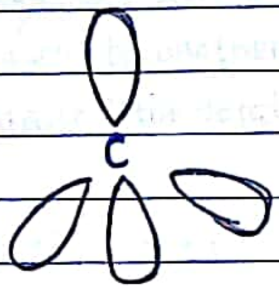
Step 3 : Construct a valid Lewis structure of the molecule in questi showing all the bonds and all of the lone pairs (non-bonded pairs) of electrons.

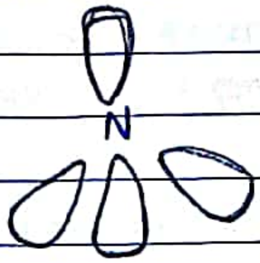


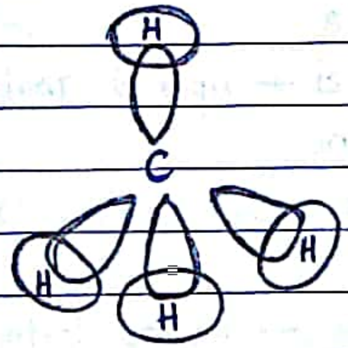
$$H - \overset{\cdot\cdot}{\underset{|}{N}} - H$$
$$H$$

Step 4 : Determine the coordination number around the central atom The coordination number is the number of electron pairs whic is also the number of electrons in the outer shell divided by 2. e.g CH_4 and NH_3 have coordinate numbers of 4 each.

Step 5 : The overall geometry of the atomic centre is determined by the mutual repulsion between the electrons pairs of the total coordination number.







Step 6 : Two adjustments are required by the VSEPR theory method to find the geometry of an atomic centre.
Lone pairs of electrons (non-bonded pairs) are taken into account in determining the total coordination number and VSEPR geometry, but are not used when defining the geometry of an atomic centre, only atoms are used.

* Resonance is simply a concept used to show a composite or average structure, where two or more structures are possible.

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THERMOCHEMISTRY

NATURE OF ENERGY

Energy is defined as the capacity to do work or heat (to produce heat). One important law to consider is the Law of Conservation of Energy. Energy can neither be created nor destroyed but can be converted from one form to another. This implies that the energy of the universe is constant (the total energy of the universe is constant).

Thermal Energy — is the the energy associated with the the random motion of atoms and molecules.

Chemical Energy — is the energy stored within the bonds of chemical substances.

Nuclear Energy — is the energy stored within the collection of neutrons and protons in an atom.

Electrical Energy — is the energy associated with the flow of electrons.

Potential Energy — is the energy available by virtue of an object's position

The Language of Thermochemistry

- Thermodynamic system.

A thermodynamic system is that part of the universe that is under consideration, for example (1) an experimental set-up in the lab, (2) a biological cell, (3) wine fermentation tank and et cet era...

Types of Systems

The system is separated from the rest of the universe by a real or imaginary boundary.

The surroundings are "where we are" and the rest of it is the universe. A type of system is often characterized by the nature of the boundary : it can either be open, closed or isolated.

1. Open System

This type of system can exchange both heat and matter with their surro for example an open beaker, boiling kettle, open gas cylinder, e.t.c

2. Closed System

In this kind of system, energy can be transferred between the system a surroundings but not matter for example a closed gas cylinder

3. Isolated System

Isolated systems are completely isolated from their surroundings, for example insulated container, thermoflask, et.c

State and Non-state Functions

The state of the system is defined by microscopic properties for example composition, volume, pressure and energy. In thermochemistry, we are concerned with the changes related to these properties.
Such functions do not depend on the path taken (used) but depends only on the initial and final states of the system.

Non-state functions are path-dependant functions, for example work and heat; these depend on the route used.
In moving from state 1 to state 2, different amount of work will be done depending on the path used.

Temperature is a property that reflects the random motions of the particles in a particular substance.
Heat involves the transfer of energy between two objects due to temperature difference.

WORK (W)

When an object is moved against an opposing force — work is done. In chemistry, chemical reactions do work when electrons are driven through a metal wire. Most commonly encountered work in chemical systems is volume – pressure. Volume changes, for example, occur due to disappearance or appearance of new gaseous products.

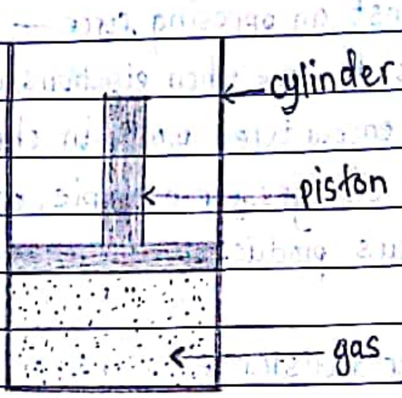
Work is the force acting over a distance.

NOTE: Always remember that there are two ways in which to transfer energy, namely, work and heat (through work and through heat).

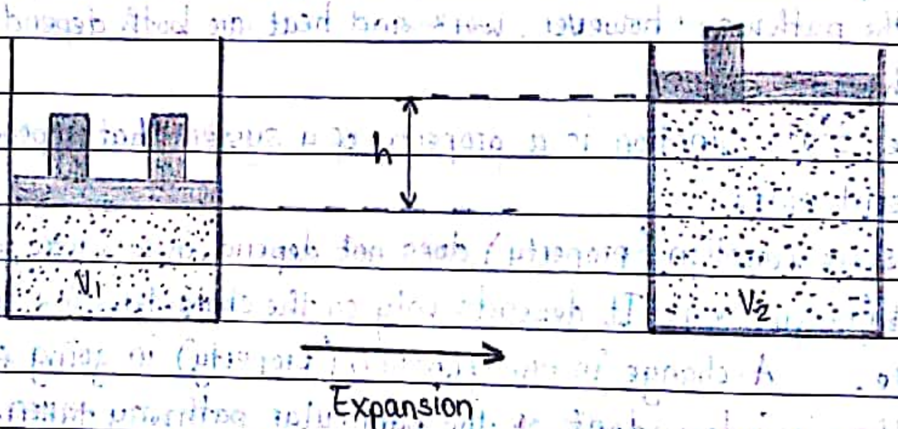
NOTE: The way energy transfer is divided between work and heat depends on the specific conditions — the pathway. Energy change is independent of the pathway; however, work and heat are both dependent upon the pathway.

NOTE: The State function is a property of a system that depends only on its present state.
A state function (property) does not depend in any way on the system's past (or future). It depends only on the characteristics of the present state. A change in this function (property) in going from one state to another is independent of the particular pathway taken.
Therefore, energy is a state function, but heat and work are not state functions.

NOTE: The system is the part of the universe on which we wish to focus attention. The surrounding, however, includes everything else in the universe. Therefore, products and reactants of a chemical reaction are defined as the system. The surroundings consist of a reaction container, e.g furnace, a room and anything else other than the reactants and products.



- If we removed one of the weights, the volume changes from V_1 to V_2.



Pressure is defined as the force per unit area.

$$P = \frac{F}{A}$$

Rearrange to express the force in terms of pressure (P) and area (A).

$$F = P \times A$$

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From classical mechanics, Work(W) = force(F) × distance(h)

$$= p \times A \times d(h)$$

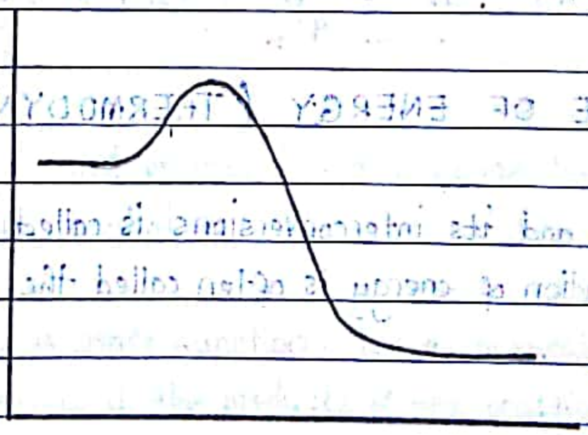
$$\text{Work} = p\Delta V$$

Heat (q)

- Heat is the thermal energy that is transferred when two bodies are in contact. It flows from a warmer body to a cooler one.
- Important! Energy is transferred between the two bodies until the average K.E between them are the same – condition of thermal equilibrium.
- Temperature is the measure of the ~~f~~ thermal energy.

Chemical changes and heat

- Energy is either evolved or released during chemical changes. It can either be absorbed or released.
- A process in which heat is released to the surroundings is known as an exothermic process e.g combustion of hydrocarbons
- Energy exits a system, – ΔE (the change in energy is negative).

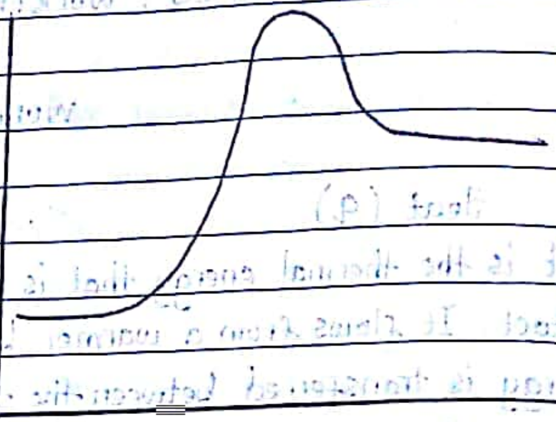


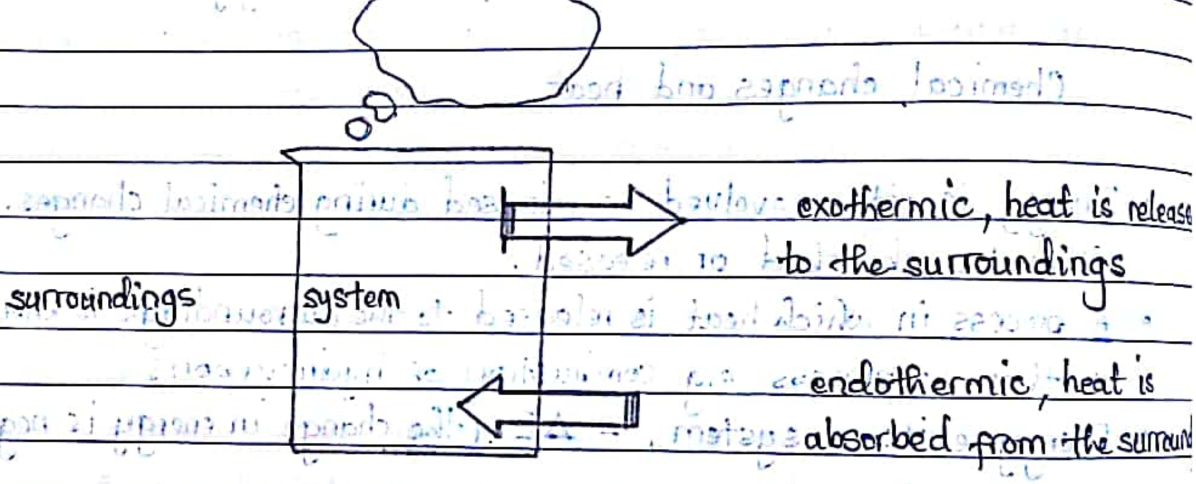
- Energy flows out of the system, e.g as heat.

- An endothermic process is where energy is absorbed by the system e.g vaporization of water.

The heat is absorbed from the surroundings by the system and consequently the temperature of the surroundings will tend to drop as the reaction or process proceeds.

Energy is added to the system, therefore the change in energy is positive, + ΔE.





THE NATURE OF ENERGY (THERMODYNAMICS)

The study of energy and its interconversions is called thermodynamics. The Law of conservation of energy is often called the first law of thermodynamics.

Internal Energy

Internal energy, E, of a system is the sum of the kinetic and potential energies of all the "particles" in the system.
To change the internal energy of a system: $\Delta E = q + w$, where q stands for heat and, w stands for work done.

NOTE: * The internal energy remains constant if there is no friction.

Thermodynamic quantities consists of two parts:

(i)

(ii)

The sign reflects the system's point of view: (i) the system does work on the surrounding's, the work done is negative, whereas (ii) when the surroundings do the work on the system, the work done is positive.

Most laboratory experiments are at constant pressure, i.e atmospheric pressure. Volume changes also do occur during reactions e.g open beakers, flasks e.t.c.

Additionally, some PV work is done. The change in internal energy is

$$\Delta E = q_p + p\Delta V$$

Rearranging, we have: $q_p = \Delta E - p\Delta V$

The energy gained or lost during a change taking place at constant pressure is known as Enthalpy (H).

Enthalpy is a state function. For a chemical reaction, $\Delta H = H_p - H_r$

ΔH is positive if the products of the reaction have a greater enthalpy than reactants.

Calorimetry is the science of measuring heat.

- Specific heat capacity is the energy required to raise the temperature one gram of a substance by one degree Celsius.
- Molar heat capacity is the energy required to raise the temperature of on mole of a substance by one degree Celsius.

A Basic Calorimeter

Two styrofoam cups nestled within one another (insulation), then fille with a specific quantity of water.
A chemical reaction or phase change takes place inside and a thermom is placed within to measure any change in temperature that occurs to t system.

$$\Delta H = \Delta H_{calorimeter} + \Delta H_{system}$$

Assumptions made in the calculation of enthalpy change

1. It is an isolated or closed system and there is no heat transfer betw the calorimeter and its surroundings.

2. The amount of heat absorbed or released by the calorimeter itself is too small to influence calculations

3. Any dilute solutions involved in the reaction are treated as if they were water.

The energy released (heat) = $s \times m \times \Delta T$

s – specific heat capacity ($J/°C\cdot g$)
m – mass of solution (g)
ΔT – change in temperature ($°C$)

HESS' LAW

In going from a particular set of reactants to a particular set of products the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

$$\begin{tikzcd}
A \arrow[rr, "\Delta H"] \arrow[dr, "\Delta H_1"'] & & D \\
& B \arrow[r, "\Delta H_2"'] & C \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Example : $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$ $\Delta H_1 = 68\ kJ$

This reaction also can be carried out in two distinct steps, with enthalpy changes designated by ΔH_2 and ΔH_3.

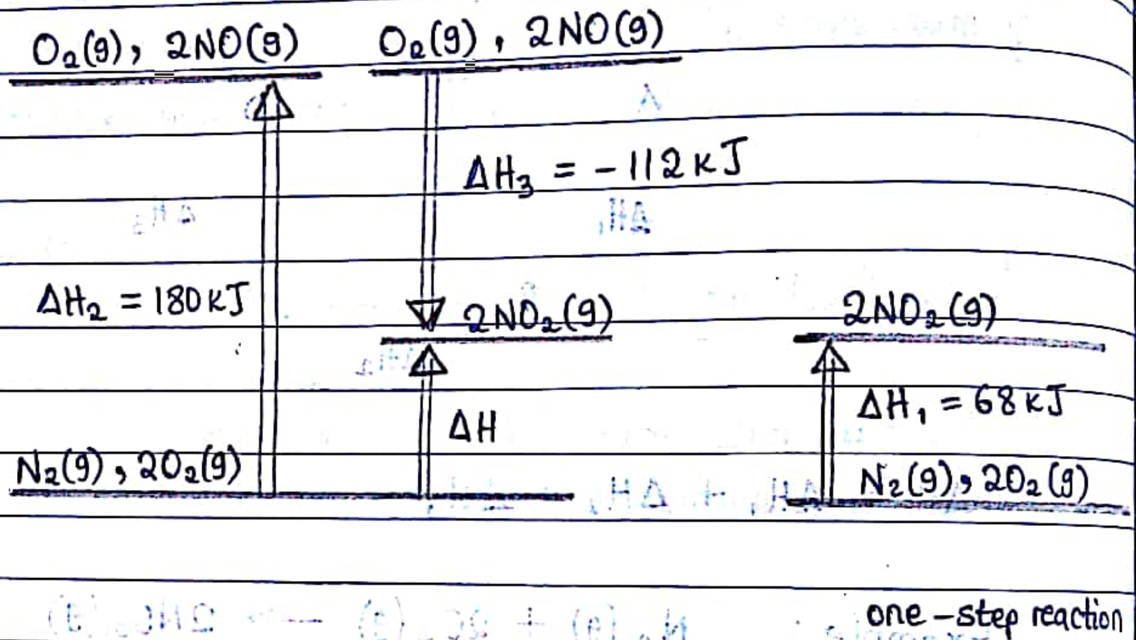
$N_2(g) + O_2(g) \longrightarrow \cancel{2NO}(g)$ $\Delta H_2 = 180\ kJ$

$\cancel{2NO}(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\Delta H_3 = -112\ kJ$

$N_2(g) + 2O_2 \longrightarrow 2NO_2(g)$ $\Delta H_2 + \Delta H_3 = 68\ kJ$

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 68\ kJ$$

The Principle of Hess' Law



Characteristics of Enthalpy Changes

- If a reaction is reversed, the sign of ΔH is also reversed.
- The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction.
- If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

Example: Consider the following data

$$NH_3(g) \longrightarrow \tfrac{1}{2} N_2(g) + \tfrac{3}{2} H_2(g) \quad \Delta H = 46 kJ \text{ ----- (i)}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \quad \Delta H = -484 kJ \text{ --- (ii)}$$

Calculate ΔH for the reaction

Problem - Solving Strategy

- Work backward from the required reaction, using the reactants and products to decide how to manipulate the other given reactions at your disposal.
- Reverse any reactions as needed to give the required reactants and products.
- Multiply reactions to give the correct numbers of reactants and products.

Example : Reverse the two reactions :

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H = -46\ kJ$

$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = +484\ kJ$

The desired reaction is : $2N_2(g) + 6H_2O(g) \longrightarrow 3O_2(g) + 4NH_3(g)$

Multiply reactions to give the correct numbers of reactants and products:

$4\left(\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)\right) \qquad 4\left(\Delta H = -46\ kJ\right)$

$3\left(2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)\right) \qquad 3\left(\Delta H = +484\ kJ\right)$

Desired reaction : $2N_2(g) + 6H_2O(g) \longrightarrow 3O_2(g) + 4NH_3(g)$

Example : The final reactions are :

$2N_2(g) + \cancel{6H_2}(g) \longrightarrow 4NH_3(g) \qquad \Delta H = -184\ kJ$

$6H_2O(g) \longrightarrow \cancel{6H_2}(g) + 3O_2(g) \qquad \Delta H = +1452\ kJ$

Desired reaction : $2N_2(g) + 6H_2O(g) \longrightarrow 3O_2(g) + 4NH_3(g) \quad \Delta H = +1268\ k$

Chemists essentially carry out experiments under a variety of condition Hess' Law has one restriction that all the enthalpies must be measured at the same temperature and pressure.

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions.

The standard state of a substance at a specified temperature is its pure form at 1 bar, for example:

$H_2O(l) \longrightarrow H_2O(g) \quad \Delta_{vap}H^\circ(373K) = +40.66\ kJ\,mol^{-1}$

Conventional Definitions of Standard States

For a compound – for a gas, pressure is exactly 1 atm
– for a solution, concentration is exactly 1 M.
– for a pure substance (liquid or solid)

For an element – the form [$N_2(g)$, $K(s)$] in which it exists at 1 atm and 25° C.

(a) Enthalpy of Physical Change

This is the standard enthalpy change that accompanies a change of hysical state, and it is called the Standard enthalpy of transition, enoted $\Delta_{trs}H^\circ$.

Standard enthalpy of vaporisation, $\Delta_{vap}H^\circ$
Standard enthalpy of fusion, $\Delta_{fus}H^\circ$

(b) Enthalpy of Chemical Change

Standard enthalpy of change that accompanies a chemical reaction.

NOTE! ΔH° is the change in enthalpy when reactants in their standard states change to products in their standard states.

It is the difference between the enthalpies of the reactants and products

ΔH = Sum of enthalpy of products − Sum of enthalpies of reactants

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

Consider the reaction : $aA + bB \longrightarrow cC + dD$

The standard enthalpy is as follows below :

$$\Delta H^\circ_R = [cH^\circ_m(C) + dH^\circ_m(D)] - [aH^\circ_m(A) + bH^\circ_m(B)]$$

A schematic diagram of the energy changes for the reaction :

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O(l).$$

$$\Delta H^\circ_{rxn} = -(-75kJ) + 0 + (-394kJ) + (-572\ kJ) = -891\ kJ.$$

Bond Enthalpy is related to the information and breaking of chemical bonds. Energy is required to break bonds whilst energy is given off in the formation of bonds.

Mean Bond Enthalpy allows us to predict the likely energy change in a chemical reaction.

Bond Dissociation energy is defined as the amount of energy required to break one mole of covalent bonds in gaseous species, e.g

$$CO_2(g) \longrightarrow C(\ ) + 2O_{(g)} \qquad \Delta H = 1609\ kJ.$$

Type of bond	ΔH^o_d (KJmol^{-1})	Molecule
N − H	389	NH_3, ammonia
O − H	464	H_2O, water
C − H	413	many organic compounds
C − C	346	many organic compounds

The enthalpy change measured during a chemical reaction is the energy needed to break all the bonds e.g combustion of methane.

$$CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2 \qquad E = 1646\ KJmol^{-1}$$

CONTINUATION OF ENTROPY FROM PAGE TWO FROM HERE.

Exothermic process: $\Delta S_{surr} = + \dfrac{\text{quantity of heat energy (J)}}{\text{temperature (K)}}$

Endothermic process: $\Delta S_{surr} = - \dfrac{\text{quantity of heat energy (J)}}{\text{temperature (K)}}$

FREE ENERGY

Free energy is defined by: $G = H - TS$

$$\Delta G = \underbrace{\Delta H}_{\text{enthalpy}} - \underbrace{T\Delta S}_{\text{entropic term}}$$

1. If ΔG is negative, then the forward reaction is spontaneous.
2. If ΔG is zero, then the system is at equilibrium.
3. If ΔG is positive, then the reaction is spontaneous in the reverse direction.

There are four C-H bonds in the molecule
Successive breaking of the bonds gives different enthalpy change.

$$CH_4(g) \longrightarrow CH_3(g) + H(g) \qquad \Delta H^\circ_d = +427 \text{ kJ mol}^{-1}$$

$$CH_3(g) \longrightarrow CH_2(g) + H(g) \qquad \Delta H^\circ_d = +371 \text{ kJ mol}^{-1}$$

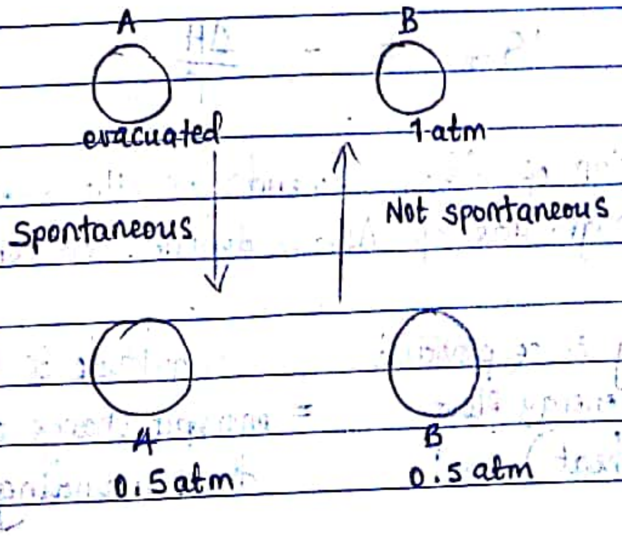
The enthalpy change for a chemical reaction can be calculated using bond dissociation enthalpies.
It is the difference between energies required to break bonds and that released in the formation of new ones.

$$\Delta H_{rxn} = \sum BE(\text{reactants}) - \sum BE(\text{products})$$

SECOND LAW OF THERMODYNAMICS

Questions to answer under this discussion:

1. Why does a reaction proceed as written in a chemical statement?
2. How far does the reaction go?
3. What factors favour spontaneous chemical processes?
4. How much energy must be supplied to drive a particular reaction in the desired direction?

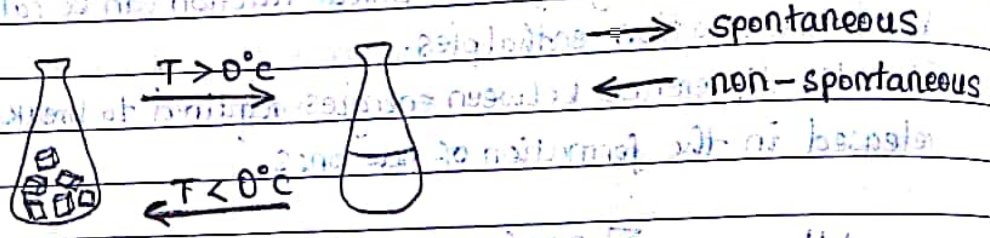


Important

Spontaneous processes are those that can proceed without any outs intervention. The gas in vessel B will spontaneously effuse into vessel A, but once the gas is in both vessels, it will not spontane go back to vessel B.

- Processes that are spontaneous at one temperature may be non-spontaneous at other temperatures.

Above 0°C it is spontaneous for ice to melt.



Below 0°C the reverse process is spontaneous.

ENTROPY

Entropy changes in the surroundings are primarily determined by heat flow.

Entropy (S) is related to the degree of randomness. It is also defined as the degree of dispersal of energy.

The driving force depends on the temperature at which the process is taking place.

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

The sign of ΔS_{surr} depends on the direction of heat flow.

The magnitude of ΔS_{surr} depends on temperature.

$$\text{Driving force provided by the energy flow (heat)} = \text{magnitude of the entropy change of the surrounding} = \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

POINTS TO REMEMBER

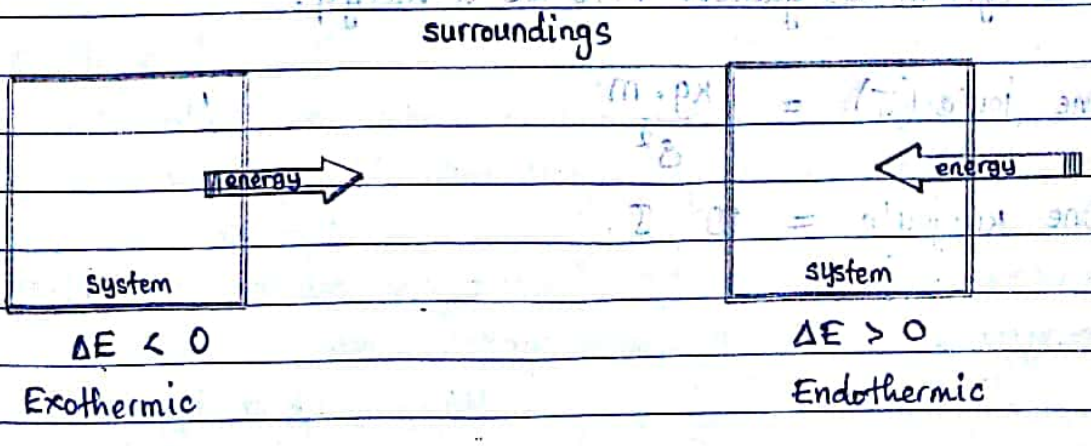
- In an exothermic reaction, the energy released as heat comes from the difference in potential energies between products and the reactants.
- The heat flow into the surroundings (in regard to an exothermic reaction) results from a lowering of the potential energy of the reaction system. This always holds true.
- In any exothermic reaction, some of the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat.
- Energy that flows into the system as heat is used to increase the potential energy of the system.
- The Law of Conservation of Energy is called the First Law of Thermodynamics.
- The Law of Conservation of Energy (first law of thermodynamics) is also stated as follows:

  The energy of the universe is constant.

- The internal energy (E) of a system is the sum of the kinetic energy and potential energy of all the particles in the system.

The Internal Energy can be changed by a flow of work, heat or both.

$\Delta E = q + w$, where q = heat, w = work and ΔE = change in the system's internal energy.



- If a system does work on the surroundings, energy flows out of the system and w is negative.
- If the surroundings do work on the system, energy flows into the system and the work (w) done is positive.
- In this conversion : $\Delta E = q(\text{heat}) + w(\text{work})$, both signs of q and w reflect what happens to the system.

This means that when work is negative, energy flows out of the system and therefore it is exothermic. When work (w) is positive (+ve), then energy flows into the system and therefore it is endothermic. In the same vein, when q is (−ve), it denotes an exothermic reaction, whereas when q is (+ve), it denotes an endothermic reaction.

Example ⇒ Calculate ΔE for a system undergoing an endothermic process in which 15.6 KJ of heat flows and where 1.4 KJ of work is done on the system.

Solution ⇒ Use the equation : $\Delta E = q + w$

$q = +15.6\ \text{KJ}$ because the process is endothermic.
$w = +1.4\ \text{KJ}$ because work is done on the system

$$\Delta E = 15.6\ \text{KJ} + 1.4\ \text{KJ}$$
$$\Delta E = \underline{\underline{17.0\ \text{KJ}}}$$

The system has gained 17.0 KJ of energy.

- One joule (J) = $\frac{\text{kg} \cdot \text{m}}{\text{s}^2}$
- One kilojoule = 10^3 J.

- The work done by a gas (through expansion) and the work done to a gas (through compression) are types of work associated with chemical processes.
- When work is done on a gas, it is called Compression.
- When work is done by a gas, it is called Expansion.
- When a gas expands against an external pressure, P, w is a negative quantity, since work flows out of the system.
- When a gas is compressed, w is a positive quantity, since work flows into the system.
- W and ~~ΔPV~~ $P\Delta V$ have opposite signs because when the gas expands, the change in volume is positive $(+\Delta V)$, work flows out of the system into the surroundings, and work is negative $(-W)$.
- Remember : ΔV = final volume − initial volume $= A \times \Delta h$

ue : Example ⇒ Calculate the work associated with the expansion of a gas from 46 L to 64 L at constant pressure of 15 atm.

Solution ⇒ For a gas at constant pressure : $w = -P\Delta V$, where $P = 15$ atm, and $\Delta V = 64 - 46\text{ L} = 18\text{ L}$.

Hence, $w = -15 \times 18$

$w = -270\text{ L}\cdot\text{atm}$

rtant! Note : since the gas expands, it does work on the surroundings; energy flows out of the gas, so work (w) is a negative quantity.

rtant! NOTE : P in $P\Delta V$ always refers to the external pressure against which work is done or which does work on the gas in the system — the pressure that causes a compression or that resists an expansion.

rtant! NOTE : For an ideal gas, work can only occur when its volume changes. Thus, if a gas is heated at constant volume, the pressure increases but no work occurs.

* Various possible combinations of ΔH and ΔS for a process and the resulting dependence of spontaneity on temperature.

	Case	Result
1.	ΔS positive, ΔH negative	spontaneous at all temperatures
2.	ΔS negative, ΔH positive	Process not spontaneous at any temperat (reverse process is spontaneous at all temperatu
3.	ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant).
4.	ΔS negative, ΔH negative	spontaneous at low temperatures (where exothermicity is dominant.)

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ELECTROCHEMISTRY

Electrochemistry is the study of energy changes from chemical energy to electrical energy or vice-versa.

Revisions of Redox Reactions

REDUCTION	OXIDATION
- gain of electrons	- loss of electrons
- gain of hydrogen	- loss of hydrogen
- loss of oxygen	- gain of oxygen
- decrease in oxidation number	- increase in oxidation number

Revision of balancing Redox Reactions (rxns) by Ion-Electron method:

Que : Balance the following redox-reaction in acidic media :

$$MnO_4^-{}_{(aq)} + Fe^{2+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + Fe^{3+}_{(aq)}$$

Step 1. Divide the reaction in two half-reactions.

$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$ (loss of O_2 : reduction)

$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)$ (increase in oxidation No : oxidation)

Step 2. Balance all other elements except oxygen and hydrogen.

Already balanced !

Step 3. Balance oxygen by adding water to the side with fewer O.

$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)$

Step 4. Balance hydrogen by adding H^+ ions on side with fewer H.

$$MnO_4^-(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l).$$
$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)$$

Step 5. Balance the charges by adding electrons on the side with higher charge.

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$

Step 6. Balance the number of electrons being gained and lost.

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l).$$
$$[\ Fe^{2+}(aq) \longrightarrow Fe^{3+} + e^-\ ] \times 5$$
$$5Fe^{2+}(aq) \longrightarrow 5Fe^{3+} + 5e^-.$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l).$$

Step 7. Combine the half-reactions

$$MnO_4^-(aq) + 8H^+(aq) + \cancel{5e^-} + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq) + \cancel{5e}$$

FINAL EQUATION: $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

Clue :- Balance the same reaction as in acidic media first and then add step 8 to balance in basic media.

Que: BALANCE THE SAME REACTION IN BASIC MEDIA.

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Step 8. Add OH^- ions equal to the numbers of H^+ ions on both sides.

$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) + 8OH^-(aq) \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O + 8OH^-$

$MnO_4^-(aq) + 5Fe^{2+}(aq) + \cancel{8H_2O}(l) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + \cancel{4H_2O} + 8OH^-(aq)$

FINAL EQUATION : $MnO_4^-(aq) + 5Fe^{2+}(aq) + 4H_2O(l) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 8OH^-(aq)$

ELECTROCHEMICAL CELLS.

Energy changes from chemical energy to electrical energy or viceversa bring about inventions for study such as electrochemical cells.

There are two types of cells that will be considered :

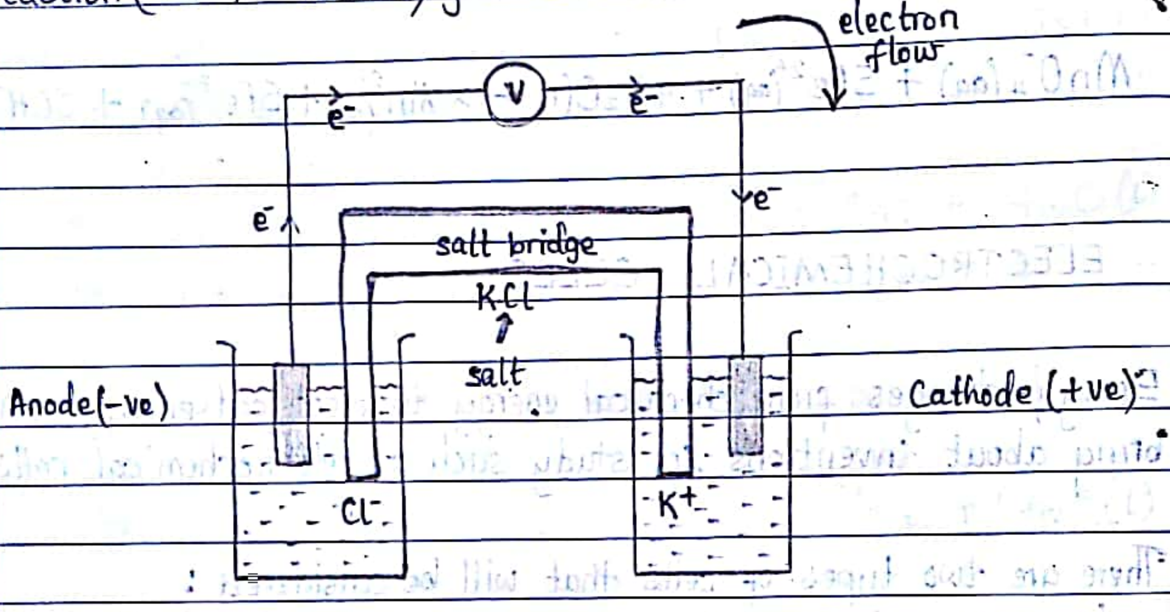
(i) GALVANIC CELLS

(ii) ELECTROLYTIC CELLS

Galvanic cells change chemical energy to electrical energy.
Electrolytic cells change electrical energy to chemical energy.

GALVANIC CELLS

Galvanic cells use spontaneous redox reactions to generate an electric current that can be used to do work.
A Galvanic cell is defined as a device in which a spontaneous chemical reaction (redox reaction) generates an electric current that can be used to do wor



Oxidation e.g
$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

Reduction e.g
$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+}$

1. Oxidation and Reduction reactions occuring in separate components. If the reactions occur in the same compartment, no amount of meaningful current can be generated.

The concentrations of the reactants in each compartment must be at standard conditions: 1 mol/L, 25°C and 1 atm.

2. Connecting wire
The two compartments must be connected by a wire through which electrons will flow from the reducing agent (oxidation reaction) to the oxidising agent (reduction reaction).

[illegible]. Electrodes

Two electrodes used in galvanic cells are (i) the Anode and (ii) the Cathode.

The anode is the electrode at which oxidation takes place (this is the proper definition). The anode in galvanic cells is negatively charged.

The cathode is the electrode at which reduction takes place (this is the proper definition). The cathode in galvanic cells is positively charged.

NOTE: Do not define the anode and cathode in terms of charges!!

The nature of the electrodes can be either active or inert.

4. Salt Bridge or Porous Disk

As electrons are leaving the anode, the solution in which it is immersed becomes more and more positive. A Salt bridge (made up of positively and negatively charged ions) will ~~not~~ provide negatively charged ions in order to neutralise the positive charge that builds up.

But as electrons enter the cathode, the solution around it becomes more and more negative. The salt-bridge will provide positively-charged ions to this compartment in order to neutralise the negative charge that has build up.

Without the salt bridge, the flow of electrons would stop.

5. Voltmetere

You can connect a voltmeter to a galvanic cell so as to measure the amount of voltage or electric current generated by the flow of electrons.

You can also connect a light bulb that lights up when there is flow of current.

NOTE: In a Galvanic cell, the appropriate unreacting ions are called Counterions

They are usually present to balance the charge.

NOTE: For a Galvanic cell, the cell potential is always positive.

ELECTRODE POTENTIAL

Important!

Electrode potential is the voltage between an electrode and the solution (or electrolyte) in which it is immersed.
The anode has an oxidation potential that arises due to loss of electron
The cathode has a reduction potential which arises due to gain of electrons; Since electrons loss (oxidation) is opposite to reduction (gai of electrons), only the reduction potential is necessary to measure. Thus sometimes electrode potential and reduction potential are used interchangeably.

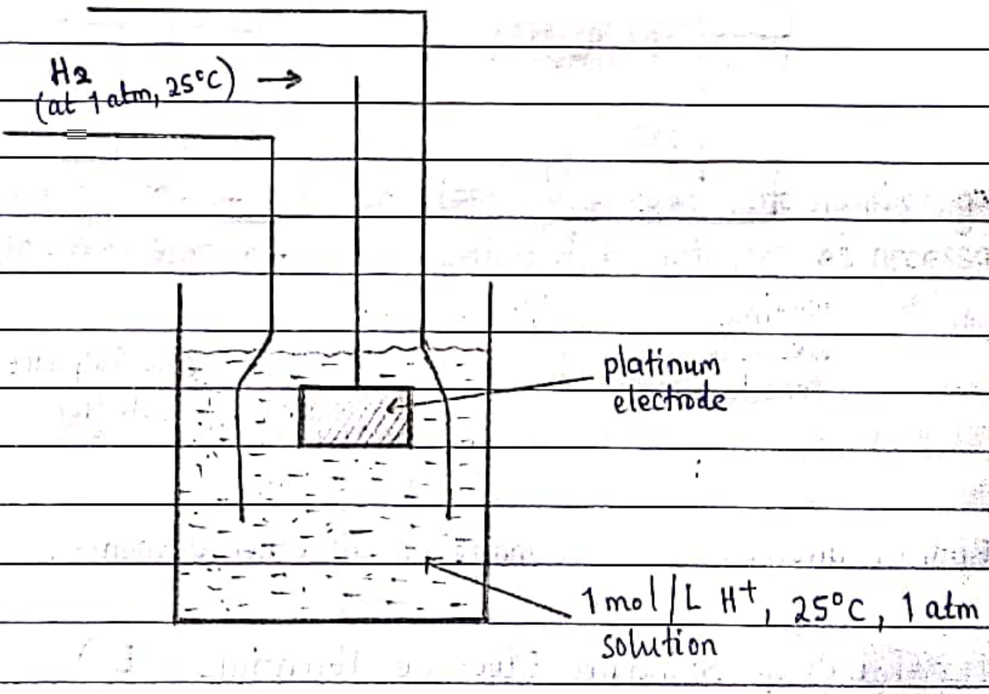
REDUCTION POTENTIAL

The reduction potential measures how easily a substance gets reduced. In other words, it measures the ability of a substance to accept electron The higher the reduction potential the more easily the element gets reduced Hence the better the element is an oxidising agent. The lower the reductio potential, the harder it is to reduce the element. Hence the better the reducing agent it is.

Important! The higher the reduction potential (E), the more easily the element gets reduced. Thus the better the oxidising agent.
The lower the reduction potential, the more difficult it is to reduce (but oxidises easily) therefore the better it is as a reducing agent.

Standard Hydrogen Electrode (S.H.E)

The reduction potential of hydrogen under standard conditions (25°C, 1 atm, 1 mol/L H^+) has been measured to be 0.000 V and is referred to as the standard hydrogen electron
Since its reduction potential is at standard conditions, the symbol is E



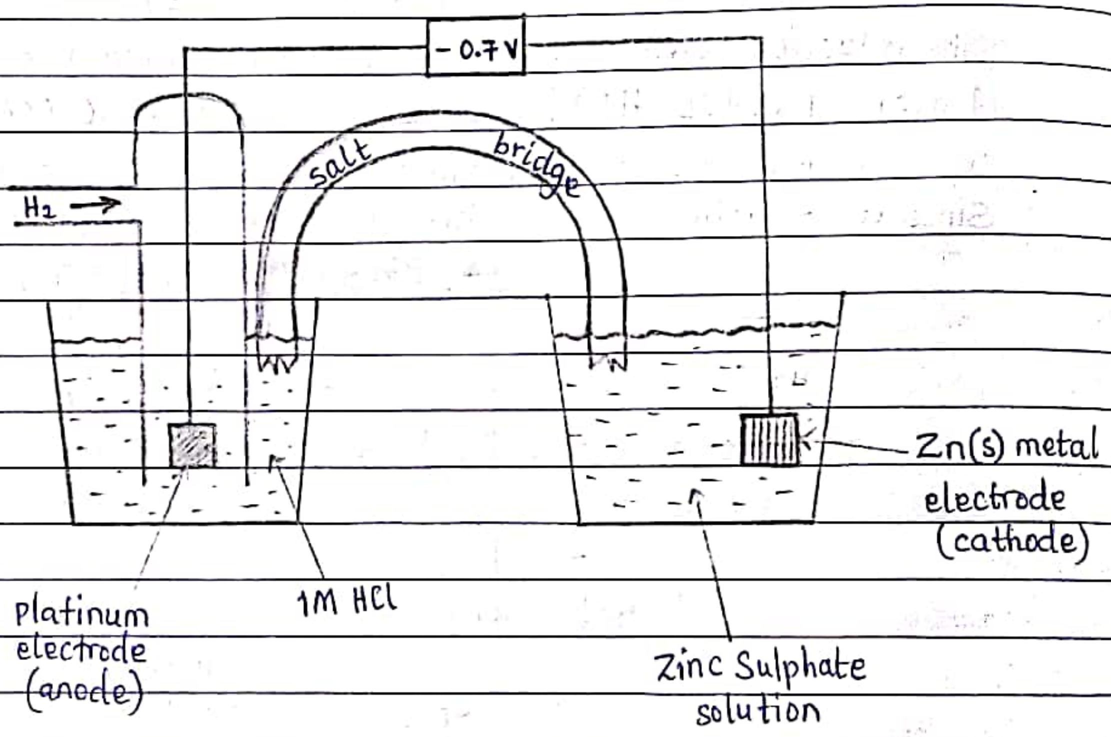
The reaction taking place in S.H.E is given below

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

Therefore, $E^\circ_{S.H.E} = 0.000\text{ V}$. The electrode used in the S.H.E is plat which is an inert electrode. Inert electrodes are used when no solids are invol in the reaction. Any metal connected to S.H.E will reflect the reduction pote for that metal (provided the S.H.E is put at the anode).

Standard Reduction Potentials (E°)

These are reduction potentials measured under standard conditions. All E° values are obtained using the S.H.E because you cannot get E of an element on its own. Therefore, S.H.E is the referrence point for all E° values.



Similar arrangements were made for all other elements.

Table of Standard Electrode Potentials (E°)

Reaction	E°	
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.03 V	↑ good reducing agents
$K^+(aq) + e^- \longrightarrow K(s)$	-2.92 V	
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76 V	
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00 V	
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	$+0.34$ V	↓ good oxidising agents
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	$+0.80$ V	

Combining Half-Cells

You can combine two half cells to make a complete galvanic cell, also known as a Voltaic cell.

Cell Potential (E_{cell})

Cell potential is the 'pull' or driving force on the electrons. It is also calle the Electromotive Force (E.M.F).

Under standard conditions, it is called Standard Cell Potential (E°_{cell})

$$E^\circ_{cell} = \underset{\substack{\text{(reduction)} \\ \text{potential}}}{E^\circ_{cathode}} - \underset{\substack{\text{(reduction)} \\ \text{potential}}}{E^\circ_{anode}}$$

NOTE: Since the number of electrons lost must equal the number gained, the half-reactions must be multiplied by integers as necessary to achieve the balanced equation. HOWEVER, the value of E° is not changed when a half-reaction is multiplied by an integer. Since a standard reduction potential is an intensive property (it do not depend on how many times the reaction occurs), the potential is not multiplied by the integer required to balance the cell reaction.

A GALVANIC CELL IS FULLY DESCRIBED BY THE FOLLOWING FOUR ITEN

1. The Cell potential (always positive) and the balanced cell reaction.
2. The direction of electron flow obtained by examining the half-reactions and using the direction that gives a positive cell potential.
3. Designation of the anode and cathode (a diagram may help).
4. The nature of each electrode and the ions present in each compartment. A chemically inert conductor is required if none of the substances takin part in the half-reaction is a conducting solid (a line notation may help.

Que : Describe completely the galvanic cell based on the following half-reactions under standard conditions :

$Ag^+ + e^- \longrightarrow Ag$ $\quad \mathcal{E}^\circ = 0.80$ volts, equation 1.

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\quad \mathcal{E}^\circ = 0.77$ volts, equation 2.

Answer : Since a positive cell potential is required, equation 2 must run in reverse.

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\quad \mathcal{E}^\circ = 0.77$ volt

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $\quad \mathcal{E}^\circ = -0.77$ volt

The cell reaction is: $Ag^+ + e^- + Fe^{2+} \longrightarrow Ag + Fe^{3+} + e^-$

$$Ag^+_{(aq)} + Fe^{2+}_{(aq)} + \cancel{e^-} \longrightarrow Ag_{(s)} + Fe^{3+}_{(aq)} + \cancel{e^-}$$

$$Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Ag(s) + Fe^{3+}(aq)$$

The cell potential is : $\mathcal{E}^\circ_{cell} = \mathcal{E}^\circ_{cathode} - \mathcal{E}^\circ_{anode}$

$$\mathcal{E}^\circ_{cell} = 0.80 - 0.77$$

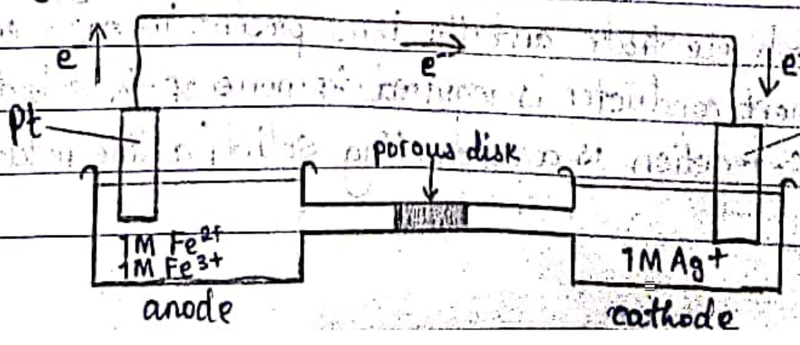
$$\mathcal{E}^\circ_{cell} = 0.03 \text{ volt}$$

* Electrons will flow from the compartment containing Fe^{2+} to the compartment containing Ag^+.

* Oxidation occurs in compartment containing Fe^{2+} hence this compartment functions as the anode. Reduction occurs in the compartment containing Ag^+, so this compartment functions as the cathode.

* The electrode in the Ag/Ag^+ compartment is silver metal and an inert conductor such as Platinum must be used in the Fe^{2+}/Fe^{3+} compartment. Appropriate counterions are assumed to be present. The line notation for this cell is : $Pt(s) \mid Fe^{2+}(aq), Fe^{3+}(aq) \parallel Ag^+(aq) \mid Ag(s)$.

The diagram for this cell is shown below :



Que 1. Construct a galvanic cell using $Mg_{(s)}$ and $Al_{(s)}$ given the standard electrode potentials below :

$$Al^{3+} + 3e^- \rightleftharpoons Al_{(s)} \Rightarrow -1.66\ V$$
$$Mg^{2+} + 2e^- \rightleftharpoons Mg(s) \Rightarrow -2.37\ V$$

st Step : Determine which reaction occurs at the anode and which one occurs at the cathode.

Remember : The standard way of setting up a Galvanic cell is by ensuring that the anode is always on the left.

Since Magnesium reaction has the lower electrode potential, it shall be on the anode (-ve), whereas the Aluminium reaction takes place at the cathode (+ve). If this is so, the reaction for magnesium will be changed, as well as the sign of it's cell potential reduction.

$$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg(s) \longrightarrow E^\circ = -2.37\ V$$
$$Mg(s) \rightleftharpoons Mg^{2+}(aq) + 2e^- \quad E^\circ = -(-2.37)\ V$$
$$E^\circ = 2.37\ V.$$

Therefore, we have :

$$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al\ (s) \quad E^\circ = -1.66\ V$$

$$Mg(s) \rightleftharpoons Mg^{2+}(aq) + 2e^- \ , \ E^\circ = 2.37\ V$$

Here we shall now balance the number of electrons for both equations:

$$2\times(Al^{3+} + 3e^- \rightleftharpoons Al) \longrightarrow E^\circ = 2\times -1.66\ V$$
$$3\times(Mg(s) \rightleftharpoons Mg^{2+} + 2e^-) \longrightarrow E^\circ = 3\times 2.37\ V$$
$$2Al^{3+} + 6e^- \rightleftharpoons 2Al \longrightarrow E^\circ = -3.32\ V$$
$$3Mg \rightleftharpoons 3Mg^{2+} + 6e^- \longrightarrow E^\circ = 7.11\ V$$

Combining the two half cell reactions, we have :

$$2Al^{3+} + 3Mg + 6e^- \rightleftharpoons 2Al + 3Mg^{2+} + 6e^-$$

LINE NOTATIONS

Anode Cathode

$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

electrode electrode

Given that $Zn(s) \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$ is at the anode and $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu(s)$ is at the cathode.

NOTE : The presentation of a reaction in line notation must not be balanced, rather it should be as simple as possible.

Construct a galvanic cell of the following two reactions :

$2e^- + Zn^{2+}(aq) \rightleftharpoons Zn(s) \quad E^\circ = -0.76\ V$ ------(i)

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\circ = +0.34\ V$ ------(ii)

Changing eqn (i) so that it is at the anode, we have

$$Zn(s) \rightleftharpoons Zn^{2+} + 2e^- \quad E^\circ = 0.76\ V$$

this is because Zn has a lower reduction potential.

We maintain the second equation because it is at the cathode:

$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \ : E^\circ = 0.34\ V$$

Calculating the Reduction Potential of the Cell, we have :

$$\begin{array}{r} 0.76\ V \\ +\ 0.34\ V \\ \hline \underline{1.10\ V} \end{array}$$

* OTHER LINE NOTATIONS ARE GIVEN BELOW :

$Pt(s) \mid ClO_3^-(aq), ClO_4^-(aq), H^+(aq) \parallel H^+(aq), MnO_4^-(aq), Mn^{2+}(aq) \mid Pt(s)$

All the components involved in the redox rxn above are ions. Since none of these dissolved ions can serve as an electrode, a nonreacting (inert) conductor mu be used. The usual choice is Platinum.

Cell potential, electrical work and free energy.

$$E_{cell} = \frac{-w}{q}$$

when work is negative, it means the work is performed by an electrochemical cell. When the work is positive, it means the electrochemical cell needs work to be performed on it.
Free energy is simply the amount of energy available to do work.
Change in free energy ⇒ ΔG
Change in standard free energy ⇒ ΔG°

$\Delta G^\circ = -nF\Delta E^\circ$, where n = number of electrons, F = the Faraday constant and E° cell = cell potential.
The equation assumes a negative because the reaction in the electrochemical cell is not spontaneous.

For spontaneous reactions, $E^\circ = +$, $w = -(ve)$ and $\Delta G^\circ = -(ve)$

For unspontaneous reactions, $E^\circ = -(ve)$, $w = +(ve)$ and $\Delta G^\circ = +(ve)$

EXAMPLE:
Calculate ΔG° and ΔE° for the reactions that follow, giving the overall reaction and starting whether it is spontaneous or not.

(i) $MnO_4^-(aq) + 5e^- + 8H^+ \rightleftharpoons Mn^{2+}(aq) + 4H_2O$ $E^\circ = 1.5V$
(ii) $ClO_4^-(aq) + 2H^+ + 2e^- \rightleftharpoons ClO_3^-(aq) + H_2O$ $E^\circ = 1.19V$

$2 \times (MnO_4^-(aq) + 5e^- + 8H^+ \rightleftharpoons Mn^{2+}(aq) + 4H_2O)$
$5 \times (ClO_4^-(aq) + 2H^+ + 2e^- \rightleftharpoons ClO_3^-(aq) + H_2O)$

$2MnO_4^- + 10e^- + 16H^+ \rightleftharpoons 2Mn^{2+} + 8H_2O$
$5ClO_4^- + 10H^+ + 10e^- \rightleftharpoons 5ClO_3^- + 5H_2O$

* Equation 2 will be reversed because it has a lower reduction potential.

$$5ClO_3^-(aq) + 5H_2O \rightleftharpoons 5ClO_4^-(aq) + 10H^+ + 10e^-,\ E^\circ = -1.1$$

* Adding the two equations, we finally have:

$$2MnO_4^-(aq) + 10e^- + 16H^+ + 5ClO_3^-(aq) + 5H_2O \rightleftharpoons 2MnO_4^-(aq) + 8H_2O + 5ClO_4^- + 1$$

* Cancel out the water, the electrons and the hydrogen ions

$$2MnO_4^-(aq) + 5ClO_3^-(aq) + 6H^+ \rightleftharpoons 2Mn^{2+}(aq) + 5ClO_4^-(aq) + 3H_2O$$

$$\Delta E^\circ_{cell} = -1.19\,V + 1.51$$
$$\Delta E^\circ_{cell} = +0.32\,V$$

$$\Delta G^\circ = -nFE^\circ$$
$$\Delta G^\circ = -10 \times 96,458 \times 0.32$$
$$\Delta G^\circ = -308,752.$$

Therefore, the reaction is spontaneous because ΔG° is negative.

NOTE: A Galvanic cell runs spontaneously in the direction that gives a positive value for E_{cell} (cell potential).

NOTE: The work that can be accomplished when electrons are transferred through a wire depends on the "push" behind the electrons. This "push" is the thermodynamic driving force, and this driving force (the emf) is defined as the potential difference (in volts) between two points in the circuit. A Volt represents a Joule of work per Coulomb of charge transferred:

$$\text{emf} = \text{potential difference (V)} = \frac{\text{work (J)}}{\text{charge (C)}}$$

111 CONTINUATION OF ANSWER FOR QUESTION ONE FOUR PAGES BACK.

Calculating the cell potential, E°_{cell}, we have :

(i) the equation : $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

(ii) just to sum up the two cell potentials which will require the use of the changed reaction's, in this case that of Magnesium, value of cell potential.

For (i)

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$E^\circ_{cell} = -3.32 - (-7.11)$$
$$E^\circ_{cell} = -3.32 + 7.11$$
$$E^\circ_{cell} = 3.79 \text{ volts}$$

For (ii)

$$\begin{array}{rl} & E^\circ \text{ for anode} \\ + & E^\circ \text{ for cathode} \\ = & E^\circ \text{ for electrochemical cell} \end{array}$$

$$\begin{array}{rr} & 7.11 \text{ volts} \\ + & (-3.32) \text{ volts} \\ \hline + & 3.79 \text{ volts} \end{array} \quad \text{OR} \quad \begin{array}{rr} & 7.11 \text{ volts} \\ - & 3.32 \text{ volts} \\ \hline + & 3.79 \text{ volts} \end{array}$$

NOTE : Work flowing out of a system is indicated by a minus sign (-ve).

NOTE : In any real, spontaneous process some energy is always wasted — the actual work realized is always less than the calculated maximum.

NOTE : The maximum cell potential is directly related to the free energy difference between the reactants and the products in the cell.

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

NOTE : A particular arrangement of electrodes of Zinc and Copper (Zn & Cu) and solutions ($ZnSO_4$ and $CuSO_4$) is called the Daniell Cell.

Que: Determine whether a pure gold watch will dissolve in 1 M HNO_3 to form a Au^{3+} solution.

Ans: $Au_{(s)} \longrightarrow Au^{3+}_{(aq)} + 3e^-$ $E^\circ = 1.50$

$4H^+_{(aq)} + NO_3^- + 3e^- \longrightarrow NO + 2H_2O$ $E^\circ = 0.90\,v$

$Au_{(s)} + 4H^+_{(aq)} + NO_3^- + 3e^- \longrightarrow Au^{2+} + NO + 2H_2O + 3e^-$

$\Delta G^\circ = -nFE^\circ$

$\Delta G^\circ = -3 \times 96458 \times (-0.54)$

$\Delta G^\circ = 156305.7$

The reaction is not spontaneous, therefore the gold watch will not dissolve.

Que: Predict whether the reaction below is spontaneous or not.

$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$

Ans: Calculate ΔE° ($\mathcal{E}^\circ_{cell}$)

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (reduction) $E^\circ = +0.34\,V$

$Fe(s) \longrightarrow Fe^{2+} + 2e^-$ (oxidation) $E^\circ = -0.44\,V$

$$E^\circ_{cell} = 0.34 + (-0.44)$$
$$= 0.34 - 0.44$$
$$= -0.10 \text{ volt}$$

Therefore, the reaction is not spontaneous.

POINTS TO REMEMBER

emember: In order for a cell reaction to take place spontaneously, it is necessary that the cell potential (EMF = electromotoric force) is positive.

- The reaction in a galvanic cell is always a redox reaction that can be divided into two half-cell reactions
- The cell potential for the entire cell is the sum of the two half-cell potentials.

- In order to determine overall cell potentials from half-cell potentials, the following Gibb's equation is used:

$$\Delta G^\circ = -z \cdot F \cdot E^\circ$$

where ΔG° denotes the change in standard Gibb's energy while z denote the number of transferred electrons for the half-cell reaction.

Free energy is symbolized by G and defined by the relationship:

$G = H - TS$, where H is the enthalpy, T is the temperat and S is the entropy.

- The magnitude of ΔS_{surr} depends on the temperature.
- The sign of ΔS_{surr} depends on the direction of the heat flow.
- Nature tends to seek the lowest possible energy.
- The transfer of a given quantity of energy as heat produces a much greater percent change in the randomness of the surroundings at a low temperature than it does at a high temperature. Thus ΔS_{surr} depends directly on the quantity of heat transferred and inversely on temperature.
- Heat flow (constant P) = change in enthalpy = ΔH
- Under conditions of constant temperature (in Kelvins) and pressure, the following relationship for ΔS_{surr} holds:

$$\Delta S_{surr} = -\frac{\Delta H}{T}.$$

- The minus sign changes the [illegible] the system to the surroundings.

- The spontaneity of a process is determined by the entropy change it produces in the universe.
- The term ΔS_{surr} is temperature-dependant.

- For a process that occurs at constant temperature, the change in free energy (ΔG) is given by the equation:

$$\Delta G = \Delta H - T\Delta S.$$ All quantities here refer to the system.

- At constant temperature and pressure, the ΔS_{univ} is given by:

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$$

$$\Delta S_{univ} = -\frac{\Delta G}{T}$$

- A process carried out at constant temperature and pressure will be spontaneous only if ΔG is negative (−ve).
- A process (at constant T and P) is spontaneous in the direction in which the free energy decreases ($-\Delta G$ means $+\Delta S_{univ}$).

- Standard free energy change (ΔG°) is the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states.

- Le Chatelier's principle suggests that an increase in the concentration of one of the reactants in a chemical reaction favours the forward reaction.

- Since $G^\circ = -nFE^\circ$ and $G = -nFE$, $\Delta G = \Delta G^\circ + RT\ln Q$ because:

$$-nFE = -nFE^\circ + RT\ln Q$$

$$E = \frac{-nFE^\circ}{-nF} + \frac{RT\ln Q}{-nF}$$

$$E = E^\circ - \frac{RT\ln Q}{nF}.$$ Q = reaction quotient.

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CONCENTRATION CELLS

A cell in which both compartments have the same components but at different concentrations is called a Concentration cell. The difference in concentration is the only factor that produces a cell potential in this case and the voltages are typically small.

A concentration cell that contains a silver electrode and aqueous silver nitrate in both compartments. Because the right compartment contains 1 M Ag^+ and the left compartment contains 0.1 M Ag^+, there will be a driving force to transfer electrons (e^-) from the left to the right. Silver will be deposited on the right electrode, thus lowering the concentration of Ag^+ in the right compartment. In the left compartment the silver electrode dissolves (producing Ag^+ ions) to raise the concentration of Ag^+ in solution.

* The Nernst Equation is given below :

① $\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log Q$ (for standard temperature).

where $Q = \frac{[\overset{\text{products}}{\text{concentrated}}]^m}{[\underset{\text{reactants}}{\text{diluted}}]^n}$, m is the stoichiometric coefficient of the concentrated solution, and n is the stoichiometric coefficient of the dilute solution.

② $\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln Q$ (for non-standard temperature).

E: The potential calculated from the Nernst equation is the maximum potential before any current flow has occured. As the cell discharges and current flows from anode to cathode, the concentrations will change and as a result $\mathcal{E}^\circ_{cell}$ will change. The cell will spontaneously discharge until it reaches equilibrium at which point $Q = K$ and $\mathcal{E}_{cell} = 0$.

K = is the equilibrium constant.

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* A "dead" battery is one in which the cell reaction has reached equilib and there is no longer any chemical driving force to push electrons thro the wire.

NOTE: At equilibrium, the components in the two cell compartments have the same free energy and $\Delta G = 0$ for the cell reaction at equilibrium concentrations. The cell no longer has the ability to do work.

NOTE: For a reaction below, Q will be given as:

$$aA + bB + cC \longrightarrow dD + eE + gG$$

$$Q = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[D]^d[E]^e[G]^g}{[A]^a[B]^b[C]^c}$$

, where small letters are the stoichiometric coefficients of the substances and bloc (capital) letters for their concentrations.

CALCULATION OF EQUILIBRIUM CONSTANTS FOR REDOX REACTIONS

The quantitative relationship between $\mathcal{E}^\circ$ and ΔG° allows calculation of equilibrium constants for redox reactions. For a cell at equilibrium,

$$\mathcal{E}_{cell} = 0 \quad \text{and} \quad Q = K.$$

Applying these conditions to the Nernst equation valid at 25°c,

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n}\log(Q)$$

gives $$0 = \mathcal{E}^\circ - \frac{0.0591}{n}\log(K)$$

or $$\log(K) = \frac{n\mathcal{E}^\circ}{0.0591} \quad \text{at } 25^\circ c \ (298.15K).$$

NOTE AND REMEMBER: The concentrations of pure solids and pure liquids do not appear in the expression of Q.

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Batteries

A battery is a galvanic cell or, more commonly, a group of galvanic cells connected in series, where the potentials of the individual cells add up to give the total battery potential.

THE LEAD STORAGE BATTERY

- This type of battery can function for several years under temperature extremes from - 30°F to 120°F.
- In this battery, lead serves as the anode and lead coated with lead dioxide serves as the cathode.
- Both electrodes dip into an electrolyte solution of sulphuric acid.

The reactions at the electrodes are given below:

Anode : $Pb + HSO_4^- \longrightarrow PbSO_4(s) + \cancel{H^+} + \cancel{2}e^-$

Cathode : $PbO_2 + HSO_4^- + \cancel{3H^+} + \cancel{2}e \longrightarrow PbSO_{4(s)} + 2H_2O$

Cell reaction : $Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O($

Sulphuric acid = $H_2SO_4(aq)$

- In this cell reaction, sulphuric acid is consumed as the battery discharges. This lowers the density of the electrolyte solution.
- The solid lead sulphate formed in the cell reaction during discharge adheres (or sticks) to the grid surfaces of the electrodes. The battery is recharged by forcing current through it in the opposite direction to reverse the cell reaction.
- The Lead storage battery is rechargeable. The battery is recharged by a process of electrolysis when an external voltage is applied at the anod and cathode. The overall of the electrolysis reaction is exactly the opposite of the normal cell reaction.

1/18 SPONTANEITY OF REDOX REACTIONS

- Chemical energy is converted to electrical energy. Electrical energy in this case is the product of the emf of the cell and the total electrical charge (in coulombs) that passes through the cell:

Electrical energy = volts x coulombs
= joules

- The total charge is determined by the number of moles of electrons (n) that pass through the circuit. By definition:

total charge = nF, where F is faraday constant (96485 c/mol and n is the number of moles of electrons exchanged between the reducing agent and the oxidizing agent in the overall redox requation

- The measured emf is the maximum voltage that the cell can achieve. This value is used to calculate the maximum amount of electrical energy that can be obtained from the chemical reaction. This is the energy that is used to do electrical work (W_{ele}) so; remember Work = charge x voltage

$$W_{max} = W_{ele}$$

$$W_{max} = -nF\mathcal{E}_{cell} = W_{ele} = -nF\mathcal{E}_{cell}$$

The negative sign on the right-hand-side of the equation indicates that the electrical work is done on the environment or surroundings by the system.

- The standard free-energy change ΔG° for a reaction is related to its equilibrium constant as follows:

$$\Delta G^\circ = -RT\,\text{In}K$$

$$\Delta G^\circ = -nF\mathcal{E}^\circ_{cell}$$

$$-nF\mathcal{E}^\circ_{cell} = -RT\,\text{In}K$$

$$\mathcal{E}^\circ_{cell} = \frac{-RT}{-nF}\,\text{In}K$$

$$\mathcal{E}^\circ_{cell} = \frac{RT}{nF}\,\text{In}K$$ where $R = 8.3145\ \text{J mol}^{-1}\text{K}^{-1}$

- When it is at standard temperature 25°C (298.15 K), $\mathcal{E}^\circ$ cell becomes:

$$\mathcal{E}^\circ_{cell} = \frac{0.0257\ V}{n}\,\text{In}K.$$

A Battery is an electrochemical cell, or a series of combined electrochemical cells, that can be used as a source of direct electric current at a constant voltage.

THE DRY CELL BATTERY (THE LECLANCHÉ CELL)

The voltage produced by a dry cell is about 1.5 V. The anode of a dry cell consists of a zinc can or container that is in contact with manganese dioxide (MnO_2) and an electrolyte. The electrolyte consists of ammonium chloride and zinc chloride in water, to which starch is added to thicken the solution to a pastelike consistency so that it is less likely to leak. A carbon (C) rod serves as the cathode, which is immersed in the electrolyte in the center of the cell.

The reactions in the cell are as follows:

Anode : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode : $2NH_4^+(aq) + 2MnO_2(s) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

CORROSION

- Corrosion can be viewed as the process of returning metals to their natural state — the ores from which they were originally obtained.
- Corrosion involves oxidation of the metal. Metals corrode because they oxidise easily. However, there are metals such as copper, gold, silver and platinum that are relatively difficult to oxidize. These are often called Noble metals.

Metals are easily oxidized because they have lower reduction potentials at standard states.

- Oxidation of most metals is spontaneous, by oxygen.
- When most metals are oxidized, they develop a thin oxide coating, which tends to protect their internal ~~organs~~ atoms against further oxidation.
- Copper forms an external layer of greenish copper carbonate called Patina.
- The corrosion of iron is an electrochemical reaction instead of being a direct oxidation process.

CORROSION OF IRON

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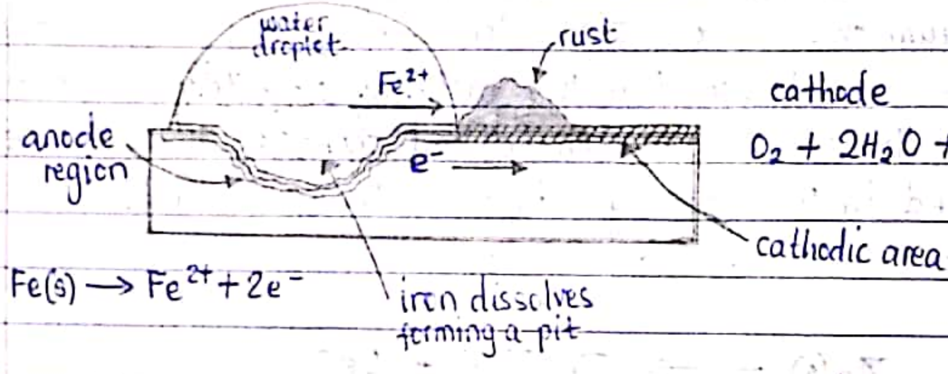
not corrosive

$O_2 + 4H^+ + 2e^-$ 1.23 Volts

corrosive



$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$Fe(s) \longrightarrow Fe^{2+} + 2e^-$

When they react, $$Fe^{2+} + O_2 + 4H_2O + (4+2n) \longrightarrow \underbrace{2Fe_2O_3}_{\text{rust}} \cdot nH_2O$$

- Steel has a nonuniform surface because the chemical composition is not completely homogenous. Physical strains leave stress points in the metal. These nonuniformities cause areas where the iron is more easily oxidized. These areas are called Anodic regions.
- In the anodic region, each iron atom gives up two electrons to form the Fe^{2+} ion: $Fe \longrightarrow Fe^{2+} + 2e^-$
  The electrons that are released flow through the steel, as they do through the wire of a Galvanic cell, to a cathodic region where they react with oxygen: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$
- The Fe^{2+} ions formed at the anodic areas travel to the cathodic areas through the moisture on the surface of the steel just as ions travel through a salt bridge in a Galvanic cell.
- In the cathodic regions Fe^{2+} ions react with oxygen to form rust, which is hydrated iron (III) oxide of variable composition.

Mass you want = mols of metal — moles of electrons — charge — tim
and curr

1. Que : Calculate the mass of copper that can be deposited onto the cathode by a current of 10 amps for 30 minutes?

Determine the amount of charge carried by the current.

1 amp = 1 coulomb/sec

$Q = It$
$Q = 10 \times 30 \times 60$
$Q = 18\,000$ c

1F = 96 485 coulomb/mole of e^-

96 485 coulombs = 1 mol of e^-
18 000 coulombs = x

$$x = \frac{18000}{96485} = 0.186557496 \text{ mols of } e^-$$

Now copper requires only 2 moles of electrons in its ionic form to m
63.55g of elemental solid copper.

$$Cu^{2+} + 2e^- \longrightarrow Cu(s)$$
$$2e^- \longrightarrow 63.55 \text{ g/mol}$$

How about $0.187\ e^- \longrightarrow x$?

Therefore, $2x = 63.55 \times 0.187$

$$\frac{2x}{2} = \frac{11.88385}{2}$$

$x = \underline{5.94\text{ g}}$ will be deposited onto the cathod

- The degree of hydration of the iron oxide affects the color of the rust, which may vary from black to yellow to the familiar reddish brown.
- Moisture has to be present to act as a kind of salt bridge between anodic and cathodic regions.
- Steel does not rust in dry air.
- Salt accelerates rusting.
- Chloride ions also accelerate rusting by forming very stable complex ions with Fe^{3+} and this factor tends to encourage the dissolving of the iron.
-

CHEMICAL KINETICS

- The area of chemistry that is concerned with the speeds, or rates, of reactions is called chemical kinetics.
  It relates how quickly a medicine is able to work, for example, and it also can relate to whether the formation and depletion of ozone in the upper atmosphere are in balance, and to industrial challenges such as the development of catalysts to synthesize new materials.
- Reactions involve the breaking and forming of bonds, the speeds of the reactions depend on the nature of the reactants themselves.

- Reactants must come together to react. The more readily molecules collide with each other, the more rapidly they react. Most reactions we consider are homogenous, involving either gases or liptuid solutions.

- Most chemical reactions proceed faster if the concentration of one or more of the reactants is increased. For example stell wool burns with difficulty in air which contains only about 21% O_2, but bursts into a brilliant flame in pure oxygen.

- **Catalysts** affect the kinds of collisions (the mechanism) that lead to **reaction**. They are agents that increase reaction rates without being used up
- **Reaction** rates also depend on the frequency of collisions between molecules
  The greater the frequency of collisions, the greater is the rate of reaction.
- For a collision to lead to a reaction, it must occur with sufficient energy to stretch bonds to a critical length and with suitable orientation for new bonds to form in the proper locations.

- The speed of a chemical reaction, also called its reaction rate is the change in the concentration of reactions or products per unit of time. Thus, the units for reaction rate are usually Molarity per second (M/s): that is, the change in concentration (measured in molarity) divided by a time interval (in seconds).

By convention, rates are always expressed as positive quantities. But because the concentration of reactants decrease with time, the change in concentration of reactants, Δ[reactant] is a negative number. Consequently, we use a negative sign to convert the negative Δ[reactant] to a positive rate.

It is typical for rates to decrease as a reaction proceeds, because the concentration of reactants decreases.

For a reaction whose stoichiometric relationships are not one to one, the rate of reaction is given by :

Reation equation : $aA + bB \longrightarrow cC + dD$

Reaction rate : $\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$

QUESTION : (a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2O_3(g) \longrightarrow 3O_2(g)$?

(b) If the rate at which O_2 appears, $\Delta[O_2]/\Delta t$, is 6.0×10^{-5} M/s at a particular instant, at what rate is O_3 disappearing at this same time $-\Delta[O_3]/\Delta t$?

ANSWER : (a) $2O_3(g) \longrightarrow 3O_2(g)$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

(b) $-\frac{\Delta[O_3]}{\Delta t} = 2 \times \frac{1}{3}\frac{\Delta[O_2]}{\Delta t} \Rightarrow \frac{2}{3}(6.0 \times 10^{-5}) = 0.00004$

$= 4.0 \times 10^{-5}$

$$-\frac{\Delta[O_3]}{\Delta t} = 4.0 \times 10^{-5} \text{ M/s.}$$

- Molecules are in continous random motion.
- As they move randomly, molecules collide with each other and energy is exchanged.
- These collisions are said to be elastic, meaning energy is conserved, not lost.
- $T \propto KE = \frac{1}{2}mv^2$

  Temperature is directly proportional to the energy of motion of the molecules (kinetic energy).
- When molecules collide, they must have sufficient energy called the Activation energy. This energy is needed to break bonds or form bond for a reaction to take place between two substances.
- In some reactions, direction of reaction also matters. An example is the reaction below:

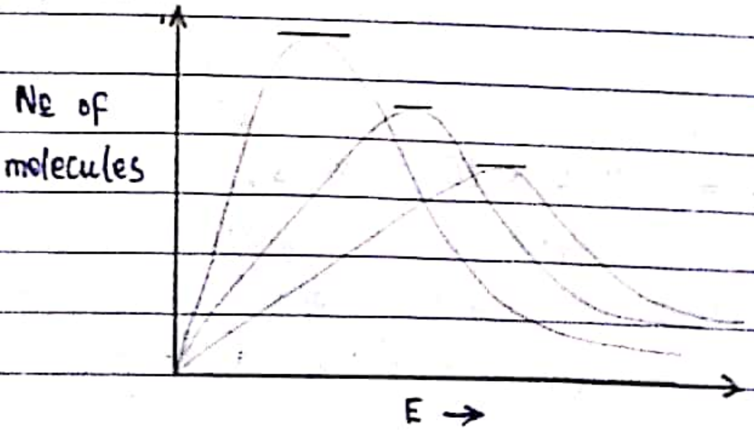
$$C_4H_9Cl + OH^- \longrightarrow C_4H_9OH + Cl^-$$

* The carbon-chloride bond is polar.

NOTE : In the case of the reaction above, the reaction will not take place because even though the reactants collide, they have a repelling force because of the like charges on the partially negative Cl atom and the negative OH ion.

- Do all particles have the same energy?

  Not all the particles have the same energy. This is called Maxwell Boltzmann distribution.



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- The higher the temperature, the lower the peak.

Every few molecules have high energy, and very few molecules have lower energy. Basically, most molecules have average energy.

FACTORS THAT AFFECT CHEMICAL REACTIONS.

1. Concentration
2. Pressure
3. Particle size
4. Temperature
5. Catalyst
6. Light

1. CONCENTRATION

An increase in concentration will increase the rate of the chemical reaction.

When there are more molecules, the chances of collision also increase.

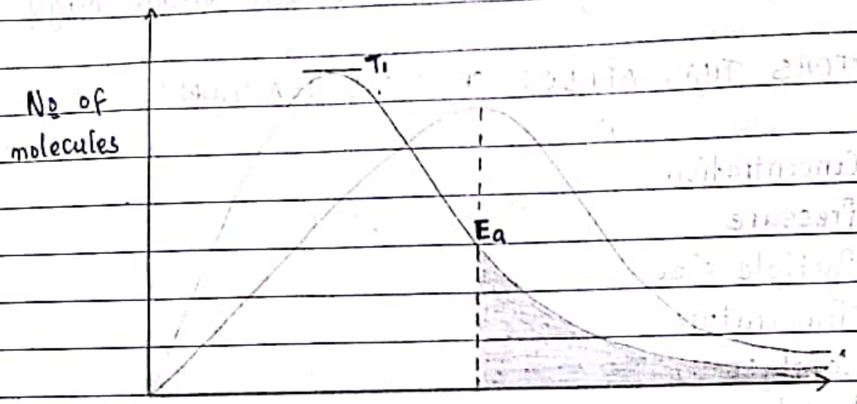
In gases, the effect of pressure is just the same as the effect of concentration on a chemical reaction.

Consider the reaction below:

$$CaCO_3 + 2HCl \longrightarrow CaCl + H_2O + CO_2$$

Putting a lump of $CaCO_3$ in 5M of HCl would trigger a reaction. However, only the particles on the surface of the lump of $CaCO_3$ will be able to react with the HCl.

If the lump is cut into four pieces, the surface area is increased and thus the reaction becomes faster. When the lump is ground into powder, the surface area increases even more and the number of particles that take part in the reaction increases. This eventually increases the overall rate of reaction.



2. TEMPERATURE

- Temperature is the measure of the average kinetic energy. The higher the temperature, the higher the velocity of the particles.

For a reaction to occur, the following are essential and inevitable:

1. Particles have to collide.
2. Particles have to be in the right orientation.
3. Particles have to have sufficient energy.

- In the graph diagram above, only the particles in the shaded region will be able to react.

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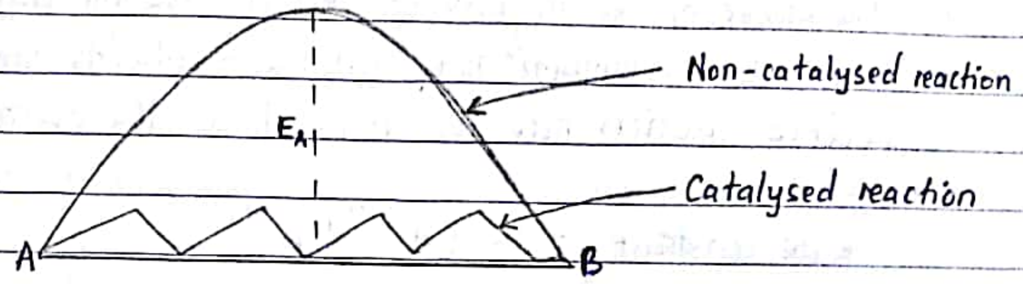
NOTE : Catalysts find the alternative route with lower activation energy. However, there are also catalysts that are able to lower the activation energy.



$$A + B \longrightarrow \text{Products}$$

- The rate of a reaction is given by the equation below:

$$\text{Rate} = k\,[A]^m\,[B]^n$$

, where k is the reaction constant, m is the order of reaction of A , n is the order of reaction of B.

$m + n$ is the overall order of reaction. They are whole numbers 0, 1, 2, 3, 4, ... (and so on.)

NOTE : Rate constant is constant at constant temperature.

$$-\frac{dx}{dt} = \text{Rate} = k\,[A]^m\,[B]^n$$

The order of reaction is related to the mechanism of the reaction.

- There are a few reactions with higher order e.g 10 or 9 e.t.c.
- Most reactions occur in lower orders, 0, 1, 2, 3, ... and so on.
- It is not necessary that the orders m and n should be the same, or in consecutive order.
- K is called the specific reaction rate.
- K is also called the rate constant.

- $m + n$ can not be determined stoichiometrically but they are determined practically in a laboratory.
- $m + n$ is the overall order of reaction.
- The order of reaction is related to the mechanism of the reaction.
- When the concentrations of all the reactants are 1 mol/dm³, the specific reaction rate will depend on the overall order of reaction.

$$\text{Rate constant} = K[A]^m[B]^n$$

$$= K(1)^m(1)^n$$

$$= K$$

$$mol\,dm^{-3}s^{-1} = K[mol\,dm^{-3}]^m[mol\,dm^{-3}]^n$$

- If $m = 1$ and $n = 0$, $rate = K[A]^1[B]^0$

$$rate = K[A]$$

$$\cancel{mol\,dm^{-3}}s^{-1} = K[\cancel{mol\,dm^{-3}}]$$

$$K = s^{-1}$$

This means that the overall order of reaction, $m+n$, is 1 because $m + n = 1 + 0 = 1$.

- K, the rate constant, changes with temperature and therefore determines how temperature affects the rate.

QUESTION ON ENTROPY AND FREE ENERGY WITH EQUILIBRIUM.

Que 1. The molar heats of fusion and vapourisation of benzene are 10.9 kJ/m and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid ⟶ liquid and liquid ⟶ vapour transitions for benzene At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.

Ans : At the melting point, solid benzene and liquid benzene are at equilibrium. Therefore, $\Delta G = 0$ and the entropy of fusion is given by : $\Delta G = \Delta H - T\Delta S$

$$\Delta G = 0 \quad ; \quad 0 = \Delta H - T\Delta S$$

$$\frac{T\Delta S}{T} = \frac{\Delta H}{T}$$

$$\Delta S = \Delta H / T$$

$$\Delta S = \frac{\Delta H_{fus}}{\Delta T_{fus}}$$

$$\Delta S = \frac{(10.9\ kJ/mol)(1000\ J/1\ kJ)}{(5.5 + 273.15)\ K}$$

$$\Delta S = \frac{10900\ J mol^{-1}}{278.65\ K}$$

$$\Delta S = \underline{\underline{39.1}}\ J/K{\cdot}mol$$

Similarly, at boiling point $\Delta G = 0$, we have then:

$$\Delta S = \Delta H_{vap} / \Delta T_{vap}$$

$$\Delta S = \frac{(31.0\ kJ mol^{-1})(1000\ J/1\ kJ)}{(80.1 + 273.15)\ K}$$

$$\Delta S = \frac{31000\ J mol^{-1}}{353.25\ K}$$

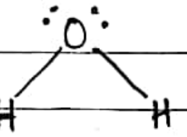
$$\Delta S = \underline{\underline{87.8}}\ J/K{\cdot}mol$$

Because $\Delta S_{vap} > \Delta S_{fus}$, vapourisation causes more disorder than the melting process.

MOLECULAR GEOMETRY

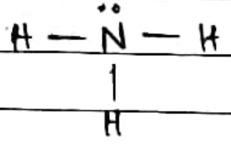
The polarity of a molecule (or lack thereof) influences physical properties such as solubility, boiling point, melting point, freezing point, vapour pressure, and chemical reactivity.

The first step in determining molecular geometry is to write the Lewis structure for a molecule, which gives the arrangement of valence electrons in terms of bonding pairs and lone pairs of electrons.



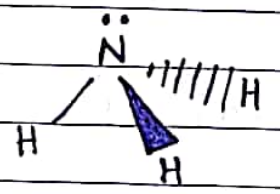
The Valence Shell Electron Pair Repulsion (VSEPR) model is then applied to determine a molecule's three-dimensional geometry (or shape). The basic premise of the VSEPR approach is that the electron pairs surrounding an atom in a molecule repel each other, and tend to minimize the repulsions by positioning themselves as far away from each other as possible. The application of VSEPR permits the prediction of molecular geometries and bond angles. This information can be used to subsequently determine other properties, such as molecular polarity.

For example, consider ammonia, NH_3, which has the Lewis structure:



The nitrogen atom (N) has four pairs of valence electrons, 3 bonding pairs (shared with H atoms) and 1 lone pair (unshared).
The VSEPR model predicts that the four pairs minimize repulsions by adopting a tetrahedral arrangement around the nitrogen (N). The arrangement of all electron pairs – bonding pairs and lone pairs – around the central atom is referred to as the electron pair arrangement

By contrast, the molecular geometry does not include the lone pairs, but only describes the geometric arrangement of the atoms in the molecule. Thus, in the example of NH_3, the electron pair arrangement is tetrahedral while the molecular geometry is trigonal pyramidal as shown below.



VSEPR allows the prediction of ideal bond angles; for the tetrahedral electron pair arrangement of the NH_3 molecule, the ideal H-N-H angle would be predicted to be 109.5°, the tetrahedral angle.

PROCEDURE FOR DRAWING LEWIS STRUCTURES

1. Add up the total # of valence electrons for all the atoms. Account for charge: If the species has a negative (-) charge: add one valence electron for each negative charge; for a positively charged (+) species, substract one electron for each positive charge.
2. Draw the molecular skeleton and connect the atoms with one bond. The central atom is generally the atom with the lowest electronegativity but never H.
3. Satisfy the Octet rule: Distribute the remaining valence electrons by adding lone pairs to complete the octets of the outer atoms first (H only requires 2 electrons), then place any remaining e^-s on the central atom.
4. If there are too few valence electrons to give each atom an octet, multiple bond(s) may be required. In this case, convert outer atom lone pairs to bond pairs to form multiple bonds.
5. There are some exceptions to the octet rule: 3rd period or heavier elements may more than have 8 electrons around them if needed (expanded valence shells). Atoms such as Be, B and Al may have less than an octet of electrons. In species with an odd number of electrons the least electronegative atom carries the odd electron.

- A way in which the rate of a reaction depends on the concentrations of the reactants can be expressed in the following equation for a hypothetical reaction:

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = k[A][B] = k[A]^m[B]^n$$

Such an equation that shows how the rate depends on the concentrations of the reactants is called a Rate Law.
The constant (k) in the rate law is called the Rate Constant.

- The magnitude of k changes with temperature and therefore determines how temperature affects rate.
- The exponents m and n are typically small whole numbers (usually 0, 1, or 2). These exponents, m and n, are called Reaction Orders. They indicate how the rate is affected by each reactant's concentration.
- If the rate law for a reaction is known and its rate for a set of reactant concentrations, the value of the rate constant, k, can be calculated.

E.G • For example, calculate the rate of reaction given the following data

$[A] = 0.100\,M$, $[B] = 0.100\,M$, $m = 1$, $n = 1$ and $k = 2.7 \times 10^{-4}\ M^{-1}s^{-1}$

$$\text{Rate} = k[A]^m[B]^n$$
$$\text{Rate} = 2.7\times10^{-4}[0.100]^1[0.100]^1$$
$$\text{Rate} = 2.7\times10^{-4} \times 0.010000$$
$$\text{Rate} = 0.0000027$$
$$\text{Rate} = 2.7\times10^{-6}\ M/s \text{ or } Ms^{-1}.$$

OTE: When the concentrations of all the reactants are 1 mol/dm³ or 1 M the specific reaction rate will depend on the overall order of reaction:
$m + n$ = overall order of reaction.

- Initial rates can be used to determine rate laws.
- The rate law for any chemical reaction must be determined experimentally
- The effects of changing the initial concentrations of the reactants are observed on the initial rate of the reaction.

$$Rate = k[\text{reactant } 1]^m[\text{reactant } 2]^n$$

Thus, the task of determining the rate law becomes one of determining the reaction orders, m and n.

NOTE • In most reactions the reaction orders are 0, 1, or 2.
If a reaction is zero-order in a particular reactant, changing its concentration will not affect the rate in any way (as long as some of the reactant is present) because any concentration raised to the power zero is equal to 1 (one).

- When the reaction order is one in a reactant, changes in the concentration of that reactant will produce proportional changes in the rate. Thus, doubling the concentration of the reactant will double the rate and so on
- When the rate law is second order in a particular reactant, doubling its concentration increases the rate by a factor of $2^2 = 4$, tripling its concentration causes the rate to increase by a factor of $3^2 = 9$, and so forth.

NOTE • It is important to realize that the rate of a reaction depends on the concentration, but the rate constant (k) does not.

NOTE • The rate constant, k, is affected only by temperature and by the presence of a catalyst.

- Energy associated with a particular orbit (energy level) is given by :

$$\boxed{E = \frac{-b}{n^2}}$$

, where $b = 2.18 \times 10^{-18}$ J

n = the principal quantum number

- The change in orbit of an electron is given by :

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = -\left(\frac{b}{n_2^2}\right) - \left(-\frac{b}{n_1^2}\right)$$

$$\Delta E = -\left[\frac{b}{n_2^2}\right] + \frac{b}{n_1^2}$$

$$\Delta E = \frac{b}{n_1^2} - \frac{b}{n_2^2}$$

$$\boxed{\Delta E = b\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]}$$

$$\Delta E = \frac{hc}{\lambda}$$

$$\Delta E = hc\left(\frac{1}{\lambda}\right)$$

$$b\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = hc\left[\frac{1}{\lambda}\right]$$

$$\frac{b}{hc}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = \frac{1}{\lambda}$$

, where $n_2 > n_1$.

Therefore, the wavelength associated with electron transition is given by:

$$\boxed{\lambda = \frac{1}{\frac{b}{hc}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]}}$$

in metres (m).

- Rydberg's equation is also given by :

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Therefore, $$\lambda = \frac{1}{R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]}$$

For Spectral Lines

n_1, n_2 are integers with values 1, 2, 3, ..., ∞ called quantum numbers.

SERIES	n_1	n_2	REGION
Lyman	1	2, 3, 4 .... ∞	U.V
Balmer	2	3, 4, 5 ... ∞	UV / visible
Paschen	3	4, 5, 6 ... ∞	IR
Brackett	4	5, 6, 7 ... ∞	IR
Pfund	5	6, 7, 8 ... ∞	IR

NOTE: $R_H = \frac{b}{hc} = 10\,966\,898.08 \approx 1.097 \times 10^7 \text{ m}^{-1}$.

- When ∞ = n, the energy is zero.

Wave Property of Matter (The Wave Particle Duality).

- When particles are bound in an atom, they behave like waves and not solids.
- De Broglie proposed that the wavelength of a matter wave, λ, is given by the equation below:

$\lambda = h/mv$, where h = Plank's constant, m = mass, and v = velocity.

mportant!
- This equation connects a wave property, wavelength to particle properties, mass and velocity.

NOTE : $m \times v = P$ (momentum).

Heisenberg's Mathematical Formula and Analysis

- Mathematically, it is impossible to measure with complete precision both the particle's position and velocity at the same instance.

To measure a particle's position or velocity we have to bounce off another particle off it.

- The exact position and velocity of a particle cannot be determined simultaneously, no matter how cleverly measurements are done.
- The mathematical expression is :

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

The combination of the error in position (Δx) times the error in momentum ($\Delta p = mv$) must always be greater than Plank's constant.

These limitations prevents us from ever knowing or predicting where an electron will be at any particular instant instead probability is used.

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WAVE MECHANICS AND FUNCTIONS

- Wave functions foro electrons are called Orbitals.
  The acceptable wave functions are characterised by three quantum numbers: n, ℓ and m_ℓ that relate to size, shape and orientation of the orbital, respectively.
- Wave mechanisms views the probability of finding an electron at a given point as equal to the square of amplitude of the electron wave given by the wave function ψ^2.
  An electron behaves as if it is spread out around the nucleus in an electron cloud. Therefore, the probability of finding an electron varies from place to place, i.e electron density.
  In regions of high probability, there is high concentration of electrical charge (and mass), the electron density is high.

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FIRST – ORDER REACTIONS

- A first-order reaction is one whose rate depends on the concentration of a single reactant raised to the first power.
- For a reaction of the type of A ⟶ Products, the rate law may be first-order :

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

This form of a rate law, which expresses how rate depends on concentration, is called the Differential Rate Law.

- Using an operation from calculus called Integration, this relationship can be transformed into an equation that relates the concentration of A at the start of the reaction, $[A]_0$, to its concentration at any other time, t, $[A]_t$:

$$\ln[A]_t - \ln[A]_0 = -kt \quad \text{or} \quad \ln\frac{[A]_t}{[A]_0} = -kt$$

This form of the rate law is called the Integrated Rate Law. The function "ln" in the equation above is the natural logarithm.
The integrated rate law can also be written as:

$$\ln[A]_t = -kt + \ln[A]_0$$

as long as the units are the same for both $[A]_t$ and $[A]_0$.

- Given any three of the following quantities, we can solve for the fourth: k, t, $[A]_0$, and $[A]_t$.
- Thus you can use these equations, for example, to determine (1) the reactant concentration remaining at any time after the reaction has started, (2) the time required for a given fraction of a sample to react, or (3) the time required for a reactant concentration to fall to a certain level.

$$\boxed{k[A] = \text{Rate} = -\frac{\Delta[A]}{\Delta t}}$$ Differential Rate Law

$$\boxed{\ln[A]_t - \ln[A]_0 = -kt}$$ Integrated Rate Law

PRACTICE EXERCISE

Que 1. The decomposition of dimethyl ether, $(CH_3)_2O$, at 510°C is a first order process with a rate constant of $6.8 \times 10^{-4}\ s^{-1}$:

$$(CH_3)_2O\,(g) \longrightarrow CH_4\,(g) + H_2\,(g) + CO\,(g)$$

If the initial pressure of $(CH_3)_2O$ is 135 torr, what is the pressure of $(CH_3)_2O$ after 1420 seconds?

Ans: 51 torr

Que 2. The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of $1.45\ years^{-1}$ at 12°C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7}\ g/cm^3$. Assume that the average temperature of the lake is 12°C.

(a) What is the concentration of the insecticide on June 1 of the following year?

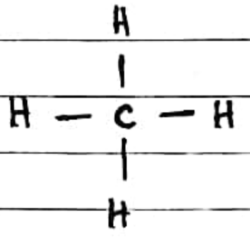
(b) How long will it take for the concentration of the insecticide to decrease to $3.0 \times 10^{-7}\ g/cm^3$?

Ans: (a) $1.2 \times 10^{-7}\ g/cm^3$

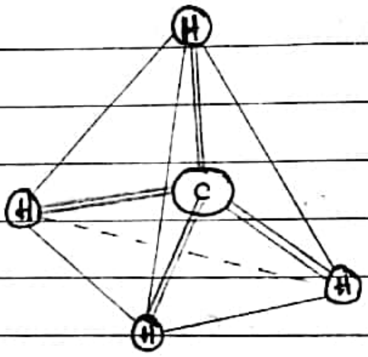
(b) 0.35 years

142 HYBRIDIZATION AND THE LOCALIZED ELECTRON MODEL

* In general we assume that bonding involves only the valence orbitals. If we consider methane and its bonding, the hydrogen atoms use 1s orbitals. The valence orbitals of a carbon atom are the 2s and 2p orbi



methane
(Lewis structure)



methane molecule
(tetrahedral molecular geometry)

Hybridization is a modification of the localized electron model to account for the observation that atoms often seem to use special atomic orbitals in forming molecules.

ALWAY
REMEM

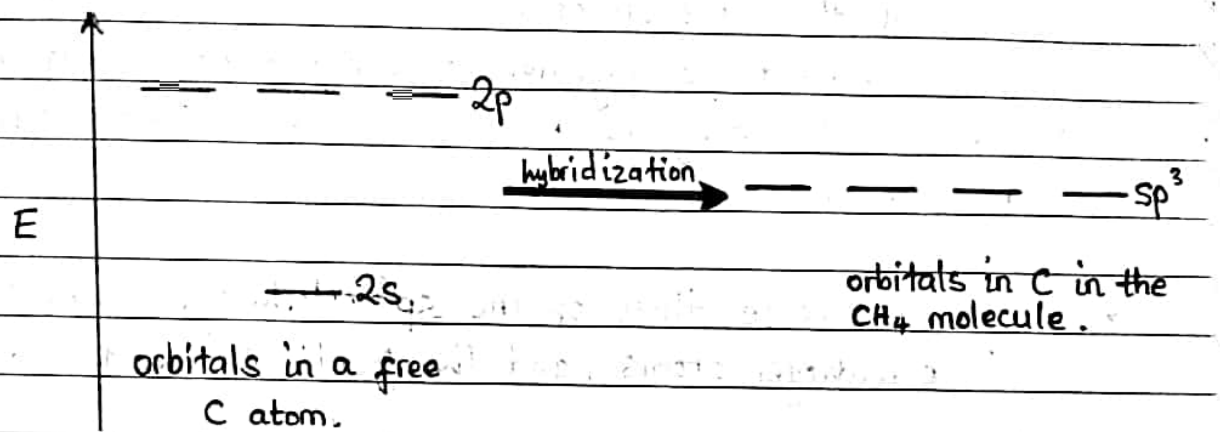
Important!

* Hybridization is the mixing of native atomic orbitals to form special orbitals for bonding.

- In the case of methane, the four new orbitals are called sp^3 orbitals because they are formed from one 2s and three 2p orbitals (s^1p^3). We say that the carbon atom undergoes sp^3 hybridization or is sp^3 hybridized.
- The four sp^3 orbitals are identical in shape, each one having a large lobe and a small lobe. The four orbitals are oriented in space so that the large lobes form a tetrahedral arrangement.

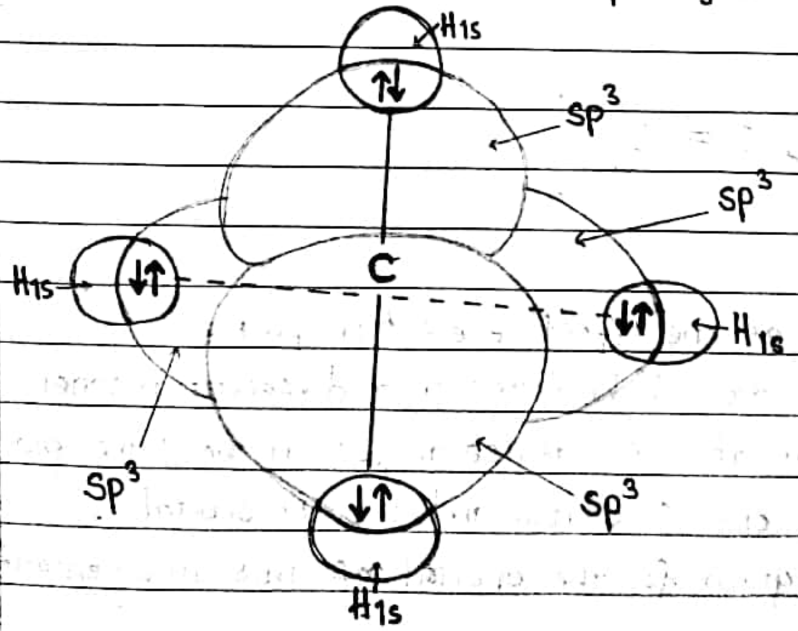
* sp^3 hybridization gives a tetrahedral set of orbitals.

- An energy-level diagram showing the formation of four sp^3 orbitals is given below:



The new sp^3 atomic orbitals on carbon are used to share electron pairs with the 1s orbitals from the four hydrogen atoms.

ALWAYS REMEMBER: Whenever a set of equivalent tetrahendral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes sp^3 hybridized.



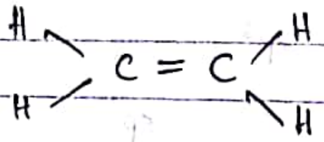
A complete description of the bonding in any compound involves three steps:

1. Writing the Lewis structure
2. Determining the arrangement of electron pairs using the VSEPR model
3. Determining the hybrid atomic orbitals needed to describe the bonding in the molecule.

- In NH_3 molecule three of the sp^3 orbitals are used to form bonds to the three hydrogen atoms, and the fourth sp^3 orbital holds the lone pair.
- The four electron pairs around the nitrogen atom in ammonia require a tetrahedral arrangement to minimize repulsions.

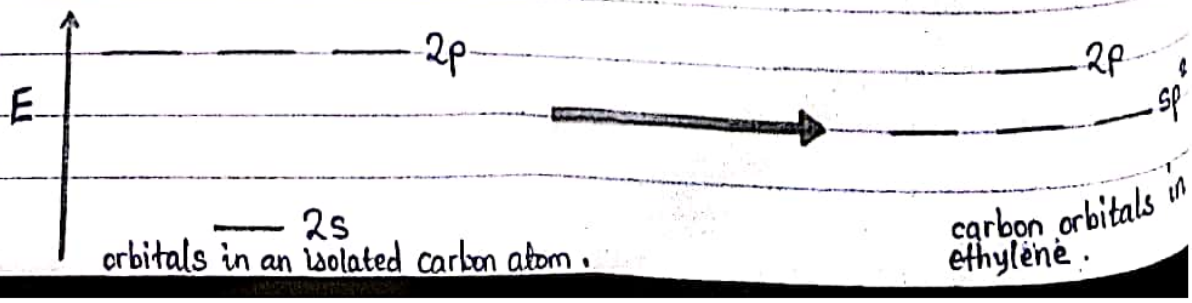
sp^2 HYBRIDIZATION

Ethylene (C_2H_4) is an important starting material in the manufacture o plastics. The C_2H_4 has 12 valence electrons and the following Lewis structure:



- A double bond acts as one effective electron pair.

In ethylene the carbon atom hybridizes in a different manner. A set o three orbitals arranged at 120-degree angles in the same plane can b obtained by combining one s orbital and two p orbitals.
The energy-level diagram for the orbital of this arrangement is giv below:



- The specific reaction rate does not change with time. However, it is characteristic of the reaction.
- Remember $mol dm^{-3} s^{-1} = M s^{-1}$

- Consider the information given below:

[A]	Rate of reaction
1. 0.50	2.00
2. 1.00	2.00
3. 1.50	2.00

TE: The data above tells us that the order of reaction of this particular reaction was 0 (zero).

- Rate is directly proportional to the concentration. This is shown in the data given below:

[A]	Rate of reaction
1. 0.50	1.00
2. 1.00	2.00
3. ~~1.50~~ 2.00	4.00

$$\text{rate} \propto [A]$$

This is true of a first order reaction, $m = 1$, $n = 0$.

Let the $\text{rate} = K[A]^m$

- Now let rate $= K[A]^M[B]^n$

	[A]	[B]	Rate of reaction
1.	0.2	0.1	1.12×10^{-3}
2.	0.2	0.2	4.48×10^{-3}
3.	0.4	0.1	2.24×10^{-3}

Let us take for example the two experiments in which the concentration of B was constant. In this case, we will take experiment 1 and 3.

$$\text{Rate} = K[A]^m[B]^n$$

$$\frac{1.12\times10^{-3}}{2.24\times10^{-3}} = \frac{\cancel{K}[0.2]^m\cancel{[0.1]^n}}{\cancel{K}[0.4]^M\cancel{[0.1]^n}}$$

$$\frac{1.12}{2.24} = \frac{[0.2]^m}{[0.4]^m}$$

$$\frac{1}{2} = \left[\frac{0.2}{0.4}\right]^m$$

$$0.5 = 0.5^m$$

$$\log 0.5 = \log 0.5^m$$

$$\log 0.5 = m\log 0.5$$

$$m = \frac{\cancel{\log 0.5}}{\cancel{\log 0.5}}$$

$$m = 1$$

Now let us take two experiments in which the concentration of A was constant. In this case, we will take experiments 1 and 2

$$\text{Rate} = K[A]^m[B]^n$$

$$1.12 \times 10^{-3} = K[0.2]^m[0.1]^n$$

$$4.48 \times 10^{-3} = \cancel{K}\,\cancel{[0.2]^m}[0.2]^n$$

$$\frac{1.12}{4.48} = \frac{[0.1]^n}{[0.2]^n}$$

$$0.25 = \left[\frac{0.1}{0.2}\right]^n$$

$$0.25 = 0.5^n$$

$$\log 0.25 = \log 0.5^n$$

$$\log 0.25 = n \log 0.5$$

$$n = \frac{\log 0.25}{\log 0.5}$$

$$\underline{\underline{n = 2}}$$

INTEGRATED RATE LAW

This law has the concentration of the reactants as the function of time.

For the first order of reaction, take for instance that we have the reaction (simple reaction) : $aA \longrightarrow \text{products}$

The rate is given by : $-\dfrac{\Delta[A]}{a\Delta t}$

$$\text{rate} = k[A]$$

$$-\frac{\Delta[A]}{a\Delta t} = k[A]$$

Rearrange and integrate as $t=0 \longrightarrow t=t$

$$[A]_0 \longrightarrow [A]_t$$

$$-\ln[A]_t = -\ln[A]_0 + akt$$

$$\underbrace{\ln[A]_t}_{} = \underbrace{\ln[A]_0}_{} - \underset{\downarrow}{\boxed{ak}}t$$

$$Y = C \quad m\,x$$

- $t_{1/2}$ is equal to half-life, i.e it is the time taken for the concentration to be reduced to half. It does not mean "half the time taken".

- $t_{1/2} = \frac{\ln 2}{ak}$

- For first order reactions, the half-life ($t_{1/2}$) is always constant.

Second Order Reactions

$$aA \longrightarrow \text{Products}$$

$$\text{rate} = -\frac{\Delta[A]}{a\Delta t}$$

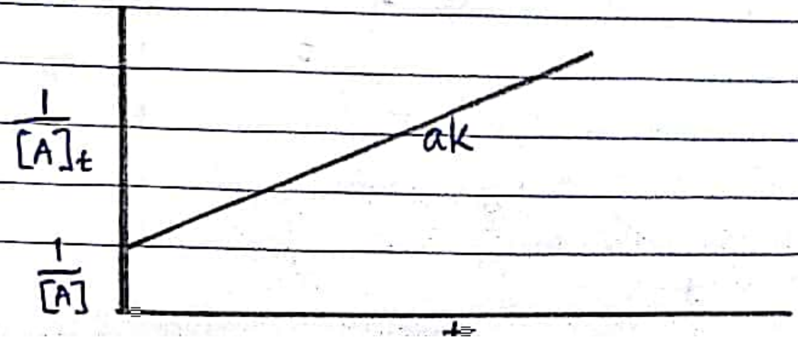
$$\text{rate} = k[A]^2$$

$$-\frac{\Delta[A]}{a\Delta t} = k[A]^2$$

Rearrange and integrate

$$\underset{y}{\underset{\uparrow}{\boxed{\frac{1}{[A]_t}}}} = \underset{c}{\underset{\uparrow}{\boxed{\frac{1}{[A]_0}}}} + \underset{mx}{\underset{\uparrow}{\boxed{ak}\,t}}$$

- If we plot the inverse of concentration, the slope will be positive.



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Half-life ($t_{1/2}$) : $t = t_{1/2}$

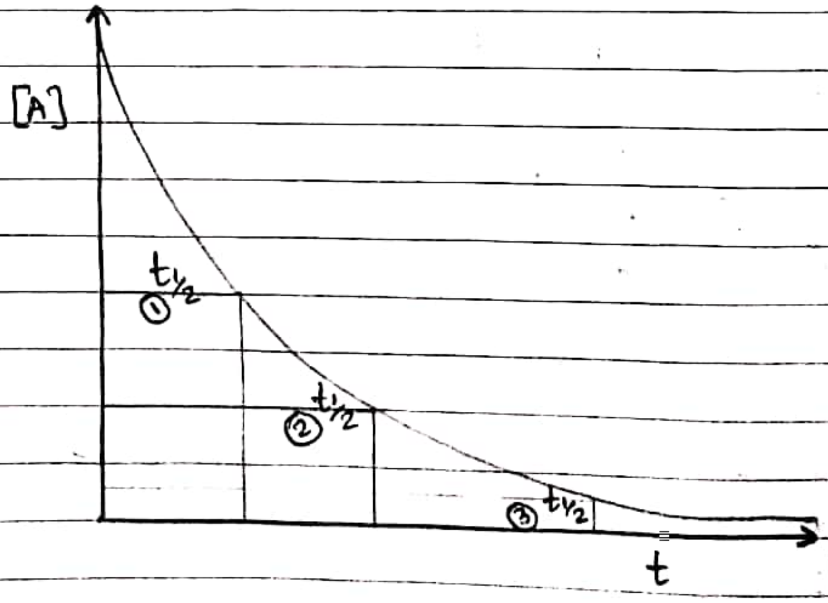
$$[A]_t = \frac{[A]_0}{2}$$

$$\frac{1}{\frac{[A]_0}{2}} = \frac{1}{[A]_0} + akt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = akt_{1/2}$$

$$\frac{1}{[A]_0} = akt_{1/2}$$

$$t_{1/2} = \frac{1}{ak[A]_0}$$



Zero Order Reactions

- Zero order reactions mean that the rate of reaction is independent of concentration.

$$\text{rate} = -\frac{\Delta[A]}{a\Delta t}$$

$$aA \longrightarrow \text{Products}$$

$$\text{rate} = ak$$

$$-\frac{\Delta[A]}{a\Delta t} = ak$$

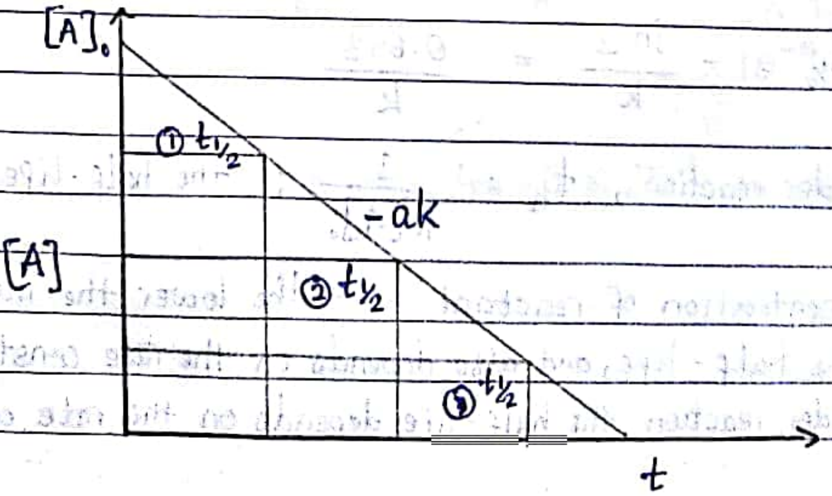
Rearrange and integrate

$$t = 0 \longrightarrow t = t$$

$$[A] = [A]_0 \longrightarrow [A]_t$$

$$[A]_t = [A]_0 - akt$$

$$y = c \quad mx$$



$$[A]_t = [A]_0 - akt$$

$$t = t_{1/2}$$

$$[A]_t = \frac{[A]_0}{2}$$

$$\frac{[A]_0}{2} = [A]_0 - akt_{1/2}$$

$$\frac{[A]_0}{2} - [A]_0 = -akt_{1/2}$$

$$\cancel{-}\frac{[A]_0}{2} = \cancel{-}akt_{1/2}$$

$$t_{1/2} = \frac{[A]_0}{2ak}$$

- Applications of half-life are the following: archaelogical dating, geological dating and carbon dating.
- Most reactions are first order reactions.
- A fast reaction will have a short half-life.
- $[A]_{t_{1/2}} = \frac{1}{2}[A]$ for first-order reactions.

$$t_{1/2} = -\frac{\ln\frac{1}{2}}{k} = \frac{0.693}{k}$$

- For second-order reactions, $t_{1/2} = \frac{1}{k[A]_0}$; the half-life depends on the initial concentration of reactant — the lower the initial concentratio the greater the half-life, and also depends on the rate constant.
- For a first-order reaction, the half-life depends on the rate constant.

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Que: A sample of a wood from an Egyptian mummy case has a half-life of 9.41. How old is the wood?

$t_{1/2} = 5730$ years

Activity in living plant = 15.3

$$t_{1/2} = \frac{\ln 2}{ak}$$

$$\ln[A]_t = \ln[A]_0 - akt$$

$$t_{1/2} = \frac{\ln 2}{ak}$$

$$ak = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730} = 1.2 \times 10^{-4}\, y^{-1}$$

Now $\ln[A]_t = \ln[A]_0 - akt$

$$\ln 9.41 = \ln 15.3 - 1.2 \times 10^{-4} t$$

$$1.2 \times 10^{-4} t = \ln 15.3 - \ln 9.41$$

$$t = \frac{\ln 15.3 - \ln 9.41}{1.2 \times 10^{-4}}$$

$$t = 4.05 \times 10^{3} \text{ years.}$$

- For some reactions, when the temperature of the reaction is increased by 10°C, the rate of reaction increases by 100%.
- Remember, temperature is the measure of kinetic energy.

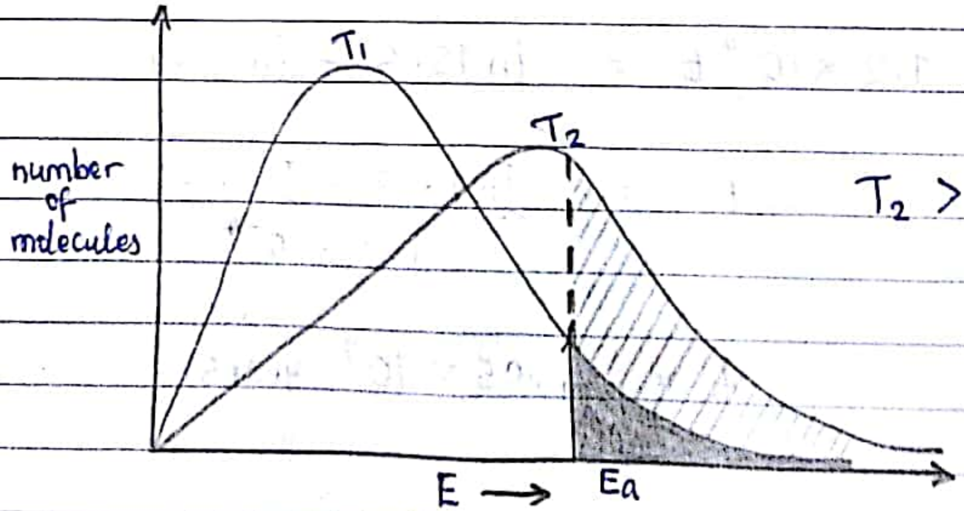
1. Collision Theory
2. Transition State Theory or Activated Complex Theory

$$T \propto KE$$
$$T \propto \frac{1}{2}mv^2$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_2}\right)^2$$

$$\frac{300}{310} = \left(\frac{V_1}{V_2}\right)^2$$

$$V_2 = 1.016\, V_1$$

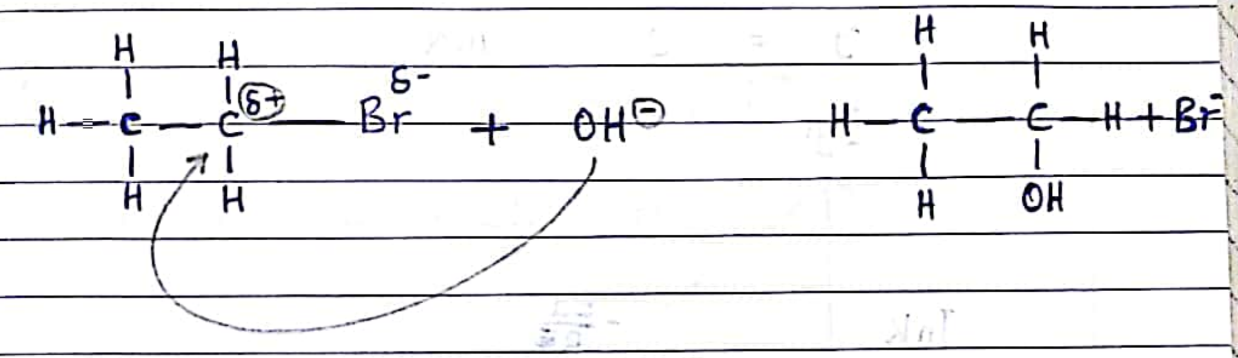


$T_2 > T_1$

- As the temperature increases, the peak lowers and the curves meet only once.

Activation Energy is the minimum energy required to start a reaction.

Activation energy = E_a.



NOTE : $e^{-\frac{E_a}{RT}}$

Fraction of molecules with sufficient energy $\propto e^{-\frac{E_a}{RT}}$

$f = e^{-E_a/RT}$ → This is the expression that gives the fraction of molecules that has an energy equal to or greater than Ea (activation energy).

rate $= k[A]^m$

A = Arrhenius constant.

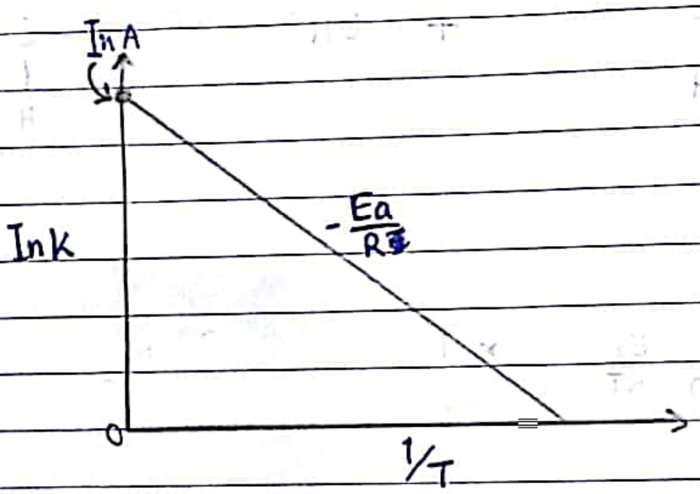
$K = Ae^{-\frac{E_a}{RT}}$

Upon collision, the Kinetic energy (K.E) of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions. That is, the kinetic energy is used to change the potential energy of the molecule.

To react, colliding molecules must have a total kinetic energy equal to or greater than some minimum value. The minimum value of energy required to initiate a chemical reaction is called the Activation Energy (E_a).

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\underset{y}{\ln k} = \underset{\boxed{c}}{\ln A} - \underset{\boxed{m}}{\frac{E_a}{R}}\underset{x}{\left(\frac{1}{T}\right)}$$



$$\text{Slope} = -\frac{E_a}{R}$$

When $T_1 \rightarrow K_1$
$T_2 \rightarrow K_2$

$$\ln K_1 = \ln A - \frac{E_a}{R}\left(\frac{1}{T_1}\right) \text{ ------ equation ①}$$

$$\ln K_2 = \ln A - \frac{E_a}{R}\left(\frac{1}{T_2}\right) \text{ ------ equation ②}$$

- The Arrhenius Equation

Arrhenius noted that most reactions show that the increase in rate wi increasing temperature is non-linear. Most reaction-rate data obeyed equation based on three factors: (a) the fraction of molecules possess an energy of Ea or greater, (b) the number of collisions occuring per sec and, (c) the fraction of collisions that have the appropriate orientation. All these three are incorporated into: $k = Ae^{-\frac{E_a}{RT}}$

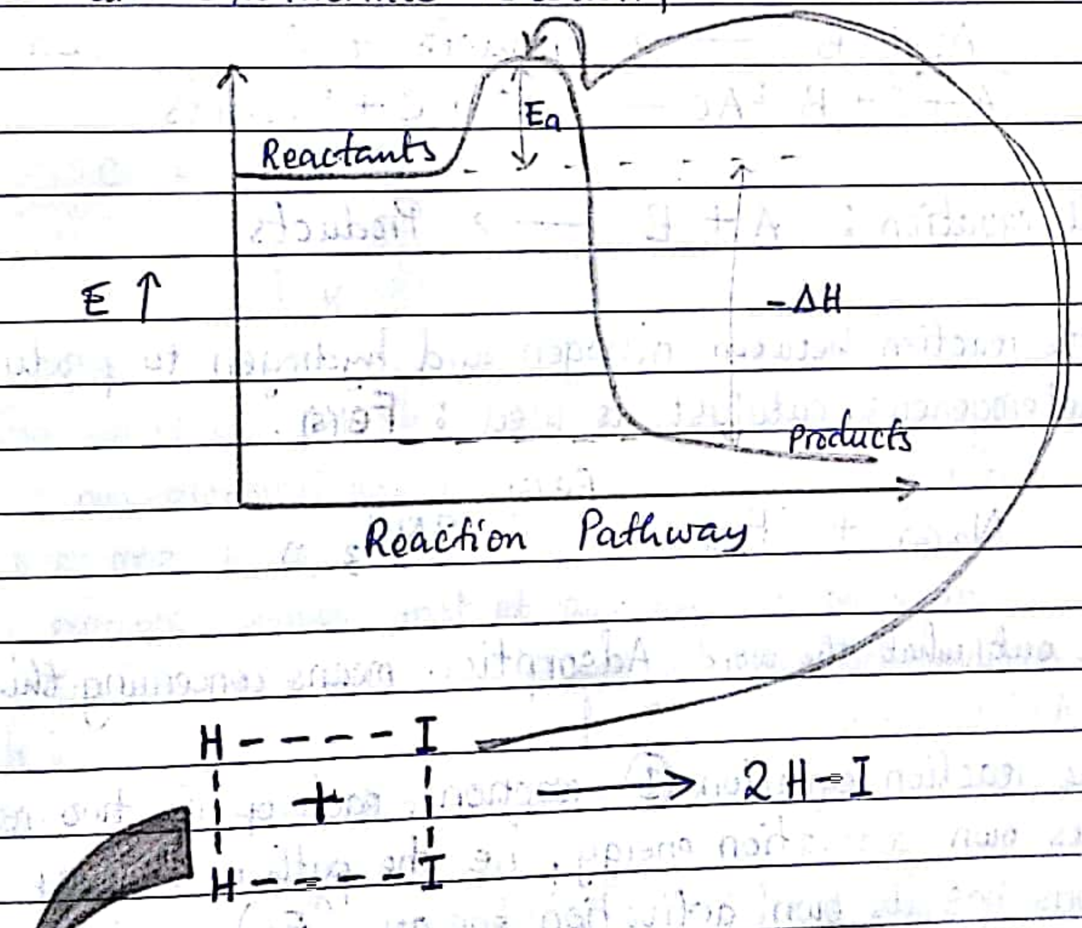
When equation ① − equation ②, we have:

$$\ln K_1 - \ln K_2 = \left(\cancel{\ln A} - \frac{E_a}{R}\left(\frac{1}{T_1}\right)\right) - \left(\cancel{\ln A} - \frac{E_a}{R}\left(\frac{1}{T_2}\right)\right)$$

$$\ln K_1 - \ln K_2 = -\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \frac{E_a}{R}\left(\frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

For an Exothermic reaction,



$$H_2 + I_2 \longrightarrow 2HI$$

This is called the Activation Complex. It occurs when weak bonds form between all the atoms for the reacting species; and there is neither the reactants or products. It is an intermediate phase.

CATALYSTS

A catalyst alters the rate of a chemical reaction.
Only a small amount of catalyst is usually required in a chemical reaction.
A catalyst is not consumed in the reaction.
A catalyst finds an alternative route with lower activation energy.

Reaction Equation ①.

$$A + B \longrightarrow \text{Products} \qquad E_a$$

$$A + C \longrightarrow AC \qquad E_a'$$

$$AC + B \longrightarrow \text{Products} + C \qquad E_a''$$

$$\overline{A + \cancel{C} + B + \cancel{AC} \longrightarrow \cancel{AC} + \cancel{C} + \text{Products}}$$

Overall equation : $A + B \longrightarrow \text{Products}$

In the reaction between nitrogen and hydrogen to produce ammonia an heterogenous catalyst is used : $Fe_{(s)}$.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{Fe_{(s)}} 2NH_{3(g)}$$

☺ * Check out what the word Adsorption means concerning this topic!

In the reaction equation ① reaction, each of the two reactions has its own activation energy, i.e the path of each of the two reactions has its own activation energy (E_a).

- A catalyst is a substance that changes the speed of a chemical reaction without undergoing a permanent change itself in the process.

- The activation energy for a given reaction can be determined by measuring k at a series of temperatures, graphing $\ln k$ versus $1/T$, and then calculating E_a from the slope of the resultant line.

  Taking the natural logarithms of $k = Ae^{-\frac{E_a}{RT}}$, we have:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$y = mx + c \quad \text{or} \quad y = bx + a.$$

A graph of $\ln k$ versus $1/T$ will be a line with a slope equal to $-E_a/R$ and a y-intercept equal to $\ln A$.

→ $m = b = -\frac{E_a}{R}$

→ $c = a = \ln A$

→ $y = \ln k$

- The equation $\ln k = -\frac{E_a}{RT} + \ln A$ can be used to evaluate E_a in a non-graphical way if we know the rate constant of a reaction at two or more temperatures.

  For example, suppose that at two different temperatures, T_1 and T_2, a reaction has rate constants k_1 and K_2. For each condition, we have:

  $\ln k_1 = -E_a/RT_1 + \ln A$ and $\ln K_2 = -E_a/RT_2 + \ln A$.

  Subtracting $\ln K_2$ from $\ln K_1$ gives:

$$\ln k_1 - \ln k_2 = \left(-E_a/RT_1 + \ln A\right) - \left(-E_a/RT_2 + \ln A\right).$$

Simplifying the above equation and rearranging it gives:

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

This provides a convienient way of calculating the rate constant, K_1, at some temperature, T_1, when u know the activation energy and the rate constant, K_2, at some temperature, T_2.

CONTINUATION ON FIRST-ORDER REACTIONS.

- The equation : $\text{In}[A]_t = -k \cdot t + \text{In}[A]_0$; can be used to verify whether a reaction is first order and to determine its rate constant. This equation has the form of the general equation for a straight line, $y = mx + c$ in which m is the slope and c is the y-intercept of the line.

$$\begin{array}{ccccc} \text{In}[A]_t & = & -kt & + & \text{In}[A]_0 \\ \updownarrow & & \updownarrow\;\updownarrow & & \updownarrow \\ y & = & m \cdot x & + & c \end{array}$$

NOTE • For a first-order reaction, a graph of $\text{In}[A]_t$ versus time gives a straight line with a slope of $-k$ and a y-intercept of $\text{In}[A]_0$.

NOTE • A reaction that is not first-order will not yield a straight line.

- As an example, consider the conversion of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN). Because experiments show that it is first order, we can write the rate equation :

$$\text{In}[CH_3CN]_t = -kt + \text{In}[CH_3CN]_0$$

Methyl isonitrile and Acetonitrile are isomers, molecules that have the same atoms arranged differently. This reaction is called Isomerization reaction.

Methyl isonitrile = CH_3NC.
Acetonitrile = CH_3CN.

NOTE • Pressure can be used as a unit of concentration for a gas because from the ideal-gas law: ($PV = nRT$), the pressure is directly proportional to the number of moles per unit volume: $P = MRT$, where M = molarity, T = temperature and R = the gas constant.

A plot of the natural logarithm of the pressure of methyl isonitrile against time as it rearranges in the gas phase at 198.9°C yields a straight line whose slope is $-5.1 \times 10^{-5}\ s^{-1}$. This equals $-k$ and therefore it is the rate constant for this reaction: $CH_3NC \longrightarrow CH_3CN$ at 198.9°C.

- This fact that a straight line fits the data confirms that the rate law is first-order.

SECOND - ORDER REACTIONS

- A second-order reaction is one whose rate depends on the reactant concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power.
- In this case, reactions of types A ⟶ Products and A+B ⟶ Product are considered.

Firstly, reactions of type A ⟶ Products or A + B ⟶ Products that are second order in just one reactant, A :

$$\text{Rate} = -\frac{\Delta [A]}{\Delta t} = k[A]^2$$

With the use of calculus, the differential rate law above can be used to derive the following integrated rate law :

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

This equation has four variables and any one of these can be found by calculation knowing the other three.

This equation also has the form of a straight-line ($y = mx + c$). If the reaction is second order, a plot of $1/[A]_t$ versus (t) will yield a straight line with a slope equal to k and a y-intercept equal to $1/[A]_0$.

- One way to distinguish between first- and second-order rate laws is to graph both $\ln[A]_t$ and $1/[A]_t$ against time t.

If the $\ln[A]_t$ plot is linear, the reaction is first-order; if the $1/[A$ plot is linear, the reaction is second-order.

PRACTICE EXERCISE

Que 1. The following data were collected for the gas-phase decomposition of nitrog dioxide at 300°C = 573.15 K, $NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$:

Time (s)	$[NO_2]$ (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Is the reaction first or second order in NO_2 ?

Ans: The reaction is second-order in NO_2.

Que 2. Consider again the reaction of decomposition of NO_2 discussed in Que. The reaction is second order in NO_2 with $k = 0.543 M^{-1}s^{-1}$. If th initial concentration of NO_2 in a closed vessel is 0.0500 M, what is the remaining concentration after 0.500 hours ?

Ans: $[NO_2] = 1.00 \times 10^{-3}$ M.

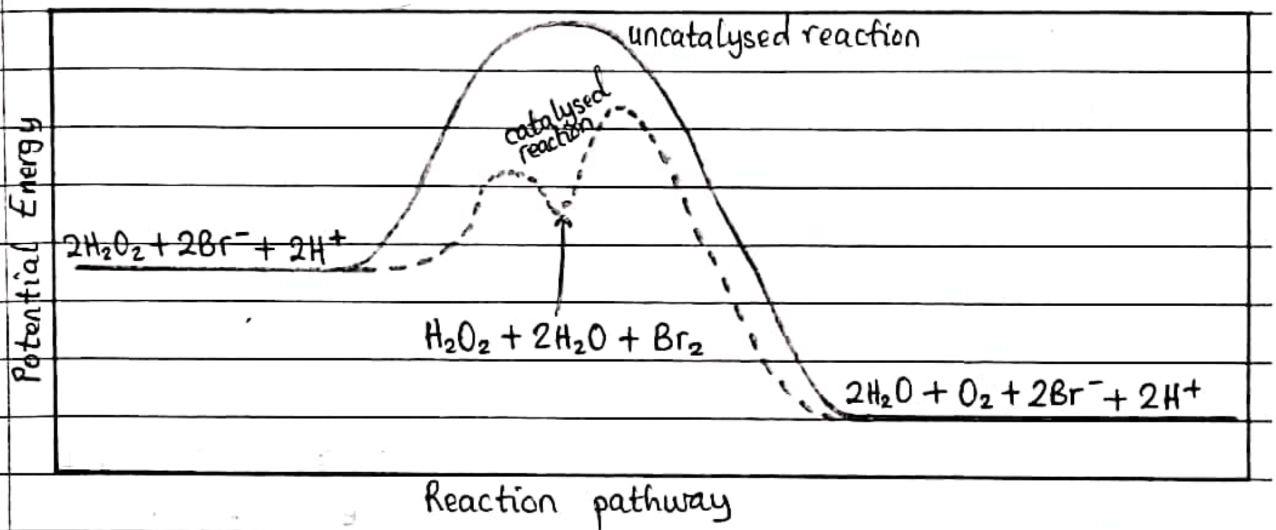
HOMOGENEOUS CATALYSIS

A Catalyst that is present in the same phase as the reacting molecules i called a Homogeneous catalyst. Examples abound both in solution and i the gas phase.

- A catalyst is there at the start of the reaction, whereas the intermedia is formed during the course of the reaction.
- On the basis of the Arrhenius equation, the rate constant (k) is determ by the activation energy (Ea) and the frequency factor (A). A catalyst affect the rate of reaction by altering the value of either Ea or A. Th most dramatic catalytic effects come from lowering Ea.

- As a general rule, a catalyst lowers the overall activation energy for a chemical reaction. This is done usually by provision of a different mechanism for the reaction.

In the decomposition of hydrogen peroxide, two successive reactions of H_2O_2, with bromide and then bromine, take place. Because these two reactions together serve as a catalytic pathway for hydrogen peroxide decomposition, both of them must have significantly lower activation energies than the uncatalysed decomposition, as shown schematically below:



NOTE: The energies of reactants and products are unchanged by the catalyst.

HETEROGENEOUS CATALYSIS

A Heterogeneous catalyst exists in a different phase from the reactant molecules, usually as a solid in contact with either gaseous reactants or with reactants in a liquid solution. Heterogeneous catalysts are often composed of metals or metal oxides. The initial step in heterogeneous catalysis is usually adsorption of reactants.

NOTE
- Adsorption refers to the binding of molecules to a surface, whereas Absorption refers to the uptake of molecules into the interior of another substance.

Adsorption occurs because the atoms or ions at the surface of a solid are extremely reactive. Also because the surface atoms and ions have unused bonding capacity. This unused bonding capacity can be used to bond molecules from the gas or solution phase to the surface of the solid.

THE RATE LAW : EFFECT OF CONCENTRATION ON RATE .

Consider the reaction below :

$$NH_4^+ (aq) + NO_2^- (aq) \longrightarrow N_2(g) + 2H_2O(l)$$

Because the exponent of $[NH_4^+]$ is 1, the rate is first-order in NH_4^+. The rate is also first-order in NO_2^-. The exponent "1" is not shown explicitly in rate laws. The overall reaction order is the sum of the orders with respect to each reactant in the rate law. Thus, the rate law has an overall reaction order of $1 + 1 = 2$, and the reaction is second-order overall.

The exponents in a rate law indicate how the rate is affected by the concentration of each reactant. Because the rate at which NH_4^+ reacts with NO_2^- depends on $[NH_4^+]$ raised to the first power, the rate doubles when $[NH_4^+]$ doubles, triples when $[NH_4^+]$ triples, and so forth. Doubling or tripling $[NO_2^-]$ likewise doubles or triples the rate.

If a rate law is second-order with respect to a reactant, $[A]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple ($[2]^2 = 4$), whereas tripling the concentration causes the rate to increase ninefold ($[3]^2 = 9$).

- Occassionally, rate laws in which the reaction order is fractional or even negative can possibly exist.
- The rate law is given by : rate $= k[A]^m[B]^n$.
- The units of the rate constant depend on the overall reaction order in the rate law.
- The rate law for any chemical reaction must be determined experimentally. it cannot be predicted by merely looking at the chemical equation
- The rate law for a reaction can be determined by observing the effect of changing the initial concentrations of the reactants on the initial rate of the reaction.

- It is important to realize that the rate of a reaction depends on the concentration, but the rate constant does not.
- The rate constant (and hence the reaction rate) is affected by temperature and by the presence of a catalyst.

Determining a Rate Law from Initial Rate Data

Que : The initial rate of a reaction $A + B \longrightarrow C$ was measured for several different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using the data given, determine (a) the rate law for the reaction, (b) the rate constant, (c) the rate of the reaction when [A] = 0.050 M and [B] = 0.100 M.

Ans : (a) As we move from experiment 1 to experiment 2, [A] is held constant and [B] is doubled. Thus, this pair of experiments shows how [B] affects the rate, allowing us to deduce the order of the rate law with respect to B. Because the rate remains the same when [B] is doubled, the concentration of B has no effect on the reaction rate. The rate law is therefore zero order in B (that is, $n = 0$).

In experiments 1 and 3, [B] is held constant so these data show how [A] affects rate. Holding [B] constant while doubling [A] increases the rate fourfold. This result indicates that rate is proportional to $[A]^2$ (that is, the reaction is second order in A).

Hence, the rate law is : Rate $= k[A]^2[B]^0 = k[A]^2$.

(b) Rate $= k[A]^2$

$16.0 \times 10^{-5} = k[0.200]^2$

$16.0 \times 10^{-5} = k(0.04)$

$k = \frac{16.0 \times 10^{-5}}{0.04}$

$k = 0.004 \ M^{-1}s^{-1}$

(c) Rate $= k[A]^2[B]^0$

Rate $= 0.004[0.050]^2[0.100]^0$

Rate $= 0.004(0.0025)(1)$

Rate $= 0.00001 \ Ms^{-1}$

Rate $= 1.0 \times 10^{-5} \ Ms^{-1}$

CHEMICAL EQUILIBRIUM

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

$PV = nRT$ → the Ideal Gas Law.

$$\frac{n}{V} = \frac{P}{RT}$$

$$[NH_3] = \frac{P_{NH_3}}{RT} \qquad [H_2] = \frac{P_{H_2}}{RT}$$

To be in equilibrium is to be in a state of balance.
A tug of war in which the two sides are pulling with equal forces so that the rope does not move is an example of a Static Equilibrium, one in which an object is at rest.
Equilibria can also be dynamic. Take for example, or illustration, an entranceway to a city. If the rate at which cars leave the city equals the rate at which they enter, the two opposing processes are in balance, and the net number of cars in the city is constant. At equilibrium these opposing processes are occuring at the same rate.

Chemical equilibrium occurs when opposing reactions are proceeding at equal rates: The rate at which the products are formed from the reactants equals the rate at which the reactants are formed from the products. As a result, concentrations cease to change, making the reaction to appear to be stopped. How fast a reaction reaches equilibrium is a matter of kinetics.

For the reaction below, consider its K_{c1} and K_{c2} :

$$2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$$

$$K_{cf} = \frac{1}{K_{cr}}$$

We have $K_{c1} = \frac{[NH_3]^2}{[N_2][H_2]^3}$ and $K_{c_2} = \frac{[NH_3]^4}{[N_2]^2[H_2]^6}$

Here we see that $K_{c_2} = (K_{c_1})^2$

Consider again the reaction below :

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$K_{c1} = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$ and $K_{c2} = \frac{[NH_3]^2}{[N_2][H_2]^3}$

We see again that $K_{c2} = (K_{c1})^2$

Consider another reaction :

$$N_2(g) + O_2 \rightleftharpoons 2NO$$

$$2NO(g) + O_2 \rightleftharpoons 2NO_2$$

$$N_2 + \cancel{2NO} + 2O_2 \rightleftharpoons \cancel{2NO} + 2NO_2$$

$$N_2 + 2O_2 \longrightarrow 2NO_2$$

Now compare the three equilibrium constant equations:

$$K_{c_1} = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_{c_2} = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$K_{c_3} = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

Multiply the equilibrium constants for the first two steps of the overall equation.

$$K_{c_1} \times K_{c_2}$$

$$\frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$\frac{[NO_2]^2}{[N_2][O_2]^2}$$

Here we see that multiplying the equilibrium constants for the first and second steps of the overall chemical equation yields the overall equilibrium of the reaction.

172 EXERCISE: $2NO_{(g)} + 2H_2(g) \rightleftharpoons N_{2(g)} + 2H_2O_{(l)}$

A mixture of 0.100 M of NO, 0.050 M of H_2, 0.100 M of H_2O and no nitrogen is allowed to reach equilibrium. At equilibrium $[NO] = 0.062\,M$. Find K_c and K_p.

	$2NO$ +	$2H_2$ $\rightleftharpoons$	N_2 +	$2H_2O$
Initial (I)	0.100 M	0.050 M	0 M	0.100 M
Change (C)	$-2x$	$-2x$	x	$+2x$
Equilibrium (E)	0.062 M	0.012 M	0.019 M	0.138 M

I + C = E ; For 2NO : $0.100M + (-2x) = 0.062\,M$

$$0.100M - 2x = 0.062\,M$$
$$2x = 0.100\,M - 0.062\,M$$
$$2x = 0.038\,M$$
$$x = 0.038\,M / 2$$
$$x = \underline{0.019}$$

For $\boxed{H_2}$: $0.050 - 2x = E$

$$0.050 - 2(0.019) = E$$
$$0.050 - 0.038 = E$$
$$E = \underline{0.012\,M}$$

and for $\boxed{H_2O}$: $0.100 + 2x = E$

$$0.100 + 2(0.019) = E$$
$$0.100 + 0.038 = E$$
$$E = \underline{0.138\,M}$$

$$K_c = \frac{[N_2]}{[NO]^2[H_2]^2}$$

$$K_c = \frac{[0.019]}{[0.062]^2[0.012]^2}$$

$$K_c = \frac{[0.019]}{[0.003844][0.000144]}$$

$$K_c = \frac{[0.019]}{[0.000000553]}$$

$$K_c = 34358.04702$$

$$K_c = \underline{\underline{34358.05}}$$

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

$$K_p = 34358.05(8.3145 \times 298)^{\text{[illegible]}-4}$$

$$K_p = 34358.05(2478.9682)^{-3}$$

$$K_p = \frac{34358.05}{(2478.9682)^3}$$

$$K_p = \cancel{13.85981877}\ \frac{34358.05}{1.5234 \times 10^{11}}$$

$$K_p \approx \cancel{13.86}$$

$$K_p = 0.000002255$$

$$K_p \approx 0.00000226$$

$$K_p \approx 2.26 \times 10^{-6}$$

THE CONCEPT OF EQUILIBRIUM

- An equilibrium state is a mixture of reactants and products whose concentrations no longer change with time.
- Let's take for example the decomposition reaction of N_2O_4, a colourless substance that dissociates to form NO_2, which is brown.

Because the chemical reaction occurs in a closed system, the reaction will eventually reach equilibrium.

The solid N_2O_4 vapourises as it is warmed above its boiling point (21.2°C = 294.35 K), and the gas turns progressively darker as the colourless NO_4 gas dissociates into brown NO_2 gas. Eventually, even though there is still some more N_2O_4 in the tube, the colour stops getting darker because the system reaches equilibrium. We are then left with an equilibrium mixture of N_2O_4 and NO_2 in which the concentrations no longer change as time passes.

$$\underset{\text{colourless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{brown}}{2NO_2(g)}$$

In this case, both the forward and reverse reactions are elementary reactions. Therefore, the rate laws for elementary reactions can be written from their chemical equations:

F (forward rxn): $N_2O_4(g) \longrightarrow 2NO_2(g)$; $Rate_f = k_f [N_2O_4]^1$

R (reverse rxn): $2NO_2(g) \longrightarrow N_2O_4(g)$; $Rate_r = k_r [NO_2]^2$

where k_f and k_r are rate constants for the forward and reverse reactions, respectively.

At equilibrium the rate at which products are produced from reactants equals the rate at which reactants are produced from products:

$$\underset{\text{forward reaction}}{k_f [N_2O_4]} = \underset{\text{reverse reaction}}{k_r [NO_2]^2}$$

Thermodynamic Equilibrium Constant

$$aA + bB \rightleftharpoons cC + dD$$

The Reaction Quotient $(Q) = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ at equilibrium,

we have a situation where $Q = K$.

$$\Delta G = \Delta G^\circ + RT\ln Q$$

At equilibrium $Q = K$, $\Delta G = 0$.

$$0 = \Delta G^\circ + RT\ln K$$

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

$R = 8.314$, K_p = gases and K_c = solution.

$R = 8.314\ J.K^{-1}mol^{-1}$

When $Q < K$ forward
$Q > K$ reverse
$Q = K$ (equilibrium) equal, hence no shift required.

- Rearranging $k_f[N_2O_4] = k_r[NO_2]^2$ gives the following equation:

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = \text{a constant}$$

NOTE : The quotient of two constants, such as k_f and k_r, is itself a constant

- The value of the equilibrium constant, say 4.5×10^{215}, which is very big a value, tells us that the numerator in the equilibrium constant formula is larger than the denominator. Conversely, when the value of the equilibrium constant is small, say 4.6×10^{-12}, this tells us that the denominator of the equilibrium constant formula is larger than the numerator.

  The equilibrium constant formula is given by:

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

where the reaction equation is : $aA + bB \rightleftharpoons cC + dD$. This is called the Law of Mass Action.

- Thus at equilibrium the ratio of the concentration terms involving the reactants and products, N_2O_4 and NO_2, equals a constant. This constant is called the Equilibrium Constant.
- At equilibrium the ratio equals a specific value. Thus, it makes no difference whether we start with N_2O_4 or with NO_2, or even with a mixture of the two. Thus, again, there is an important constraint on the proportions of N_2O_4 and NO_2 at equilibrium.
- If the composition of the equilibrium mixture remains constant with time it does not mean, however, that N_2O_4 and NO_2 stop reacting. On the contrary, the equilibrium is dynamic.

NOTE • For equilibrium to occur, neither reactants nor products can escape from the system.

NOTE • At equilibrium a particular ratio of concentration terms equals a constant.

NOTE • The equilibrium condition can be reached from either direction.

NOTE • $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ is called the equilibrium-constant expression for a particular reaction.

LE CHATELIER'S PRINCIPLE

- Consider the equations representing different reactions that take place chemically:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad 4 \longrightarrow 2$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad 2 \longrightarrow 2$$

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad 1 \longrightarrow 2$$

① Concentration

- For equation number one, if we increase the concentration of the gas nitrogen, a reactant, the equilibrium constant will move to the right. However, the concentration of ammonia (NH_3) will also increase so that the equilibrium state is reached again; this time the concentrations of the species taking part in this chemical reaction will be different from those at the beginning. Also, the equilibrium constant shall not change unless the temperature is changed.
- When the concentration of the products is increased, the equilibrium constant will shift to the left. Similarly, the system will try to oppose the effect and the concentrations of the reactants will also increase so that the equilibrium position is reached again.

TE • The subscript c on the K in K_c indicates that concentrations expressed in molarity are used to evaluate the constant.
K_c is the numerical value obtained when we substitute equilibrium concentrations into the equilibrium-constant expression.

- For the Haber process the equilibrium-constant expression is given below:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Once we know the balanced chemical equation for an equilibrium, we can write the equilibrium-constant expression even if we do not know its reaction mechanism.

② Pressure

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$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$\frac{n}{V} = \frac{P}{RT} = \frac{\text{mole fraction}}{RT} \times P_{total}$$

Partial pressure = mole fraction x P_{total}

Consideration of chemical equation 2, we know that there will be no shift of the equilibrium constant if there is no change in the number of moles of both the reactants and products. In other words, pressure will have no effect on the reaction state or the equilibrium constant / quotient. If pressure is increased, for equatio one, the equilibrium shifts to the right.
There is no change in equilibrium position if there is no change in the number of moles of either the reactants or products.

③ Temperature

Increasing the temperature of an exothermic reaction, the equilibrium shifts to the left.

$$\text{In}K = \frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

The equilibrium constant value is reduced by increasing the temperature.
Increasing the temperature of an endothermic reaction

* Increasing the temperature favours the endothermic reaction.

④ Catalysts

Catalysts affect both the forward and the reverse reactions in the same way. They affect neither the position of equilibrium not the value of the equilibrium constant.
If the forward reaction is increased by 100% by a catalyst, the reverse reaction will also be increased by 100%.

NOTE • The equilibrium-constant expression depends only on the stoichiometry of the reaction, not on its mechanism.

NOTE • The value of the equilibrium constant depends only on the particular reaction and on the temperature.

At any given temperature, the value of the equilibrium constant does not depend on the initial amounts of reactants or products. It also does not matter whether other substances are present, as long as they do not react with a reactant or a product.

EQUILIBRIUM CONSTANTS IN TERMS OF PRESSURE, K_p.

When the reactants and products in a chemical reaction are gases, we can formulate the equilibrium-constant expression in terms of partial pressures instead of molar concentrations.
When partial pressures in atmospheres are used in the equilibrium-constant expression, we can denote the equilibrium constant as K_p (where the subscript 'p' stands for pressure).
For a hypothetical chemical reaction $aA + bB \rightleftharpoons cC + dD$, the right expression for K_p is:

$$K_p = \frac{(P_D)^d (P_C)^c}{(P_A)^a (P_B)^b}$$

, where P_A is the partial pressure of A in atmospheres (atm), and so forth. For example; for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ we have:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

Heterogenous Equilibrium

$$CaCO_3\,(s) \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

This expression of equilibrium constant is wrong, not correct, for this reaction.

Probably because CO_2 is a gas and the rest of the species are solids.
How do we express the concentration of a solid substance?

$$\text{Concentration } ([\,]) = n/v = \frac{m/M_r}{V}$$

$$= \frac{m}{V} \times \frac{1}{M_r} = \text{density}/M_r$$

where M_r = molar mass
m = mass
V = volume
n = number of moles

Remember, for gases and liquids the density is not constant.
Solids are not included in the equilibrium expression.

Many equilibria, such as the hydrogen-nitrogen-ammonia system, involve substances all in the same phase. Such equilibria are called homogeneous equilibria.
Whenever a pure solid or a pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium-constant expression for the reaction.
Thus, for a reaction like: $PbCl_2\,(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-\,(aq)$, the equilibrium-constant expression is given below:

$$K_c = [Pb^{2+}][Cl^-]^2.$$

ACIDS AND BASES

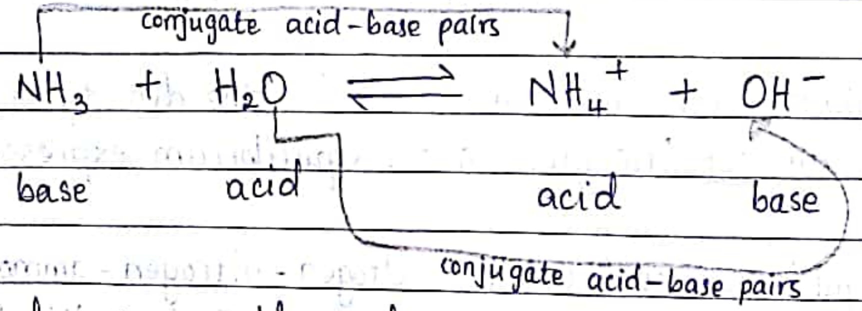
An ancient definition of an acid was that it was sour, whereas that of a base was that it was bitter.

THE BRØNSTED - LOWRY DEFINITIONS

In the Bronsted and Lowry definition of acids and bases, a hydrogen ion is called a Proton (H^+).
In this definition, acids are substances that donate a proton whereas bases are substances that accept a proton.
In other words, acid-base reactions were defined as proton transfer reactions.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{Cl^-}$$

$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{CH_3COO^-} + \underset{\text{acid}}{H_3O^+}$$



- Proton donors as acids and proton acceptors as bases.

- Substances that act or behave both as bases and acids are known as Amphiprotic. E.g water (H_2O) and ethanoic acid (CH_3COOH), even ammonia (NH_3).
- Acidity increases as the electronegativity of the element X (as in HX or $H-X$) increases, as it generally doest moving from left to right in a row on the periodic table.

THE LEWIS DEFINITION

According to the Lewis definition, electron pair donors are called bases whereas electron pair acceptors are acids.

$$\ddot{N}H_3 + H^+ \longrightarrow NH_4^+$$

* Ammonia is a Lewis base.

$$K_c = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

K_a = acid dissociation constant

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$NH_3 + H_2O \rightleftharpoons NH^+ + OH^-$$

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

Strong acids are acids that dissociate completely in water.
Strong bases are bases that dissociate completely in water.
Weak acids are acids that dissociate partially in water.
Weak bases are bases that dissociate partially in water.

- For amphiprotic substances like water, H_2O, they also dissociate.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

- Auto ionization: $K_w = k[H_2O]^2 = [H_3O^+][OH^-] = 10^{-14}$

This is the autoionization constant (K_w).

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

$$[H^+] = [OH^-] = x$$

$$K_w = 10^{-14} = x^2$$

$$x = 10^{-7}$$

$-\log[H^+] = pH \Rightarrow pH = -\log[1.0 \times 10^{-7}]$

$pH = \underline{\underline{7}}$ of water.

- The larger the equilibrium constant, the stronger the acid.

WEAK ACIDS

$HA \rightleftharpoons H^+ + A^-$ % degree of dissociation

% α

I	a	0	0
C	$-a\alpha$	$+a\alpha$	$+a\alpha$
E	$a(1-\alpha)$	$a\alpha$	$a\alpha$

$$K_a = \frac{(a\alpha)^2}{a(1-\alpha)}$$

PH (potential Hydrogen)

pH is the acidity of a solution.

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

- Lower the pH, stronger the acid.
- Higher the pH, stronger the base.

- Concentrated acid ⟶ amount of acid
- Strong acid ⟶ dissociation
- Weak acid ⟶ dissociation
- Dilute acid ⟶ amount of acid

- The higher the concentration, the stronger the acid.

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

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$pH \text{ of base} = -\log\left(\frac{K_w}{[OH^-]}\right)$$

STRONG ACIDS AND BASES

Strong acids and bases are strong electrolytes, existing in aqueous solution entirely as ions. There are relatively few common strong acids and bases.

Strong Acids

The seven most common strong acids include six monoprotic acids (HCl, HBr, HI, HNO_3, $HClO_3$, and $HClO_4$), and one diprotic acid (H_2SO_4).

NOTE
- In aqueous solutions of strong acids, the acids are normally the only source of H^+ ions. If the concentration of the acid is 10^{-6} M or les we also need to consider H^+ ions that result from the autoionization of H_2O (water). Normally, the concentration of H^+ from H_2O is so small that it can be neglected.
- For all practical purposes, an aqueous solution of HNO_3 consists entirely of H_3O^+ (or H^+) and NO_3^- ions. (Since it is a strong acid, it dissociates completely).

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \quad \text{(complete ionization)}$$

Thus, simplifying this equation for the ionization of HNO_3 acid, we have:

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

NOTE
- Calculating the pH of a solution of a strong monoprotic acid is straig forward because $[H^+]$ equals the original concentration of the acid.

In a 0.20 M solution of $HNO_3(aq)$, for example, $[H^+] = [NO_3^-] = 0.20M$

Question: An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the acid?

Answer:

$$HNO_3 \longrightarrow H^+ + NO_3^- \quad ; \quad [H^+] = [NO_3^-] = x$$

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

$$pH = -\log x = 2.34$$

$$x = 1/10^{2.34}$$

$$x = 0.004570881$$

$$x = 0.0046 \text{ M}$$

Strong Bases

There' relatively a few common bases that are strong. The most common soluble strong bases are the ionic hydroxides of the alkali metals (group 1A) and the heavier alkaline earth metals (group 2A), such as NaOH, KOH, and $Ca(OH)_2$. These compounds completely dissociate into ions in aqueous solution. Thus, a solution labelled 0.30M NaOH consists of 0.30 M $Na^+(aq)$ and 0.30M $OH^-(aq)$; there is essentially no undissociated NaOH.

$$NaOH \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$[Na^+] = [OH^-] = 0.30$, in a case where there is 0.30m of NaOH (aq) solution.

estion: What is the pH of a 0.0011 M solution of $Ca(OH)_2$?

swer:

$$Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

$$[Ca^{2+}] = 2[OH^-] = 0.0011\,M$$

$$2[OH^-] = 0.0011\,M$$

$$[OH^-] = 2 \times 0.0011\,M$$

$$[OH^-] = 0.0022\,M$$

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

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.0022}$$

$$[H^+] = 4.45454545 \times 10^{-12}$$

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

$$pH = -\log[4.545454545 \times 10^{-12}]$$

$$pH = 11.34242268$$

$$pH \approx 11.34$$

- The most common of strongly basic solutions that are created by certain substances that react with water to form $OH^-(aq)$ contain the oxide ion (O^{2-}). The O^{2-} reacts with water to form OH^-, leaving virtually no O^{2-} remaining in the solution: $O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$.

Neutralisation Reactions

Given the concentration of NH_4Cl solution and $K_b = 1.8 \times 10^{-5}$, find the pH.

0.1 M NH_4Cl solution, P.H=?

$K_{b_{NH_3}} = 1.8 \times 10^{-5}$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$K_a = \frac{K_w}{K_b}$$

K_a = for acid, K_b = for base, K_w = for water

$$K_a = 5.56 \times 10^{-10}$$

	NH_4^+	NH_3	H_3O^+
I	0.1	0	0
C	$-x$	x	x
E	$0.1-x$	x	x

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.1-x}$$

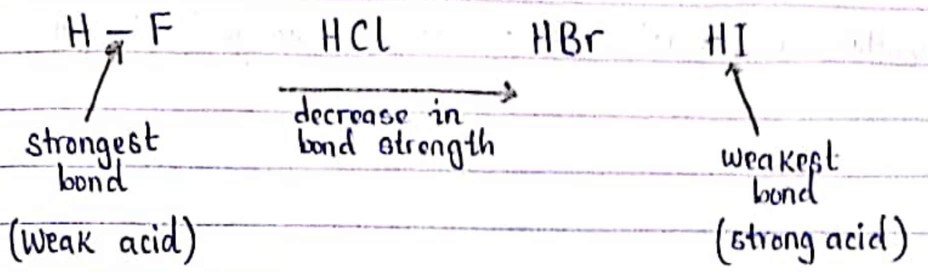
0.1 is too large as compared to $0.1 - x \approx 0.1$

Therefore, 0.1 is considered alone, not as $0.1 - x$, as the denominat

$x = 7.46 \times 10^{-6}$ M

pH = 5.13

Effect of Structure



NOTE • Weak acids ionize partially because of the strength of their bonds which require much energy to break.

Oxyacids

weakest

$HClO$

$HClO_2$

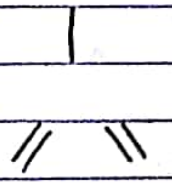
$HClO_3$

$HClO_4$

strongest

NOTE • As more electronegative elements appear in an acid, the more polar the solution will be and hence the stronger the acid.

A molecule containing H will transfer a proton only if the H—X bond is polarized in the following way: $\overset{\longmapsto}{H - X}$.



Very strong bonds are less easily dissociated than weaker ones. The H—F bond is the most polar H—X bond. HF would be expected to be the strongest acid if only electronegativity was all that mattered. However, HF has the highest bond strength among the hydrogen halides. Consequently, HF is a weak acid, whereas all the other hydrogen halides are strong acids in water.

- Also, the greater the stability of the conjugate base, the stronger the acid.

NOTE • The strength of an acid is combination of all three factors: ① the polarity of the H—X bond, ② the strength of the H—X bond, and ③ the stability of the conjugate base, X^-.

BUFFER SOLUTIONS

Buffer solutions are solutions that resist a change in the pH.

Acidic

Basic

Common - Ion Effect

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[CH_3COO^-]_{eq} \approx [CH_3COONa]_{initial}$$

$$[CH_3COOH]_{eq} \approx [CH_3COOH]_{initial}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[CH_3COONa][H^+]}{[CH_3COOH]}$$

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COONa]}$$

$$\log[H^+] = -\log K_a + \left(-\log \frac{[CH_3COOH]}{[CH_3COONa]}\right)$$

$$= pK_a - \log \frac{[Acid]}{[Conjugate\ Base]}$$

$$= pK_a + \log \frac{[Conjugate\ Base]}{[Acid]}$$

The Handiuson Handbatch Equation
Henderson – Hasselbalch Equation.

$$pOH = pK_b - \log \frac{[\text{Base}]}{[\text{Conjugate Base}]}$$

$$= pK_b + \log \frac{[\text{Conjugate Base}]}{[\text{Base}]}$$

$$= pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$pOH = pK_b \qquad [\text{Salt}] = [\text{Base}]$$

$\pm$ 1 pK_a

$\pm$ 1 pK_b

Because conjugate acid-base pairs share a common ion, we can use the sam procedures to calculate the pH of a buffer that we used to treat the com ion effect. However, an alternate approach is taken that is based on an equation that is derived from $[H^+] = K_a \frac{[HX]}{[X^-]}$.

Taking the negative log of both sides of $[H^+] = K_a \frac{[HX]}{[X^-]}$, we have:

$$-\log[H^+] = -\log\left(K_a \frac{[HX]}{[X^-]}\right) = -\log K_a - \log \frac{[HX]}{[X^-]}$$

Because $-\log[H^+] = pH$ and $-\log K_a = pK_a$, we have:

$$pH = pK_a - \log \frac{[HX]}{[X^-]}$$

$$pH = pK_a + \log \frac{[X^-]}{[HX]}$$

- where [base] and [acid] refer t the equilibrium concentrations of the conjugate acid-base pair.

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

(buffer solutions)

- When [base] = [acid], pH = pKa.

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WEAK ACIDS

Most acidic substances are weak acids and are therefore only partially ionized in aqueous solution.

- The equilibrium constant for a weak acid can be used to express the extent to which a weak acid ionizes.
- A general weak acid, say HA, can have its equation for ionization reaction written in the following ways, depending on whether the hydrated proton is represented as $H_3O^+(aq)$ or $H^+(aq)$:

$$HA(aq) + H_2O \longrightarrow H_3O^+(aq) + A^-(aq)$$

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

NOTE: Because H_2O is the solvent, it is omitted from the equilibrium-constant expression as either:

$$K_c = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_c = \frac{[H^+][A^-]}{[HA]}$$

As the ion-product constant for the autoionization of water is, the subscript on this equilibrium constant to indicate the type of equation to which it corresponds.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

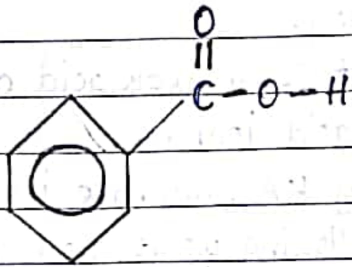
The subscript a on K_a denotes that it is an equilibrium constant for the ionization of an acid, so K_a is called the Acid-Dissociation constant.

NOTE • The magnitude of K_a indicates the tendency of the acid to ionize in water. The larger the value of K_a, the stronger the acid.

Calculating K_a from pH

Proton-transfer reactions are generally very rapid, as a result the measured or calculated pH for a weak acid always represents an equilibrium condition.

192 Question: Niacin, one of the B vitamins, has the following molecular structure:



A 0.020M solution of niacin has a pH of 3.26. What is the acid-dissociation constant, K_a, for niacin?

Answer :

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Percent Ionization

- The magnitude of Ka indicates the strength of a weak acid. Yet another measure of acid strength is percent ionization, which is defined as : $\text{Percent ionization} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$
- The stronger the acid, the greater its percentage of ionization.

Remember! For any acid, the concentration of acid that undergoes ionization equals the concentration of $H^+(aq)$ that forms, assuming that the autoionization of water is negligible.

$$[\text{of ionization of acid}] = [H^+].$$

Thus, the percent ionization for an acid HA is also given by :

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HA]_{\text{initial}}} \times 100\%$$

Question : A 0.035 M solution of HNO_2 contains 3.7×10^{-3} M $H^+(aq)$. Calculate its percent ionization.

Answer : $\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HNO_2]_{\text{initial}}} \times 100\%$

$$\text{Percent ionization} = \frac{3.7 \times 10^{-3}\ M}{0.035\ M} \times 100\%$$

$$\text{Percent ionization} = \underline{\underline{11\%}}.$$

194 Using K_a to Calculate PH

- Knowing the value of K_a and the initial concentration of the weak acid, we can calculate the concentration of $H^+(aq)$ in a solution of a weak acid.

Question: Calculate the pH of a 0.30M solution of acetic acid (CH_3COOH), the weak acid responsible for the characteristic odour and acidity of vinegar, at 25°C, given $K_a = 1.8 \times 10^{-5}$.

Answer: The ionization equilibrium for acetic acid is

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

The equilibrium-constant expression and the value of the equilibrium constant are :

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

The concentrations involved in the equilibrium equation are given in the table of I, C, E :

	$CH_3COOH(aq) \rightleftharpoons$	$H^+(aq)$ +	$CH_3COO^-(aq)$
Initial (I)	0.30M	0	0
Change (C)	$-x$ M	$+x$ M	$+x$ M
Equilibrium (E)	$(0.30-x)$ M	x M	x M

Substituting the equilibrium concentrations into the equilibrium-constant expression, we have :

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{(0.30-x)} = 1.8 \times 10^{-5}$$

$$K_a = \frac{x^2}{(0.30-x)} = 1.8 \times 10^{-5}$$

$$x^2 = 5.4 \times 10^{-6} - 1.8 \times 10^{-5} x$$

$$\boxed{x^2 + 1.8 \times 10^{-5} x - 5.4 \times 10^{-6} = 0}$$

Solve the quadratic equation above so as to obtain x.

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

$$x = \frac{-1.8\times10^{-5} \pm \sqrt{(1.8\times10^{-5})^2 - 4(1)(-5.4\times10^{-6})}}{2(1)}$$

$$x = \frac{-1.8\times10^{-5} \pm 0.00464758}{2}$$

$$x = \frac{-1.8\times10^{-5} + 0.00464758}{2} \quad \text{or} \quad x = \frac{-1.8\times10^{-5} - 0.00464758}{2}$$

$$x = \frac{0.00462958}{2}$$

$$x = 0.00231479$$

$$x = 2.3\times10^{-3}$$

Here, x is not applicable because its value turns out to be negative, which is not the case with the concentration change in $H^+(aq)$ and $CH_3COO^-(aq)$.

Therefore, now $x = [H^+] = 2.3\times10^{-3}$.

Hence, the pH of 0.30M acetic acid can be calculated by :

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

$$pH = -\log[2.31479\times10^{-3}]$$

$$pH = 2.635488402$$

$$pH = 2.64 \quad \text{(answer)}.$$

The percent ionization of CH_3COOH is given by :

$$\text{Percent ionization} = \frac{0.0023}{0.30} \times 100\%$$

$$\text{Percent ionization} = 0.77\%$$

- As a general rule, if the quantity x is more than about 5% of the init value, it is better to use the quadratic formula.
- The stronger the acid, the faster the rate of reaction in which the acid is part of the reacting species. Conversely, the weaker an acid is, the slower the rate of reaction in which the weak acid is part of the reactin species.

NOTE • The percent ionization for a weak acid decreases as its concentration increases. Thus, the concentration of $H^+(aq)$ is not directly proportional to the concentration of the weak acid.
For example, doubling the concentration of a weak acid does not doub the concentration of $H^+(aq)$.

WEAK BASES

- Many substances behave as weak bases in water. Weak bases react with water, abstracting protons from H_2O (water), thereby forming the conjugate acid of the base and OH^- ions.

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

The equilibrium-constant expression for this reaction can be written as:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

NOTE • Water is a solvent, so it is omitted from the equilibrium-constant expression.

- The most commonly encountered weak base is ammonia.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

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

NOTE • The constant K_b always refers to the equilibrium in which a base react with H_2O to form the corresponding conjugate acid and OH^-.
The constant K_b is called the Base-Dissociation constant.

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- As with Kw and Ka, the subscript "b" denotes that this equilibrium constant refers to a particular type of reaction, namely the ionization of a weak base in water.

THE COMMON-ION EFFECT

Consider solutions that contain a weak acid, such as acetic acid which has a chemical formula of CH_3COOH, and a soluble salt of that acid, such as sodium acetate (CH_3COONa). Notice that these solutions contain two substances that share a common ion which is CH_3COO^-.
Since sodium acetate is a soluble ionic compound, and is therefore a very strong electrolyte, it dissociates completely in aqueous solution to form Na^+ and CH_3COO^- ions:

$$CH_3COONa\,(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$

In contrast, CH_3COOH is a weak electrolyte that ionizes as follows:

$$CH_3COOH\,(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

The CH_3COO^- from CH_3COONa causes the equilibrium for CH_3COOH dissociation and reassociation to shift to the left, thereby decreasing the equilibrium concentration of $H^+(aq)$.
In other words, the presence of the added acetate ion causes the acetic acid to ionize less than it normally would.

OTE • Whenever a weak electrolyte and a strong electrolyte contain a common ion, the weak electrolyte ionizes less than it would if it were alone in solution.

BUFFERED SOLUTIONS

A buffer resists changes in pH because it contains both an acid to neutralize OH^- ions and a base to neutralize H^+ ions. The acid and base that make up the buffer, however, must not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid-base conjugate pair such as $CH_3COOH - CH_3COO^-$ or $NH_4^+ - NH_3$.

Buffers are often prepared by mixing a weak acid or weak base with a salt of that acid or base.

POLY PROTIC ACIDS

Polyprotic acids are acids that have more than one protons.

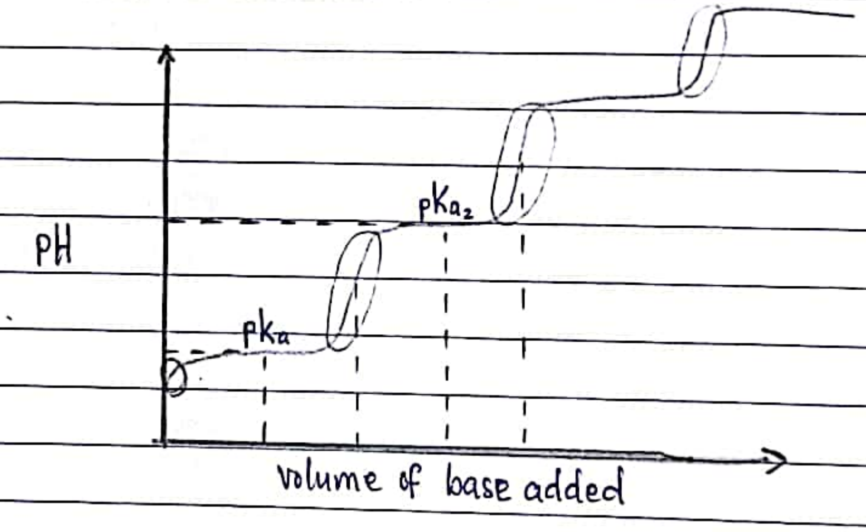
Examples: H_2SO_4 : $H_2SO_4 \longrightarrow H^+ + HSO_4^-$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

$$H_3PO_4 \xrightarrow{Ka} H_2PO_4^- + H^+$$

$$H_2PO_4^- \overset{Ka}{\rightleftharpoons} HPO_4^{2-} + H^+$$

$$HPO_4^{2} \rightleftharpoons PO_4^{3-} + H^+$$



- Many acids have more than one ionizable H atom. These are acids ar as Polyprotic acids.
  For example, each of the H atoms in sulphurous acid (H_2SO_3) can ionize in successive steps:

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq), \; K_{a_1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq), \; K_{a_2} = 6.4 \times 10^{-8}$$

- The numbers on the constants refer to the particular proton of the acid that is ionizing. Thus, K_{a2} refers to the equilibrium involving remova of the second proton of a polyprotic acid.

20/ NOTE !

- It is always easier to remove the first proton from a polyprotic acid than to remove the second.

Similarly, it is easier to remove the second proton than the third from an acid with three ionizable protons (H^+). Thus, the K_a values become successively smaller as successive protons are removed.

- As long as successive K_a values differ by a factor of 10^3 or more, it is possible to obtain a satisfactory estimate of the pH of polyprotic acid solutions by treating them as if they were monoprotic acids, and considering only K_{a1}.

SOLUBILITY EQUILIBRIUM

By increasing the temperature, usually solubility increases.

maximum amount x mol in 1 L of solution at 25° C.

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

$$K = \frac{[Pb^{2+}][Cl^-]^2}{[PbCl_2]}$$

$$K_{sp} = K[PbCl_2] = [Pb^{2+}][Cl^-]^2$$

sp = solubility product.

Que: Calculate the molar solubility of $PbCl_2$, if $K_{sp} = 1.7 \times 10^{-5}$.

Ans: $PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

A =	0	0
$-x$ =	$+x$	$+2x$
$(A-x)$	x	$2x$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$
$$K_{sp} = (x)(2x)^2$$
$$K_{sp} = (x)(4x^2)$$
$$K_{sp} = 4x^3$$
$$1.7 \times 10^{-5} = 4x^3$$
$$x = \frac{\sqrt[3]{1.7 \times 10^{-5}}}{\sqrt[3]{4}} = \underline{0.0162 \text{ moldm}^{-3}}.$$

The solubility of $BaSO_4$ is 0.0091 $g dm^{-3}$, calculate K_{sp}:

Molar solubility $= \frac{n}{dm^3} = \frac{\frac{mass}{m_r}}{dm^3}$

$= \frac{0.0091}{233}$ $mol dm^{-3}$

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$\left(\frac{0.0091}{233}\right)\left(\frac{0.0091}{233}\right)$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$K_{sp} = \left(\frac{0.0091}{233}\right)\left(\frac{0.0091}{233}\right)$$

$$K_{sp} = 1.5 \times 10^{-9}$$

Solubility decreases when a salt is dissolved into another salt having common ions.

$BaSO_{4(s)} \rightleftharpoons$	$Ba^{2+}_{(aq)} +$	$SO^{2-}_{4(aq)}$
A	0	B
	x	x
	x	$B + x$

$$K_{sp} = (x)(B + x)$$

- K_3 is a product of K_1 and K_2

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \qquad K_1$$

$$Ag^+ + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ \qquad K_2$$

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ + Cl^- \qquad K_3$$

- Q = ionic product
  k = [ ][ ]

- Solubility product determines the precipitation of precipitates.

- For AgCl , $K_{sp} = [Ag^+][Cl^-]$

Ionic Product = $[Ag^+][Cl^-]$
(the ionic product is in equilibrium whereas
the solubility product is not in equilibrium.)

Just when the ionic product exceeds the solubility product, precipitation will occur.

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THE pH SCALE

- The molar concentration of $H^+(aq)$ in an aqueous solution is usually very small.
- The pH of a neutral solution is 7.00 at 25°C. Always remember that the numbers to the right of a decimal are always significant therefore the corresponding pH must be expressed to two decimal places.
- A change in $[H^+]$ by a factor of 10 causes the pH to change by 1. Thus, a solution of pH 6 has 10 times the concentration of $H^+(aq)$ as a solution of pH 7.
- If $[H^+]$ is part of a kinetic rate law, then changing its concentration will change the rate. Thus, if the rate law is first-order in $[H^+]$ doubling its concentration will double the rate even if the change is merely from 1.0×10^{-7} M to 2×10^{-7} M.

Question: In a sample of lemon juice $[H^+]$ is 3.8×10^{-4} M. What is the pH?

Answer:

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

$$pH = -\log[3.8 \times 10^{-4}]$$

$$pH = -(-3.420216403)$$

$$pH = +3.42.$$

Question: A commonly available window-cleaning solution has $[OH^-] = 1.9 \times 10^{-}$ What is the pH?

Answer:

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

$$[H^+][1.9 \times 10^{-6}] = 1.0 \times 10^{-14}$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-6}} = 5.0 \times 10^{-9}$$

$$pH = -\log[H^+] = -\log[5.0 \times 10^{-9}] = 8.278753601 = 8.2$$

Question: A sample of freshly pressed juice from apples has a pH of 3.76. Calculate $[H^+]$.

THE pOH and other "p" Scales.

- The negative log is a convenient way of expressing the magnitudes of small quantities. The convention of the negative log of a quantity is labelled "p". Thus, the concentration of OH^- can be expressed as pOH.

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

- Likewise, $pK_w = -\log K_w$

Therefore, $-\log[H^+] + (-\log[OH^-]) = -\log K_w$

$$p[H^+] + pOH = 14.00 \quad \text{(at } 25°C\text{)}.$$

$$pH + pOH = 14.00$$

ACID-BASE PROPERTIES OF SOLUTIONS OF SALTS

Most metal ions can also react with water to decrease the pH of an aqueous solution. The mechanism by which metal ions produce acidic solutions is called the Combined Effect of Cation and Anion in Solution.

NOTE • Ions of alkali metals, of the heavier alkaline earth metals do not react with water and therefore do not affect pH. These exceptions are those cations found in strong bases.

If an aqueous solution (salt solution) contains an anion that does not react with water and a cation that does not react with water, we expect the pH to be neutral. If the solution contains an anion that reacts with water to produce hydroxide, and a cation that does not react with water, we expect the pH to be basic. If the solution contains a cation that reacts with water to produce hydronium, and an anion that does not react with water, we expect the pH to be acidic.

Finally, in a case where a solution contains an anion and a cation both capable of reacting with water, the nature of the solution would depend upon the relative abilities of the ions to react with water.

To summarize,

① An anion that is a conjugate base of an acid that is strong will not affect pH.
② An anion that is a conjugate base of a weak acid will cause an increase in pH.
③ A cation that is the conjugate ~~base~~ acid of a strong base will not affect pH.
④ A cation that is the conjugate acid of a weak base will cause a decrease in pH.

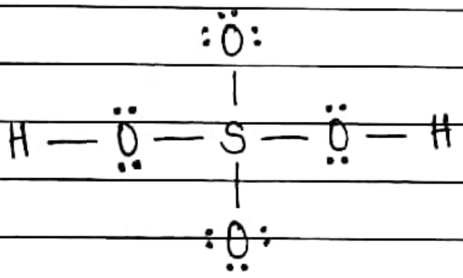
⑤ Other metals ions will cause a decrease in pH.

⑥ When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the ion with the larger equilibrium constant, Ka or Kb, will have the greater influence on the pH.

⑦ The cations of group 1A and heavier members of group 2A (Ca^{2+}, Sr^{2+}, and Ba^{2+}) will not affect pH. These are the cations of the strong Arrhenius bases They will be spectator ions in acid-base chemistry.

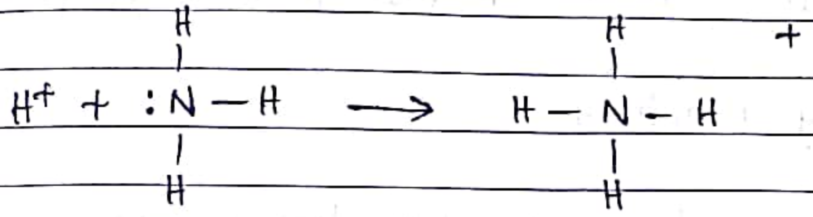
OXYACIDS

Acids in which OH groups and possibly additional oxygen atoms are bound to the central atom are called Oxyacids. Many common acids, such as, sulphuric acid, contain one or more O – H bonds.



MORE ON LEWIS ACIDS AND BASES

For a substance to be a proton acceptor (a Brønsted-Lowry base), it must have an unshared pair of electrons for binding a proton, or the proton. NH_3, e.g, acts as a proton acceptor. Using Lewis structures, we can write the reaction between H^+ and NH_3 as follows:



$$H^+ + :NH_3 \longrightarrow [NH_4]^+$$

G.N Lewis was the first to notice this aspect of acid-base reactions. He proposed a definition of acid and base that emphasizes the shared electron pair.

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

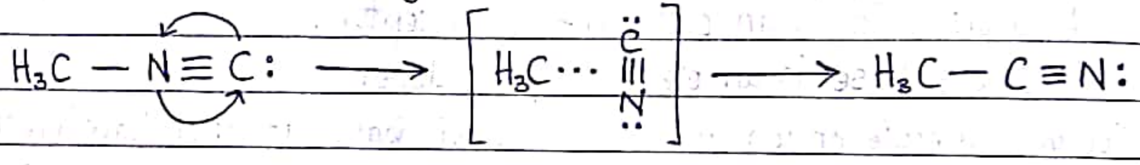
For any molecule or ion to act as a Lewis base, it must have an electron pair. It is the hydration interaction between positively-charged metal ions and the unshared electron pairs of water molecules that causes salts to dissolve in water.

REACTION MECHANISMS

- The process by which a reaction occurs is called the Reaction Mechanism. At the most sophisticated level, a reaction mechanism will describe in great detail the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction.

Elementary Reactions

We have learnt that reactions take place because of collisions between reacting molecules. For example, the collisions between molecules of methyl isonitrile (CH_3NC) can provide the energy to allow the CH_3CN to form after the rearrangement of CH_3NC, as shown below:



Similarly, the reaction of NO and O_3 to form NO_2 and O_2 appears to occur as a result of a single collision involving suitably oriented and sufficiently energetic NO and O_3 molecules:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Both of these processes occur in a single step or event and are called Elementary reactions (or elementary processes).

- The number of molecules that participate as reactants in an elementary reaction defines its Molecularity.
- If a single molecule is involved, the reaction is Unimolecular. The rearrangement of methyl isonitrile is a unimolecular process. Elementary reactions involving the collision of two reactant molecules are Bimolecular. The reaction between NO and O_3 is bimolecular.
- Elementary reactions involving the simultaneous collision of three molecules are Termolecular.

Termolecular reactions are far more less probable than unimolecular or bimolecular processes and are rarely encountered. The chance that four or more molecules will collide simultaneously with any regularity is even more remote; consequently, such collisions are never proposed as part of a reaction mechanism.

Multistep Mechanisms

The net change represented by a balanced chemical equation often occurs by a multistep mechanism, which consists of a sequence of elementary reactions. For example, consider the reaction of NO_2 and CO :

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Below 225° C, this reaction appears to proceed in two elementary reactions (or elementary steps), each of which is bimolecular.

First, two NO_2 molecules collide, and an oxygen atom is transferred from one to the other. The resultant NO_3 then collides with a CO molecule and transfers an oxygen atom to it:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$$

Thus, we say that the reaction occurs by a two-step mechanism.

The chemical equations for the elementary reactions in a multistep mechanism must always add to give the chemical equation of the overall process.

In the present example, the sum of the two elementary reactions is:

$$2NO_2(g) + NO_3(g) + CO(g) \longrightarrow NO_2(g) + NO_3(g) + NO(g) + CO_2(g)$$

Simplifying this equation by eliminating substances that appear on both sides of the arrow gives the equation: $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$, which is the net equation for the process. Because NO_3 is neither a reactant nor a product in the overall reaction — it is formed in the one elementary step/reaction and consumed in the next — it is called an Intermediat Multistep mechanisms involve one or more intermediates.

212 EQUILIBRIUM CONSTANTS IN TERMS OF PRESSURE, K_p.

For a given reaction, the numerical value of K_c is generally different from the numerical value of K_p. However, it is possible to calculate one from the other using the ideal-gas equation, to convert between the concentration (in molarity, M) and pressure (in atm):

$$PV = nRT \quad , \text{ so } \quad P = \frac{n}{V}RT$$

For a substance A, we have: $P_A = \dfrac{n_A}{V}RT = [A]RT$.

$$\boxed{P_A = [A]RT}$$

By substituting $P_A = [A]RT$ into $K_p = \dfrac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$ for a hypothetical chemical reaction $aA + bB \rightleftharpoons dD + eE$, we get to a general expression relating K_p and K_c, given by:

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

where Δn is the change in the number of moles of gas in the chemical equation for the reaction. It equals the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.

$$\boxed{\bullet \text{Remember: } M(\text{molarity}) = \text{mol } L^{-1}}$$

Δn = (moles of gaseous product) − (moles of gaseous reactant)

Δn = (summation of moles of gaseous products) − (summation of moles of gaseous reactants)

NOTE • For $aA + bB \rightleftharpoons dD + eE$, the relation expression between K_p and K_c is given by:

$$\boxed{K_p = K_c\left(RT^{(d+e)-(a+b)}\right)}$$

As an example, consider the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. There are two moles of the product NO_2 (the coefficient in the balanced eqn) and one mole of the reactant N_2O_4. Therefore, Δn is given by:

$$\Delta n = 2 - 1$$

$$\Delta n = 1.$$

And so, $K_p = K_c(RT)$ for this reaction.

NOTE • $K_p = K_c$ only when the same number of moles of gas appears on both sides of the balanced chemical equation, which means that $\Delta n = 0$.

MAGNITUDE OF EQUILIBRIUM CONSTANTS

- Equilibrium constants can vary from very large to very small.
- The magnitude of the constant shows important information about the composition of an equilibrium mixture.
- For example, consider the reaction of carbon monoxide (CO) gas and chlorine (Cl) gas at 100°c to form Phosgene ($COCl_2$), a toxic gas used in manufacturing certain polymers and insecticides:

$$CO(g) + Cl(g) \rightleftharpoons COCl_2(g) \; ; \; K_c = \frac{[COCl_2]}{[CO][Cl_2]} = 4.56 \times 10^9$$

For the equilibrium constant to be so large, the numerator of the equilibrium-constant expression must be larger than the denominator. Thus, the equilibrium concentration of $COCl_2$ must be greater than that of CO or Cl_2, and this is found true experimentally.

NOTE: We say this equilibrium lies to the right (toward the product side). Likewise, conversely, a very small equilibrium constant indicates that the equilibrium mixture contains mostly reactants, it lies to the left.

NOTE: If $K \gg 1$: Equilibrium lies to the right ; products predominate.
If $K \ll 1$: Equilibrium lies to the left ; reactants predominate.

REMEMBER! Opposing rates, not concentrations, are equal at equilibrium.

DIRECTION OF THE CHEMICAL EQUATION AND K.

Equilibrium can be approached from either direction. Because this is so, the direction in which we write the chemical equation for an equilibrium is arbitrary.

For example, the $N_2O_4 - NO_2$ equilibrium can be represented as:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \; ; \; K_c = \frac{[NO_2]^2}{[N_2O_4]} = \underline{0.212} \text{ at } 100°C.$$

Equally, the same equilibrium reaction can be represented as:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \; ; \; K_c = \frac{[N_2O_4]}{[NO_2]^2} = \underline{4.72} \text{ at } 100°C.$$

NOTE : For $2NO_2(g) \rightleftharpoons N_2O_4(g) \; ; \; K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72$ at 100°C.

MEMBER : The equilibrium-constant expression for a reaction written in one direction is the reciprocal of the one for the reaction written in the reverse direction. Consequently, the numerical value of the equilibrium constant for the reaction written in one direction is the reciprocal of that for the reverse reaction.

For reactions that utilize Hess' Law, we obtain the net equation by adding the individual equations and cancelling identical terms. However, for such reactions, the equilibrium-constant expression for the net equation is the product of the expressions for the individual steps, for instance:

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g) \; ; \; K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \underline{0.014}$$

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g) \; ; \; K_c = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \underline{7.2}$$

The net sum of these two equations is :

$$2NOBr(g) + Cl_2(g) \rightleftharpoons 2NO(g) + 2BrCl(g)$$

, and the equilibrium constant expression for the net equation is the product of the individual steps :

$$K_c = \frac{[NO]^2[BrCl_2]^2}{[NOBr]^2[Cl_2]} = \frac{[NO]^2[Br_2]}{[NOBr]} \times \frac{[BrCl]^2}{[Br_2][Cl_2]}$$

$$K_c = 0.014 \times 7.2 = \underline{\underline{0.10}}$$

SUMMARY

- The equilibrium constant of a reaction in the reverse direction is the inverse of the equilibrium constant of the reaction in the forward dirn.
- The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power equal to that nº.
- The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

HETEROGENEOUS EQUILIBRIA

The omission of pure solids and pure liquids which are excluded from equilibrium

The omission of pure solids and pure liquids from equilibrium-constant expressions can also be rationalized in a second way.
What is substituted into a thermodynamic equilibrium expression is the activity of each substance, which is the ratio of the concentration to a reference value. Now, for a pure substance, the reference value is the concentration of the pure substance itself, so that the activity of any pure solid or liquid is always simply 1.

- When a solvent is involved as a reactant or product in an equilibrium, its concentration is also excluded from the equilibrium-constant expression, provided the concentrations of reactants and products are low, so that the solvent is essentially a pure substance.

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- An equilibrium involving water as a solvent whose reaction equation is:
  $H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons OH^-(aq) + HCO_3^-(aq)$
  gives an equilibrium-constant expression in which $[H_2O]$ is excluded:

$$K_c = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]}$$

CALCULATING EQUILIBRIUM CONSTANTS

We often do not know the equilibrium concentrations of all chemical species in an equilibrium mixture.
If we know the equilibrium concentration of atleast one species, however, we can generally use the stoichiometry of the reaction to deduce the equilibrium concentrations of the others. The following are the steps in which the procedure is outlined to do this:

Step 1: Tabulate all the known initial and equilibrium concentratio of the species that appear in the equilibrium-constant expressio

Step 2: For those species for which both the initial and equilibrium concentrations of the species are known, calculate the change i concentration that occurs as the system reaches equilibrium.

Step 3: Use the stoichiometry of the reaction (that is, use the coeffici in the balanced chemical equation) to calculate the changes in concentration for all the other species in the equilibrium.

Step 4: From the initial concentrations and the changes in concentrati calculate the equilibrium concentrations. These are then used to evaluate the equilibrium constant.

The magnitude of K indicates to what extent a reaction will proceed. The equilibrium constant also allows us to :

① predict the direction in which a reaction mixture will proceed to achieve equilibrium, and

② calculate the concentrations of reactants and products when equilibrium is reached.

PREDICTING THE DIRECTION OF REACTION

For the formation of NH_3 from N_2 and H_2, $K_c = 0.105$ at 475°C. Suppose we place a mixture of 2.00 mol of H_2, 1.00 mol of N_2, and 2.00 mol of NH_3 in a 1.00 L - container at 472°C. How will the mixture react to form or reached equilibrium? Will N_2 and H_2 react to form more NH_3, or will NH_3 decompose to form N_2 and H_2?

To answer this question, we can substitute the starting concentrations of N_2, H_2 and NH_3 into the equilibrium-constant expression and compare its value to the equilibrium constant :

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2.00)^2}{(1.00)(2.00)^3} = 0.500 \quad \text{whereas} \quad K_c = 0.105.$$

To reach equilibrium, the quotient $[NH_3]^2/[N_2][H_2]^3$ will need to decrease from the starting value of 0.500 to the equilibrium value of 0.105. Because the system is closed, this change can only happen if the concentration of NH_3 decreases and the concentrations of N_2 and H_2 increase. Thus, the reaction proceeds towards equilibrium by forming N_2 and H_2 from NH_3; that is, the reaction proceeds from right to left.

The reaction quotient, Q, is a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium-constant expression. Therefore,

$$Q_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}, \quad \text{for the general reaction } aA + bB \rightleftharpoons dD + eE.$$

- The concentrations that are used in the reaction-quotient equation expression are not restricted to the equilibrium state.

NOTE : The equilibrium constant has only one value at each temperature. The reaction quotient, however, varies as the reaction proceeds.

To determine the direction in which a reaction will proceed to achieve equilibrium, we compare the values of Q_c and K_c, or Q_p and K_p. Three possible situations arise :

- $Q = K$: The reaction quotient will equal the equilibrium constant only if the system is at equilibrium already.
- $Q > K$: The concentrations of the products is too large and that of reactants too small. Thus, substances on the right side of the chemical equation will react to form substances on the left ; the reaction moves from right to left in approaching equilibrium.
- $Q < K$: The concentration of products is too small and that of the reactants too large. Thus, the reaction will achieve equilibrium by forming more products; it moves from left to right.

(2) CALCULATING EQUILIBRIUM CONCENTRATIONS

In order to calculate equilibrium concentrations, we tabulate the initial concentrations or partial pressures, the changes therein, and the final equilibrium concentrations or partial pressures. Usually the equilibrium-constant expression is used to derive an equation that must be solved for an unknown quantity.

Que : For the Haber process, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_p = 1.45 \times 10^{-5}$ at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture ?

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$P_{N_2} = 0.432$ atm, $P_{H_2} = 0.928$ atm, and $P_{NH_3} = x$.

$K_p = 1.45 \times 10^{-5}$

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

$$K_p = \frac{x^2}{(0.432)(0.928)^3}$$

$$1.45 \times 10^{-5} = \frac{x^2}{0.34524522}$$

$$x^2 = 0.34524522 \times 1.45 \times 10^{-5}$$
$$x^2 = 0.0000005006$$
$$x = \sqrt{0.0000005006}$$
$$x = 0.002237421$$
$$x = \underline{\underline{2.24 \times 10^{-3}}}$$

LE CHATELIER'S PRINCIPLE

If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

CONCENTRATION CHANGES

If a chemical system is at equilibrium and we increase the concentration of a substance (either a reactant or product), the system reacts to consume some of the substance. Conversely, if we decrease the concentration of a substance, the system reacts to produce some of the substance.

2. VOLUME AND PRESSURE CHANGES

At constant temperature, reducing the volume of a gaseous mixture at equilibrium causes the system to shift in the direction that reduces the number of moles of gas. Conversely, increasing the volume causes a shift in the direction that produces more gas molecules.

For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, four molecules of reactants are consumed for every two molecules of the product formed or produced. Consequently, an increase in pressure (decrease in volume) causes a shift to the side with fewer gas molecules, which leads to the formation of more NH_3, as indicated in the Haber process.

For the case of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the number of molecules of gaseous products (two) equals the number of molecules of gaseous reactants; therefore, changing the pressure will not influence the position of the equilibrium.

TE : The pressure–volume changes do not alter the value of K as long as the temperature remains the same (constant). Rather, they change the partial pressures of the gaseous substances.

3. TEMPERATURE CHANGES

When the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts to the direction that consumes the excess reactant (or product), namely heat.

Endothermic : Reactants + heat $\rightleftharpoons$ Products
Exothermic : Reactants $\rightleftharpoons$ Products + heat

Increasing the temperature causes the equilibrium to shift to the right and K to increase. Lowering the temperature shifts ~~to~~ the equilibrium in the direction that produces heat, to the left, decreasing K.

In an endothermic reaction, heat is absorbed as reactants are converted to products. Thus, increasing the temperature causes the equilibrium to shift to the right, in the direction of products, and K increases.

In an exothermic reaction, the opposite occurs. Heat is absorbed as products are converted to reactants; therefore, the equilibrium shifts to the left and K decreases.

Endothermic : Increasing T results in an increase in K.
Exothermic : Increasing T results in a decrease in K.

Cooling a reaction has the opposite effect. As we lower the temperature, the equilibrium shifts to the side that produces heat. Thus, cooling an endothermic reaction shifts the equilibrium to the left, decreasing K. Cooling an exothermic reaction shifts the equilibrium to the right, increasing K.

EFFECTS OF CATALYSTS

A catalyst increases the rate at which equilibrium is achieved, but it does not change the composition of the equlibrium mixture.

Some important questions to ask?

- Why do some solids dissolve in water while others do not?
- Why are some substances gases at room temperature, but others are liquids and solids?
- What gives metals the ability to conduct electricity, what makes non-metals brittle?

The answers have to do with Intermolecular forces.

Que: What are Intermolecular forces?

Ans: Electrical forces between molecules causing one molecule to influence the other.

Ans: Attractive forces between molecules, responsible for the nonideal behaviour of gases.

Intermolecular attractions are attractions between a molecule and a neighbouring molecule.
The forces of attraction which hold individual molecules together (for example, the covalent bonds) are known as Intramolecular attractions.

NOTE • All molecules experience intermolecular attractions, although in so cases those attractions are very weak.

• Even in a gas like hydrogen gas, H_2, if you slow the molecules do by cooling the gas, the attractions are large enough and the molecules stick together to form a liquid and eventually a solid.
In hydrogen's case, the attractions are so weak that the molecules have to be cooled to 21 K (−252 °c) before the attractions ar enough to condense the hydrogen as a liquid.
Helium's intermolecular attractions are even weaker — the molecules won't stick together to form a liquid until the temperature drops to

Intermolecular vs Intramolecular forces

41 KJ to vapourize 1 mole of water (inter).
930 KJ to break all O-H bonds in 1 mole of water (intra).

NOTE
- Generally, intermolecular forces are much weaker than intramolecular forces.
- Measures of intermolecular forces are as follows: boiling point, melting point, enthalpy of fusion, vapourization and sublimation.

NOTE
- Intramolecular forces hold atoms together in a molecule.

Types of Intermolecular Forces

1. London forces.
2. Dipole – dipole interactions.
3. Ion - dipole interactions (salt dissolving in solution)
4. Hydrogen bonding.

Between H_2O (water), CH_3CH_2OH (ethanol) and Toluene which compound has the greatest intermolecular forces?
Water (H_2O) has the greatest intermolecular forces because it has the highest boiling point of the three.

DIPOLE – DIPOLE ATTRACTIONS

Recall that molecules can have a separation of charge
These attractions occur in both ionic and polar bonds – the greater the difference in electronegativity the more polar.
The molecules are attracted to each other in a compound by these positive and negative forces.

$$\overset{\delta+}{H} — \overset{\delta-}{Cl}$$

- Molecules that have a permanent dipole moment tend to align with opposite polarities in the solid phase for maximum attractive interaction.
- Dipole – dipole forces are attractive forces between polar molecules, that is, between molecules that possess dipole moments. Their origin is electrostatic.

HYDROGEN BONDING

Hydrogen bonding is a special type of dipole-dipole interaction, and it is very strong. It occurs when N, O, or F are bonded to H. It is the high change in electronegativity (ΔEN) of NH, OH and HF bonds that cause these to be strong forces (about 5x stronger than normal dipole-dipole forces).
They are given a special name because compounds containing these bonds are important in biological systems

NOTE • The energy of the H-bond is always dependant on the electronegativit of the X-atom : F > O > N > Cl.

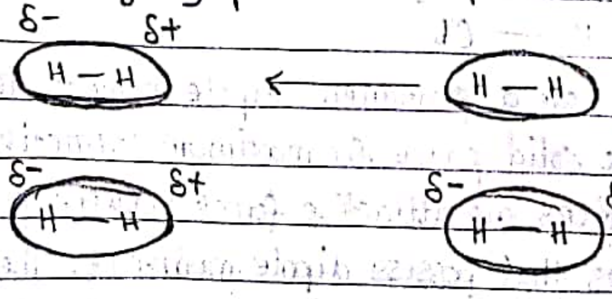
DISPERSION FORCES (LONDON FORCES)

- Non-polar molecules do not have dipoles like polar molecules. How can non-polar compounds form solids or liquids?
London forces are due to small dipoles that exist in polar-non molecules.

NOTE: Because electrons are moving around in atoms there will be instants wh the charge around an atom is not symmetrical. Hence the resulting tiny dipoles cause attractions between atoms or molecules.

- F_2 is not polar, but because electrons are on the move and tend to concentrate on one part of the molecule, an instantaneous dipole is created. These instantaneous dipoles are what makes F_2 to become polar.
- Temporary dipoles give rise to intermolecular attractions

As the right hand molecule approaches, its electrons will tend to be attracted to the slightly positive end of the right hand one



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NOTE : London forces are the only forces found in non-polar molecules that have intermolecular attractions between themselves, i.e London forces are the only intermolecular forces that are found in non-polar molecules.

- Even molecules without dipole moments must exert forces on each other.

Strengths of London Forces

Factors affecting the strength of intermolecular forces are :

1. Polarizability

As the volume of electrons increase, so does polarizability. Outer electrons tend to be loosely held.
Particles with large electron clouds experience stronger London forces than small electron clouds.

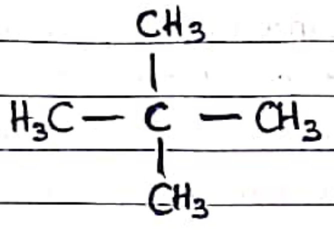
- Polarizability is the ease with which the electron cloud of a molecule or ion is distorted. It is a measure with which instantaneous dipoles are formed.

2. Number of atoms in the molecule

For molecules containing the same elements, London forces increase with increase in the number of atoms.
Comparing two hydrocarbons of different chain length C_3H_8 and C_6H_{14}, one with a longer chain has the higher boiling point. This is because molecules with longer chains experience stronger intermolecular attractions.

3. Shape of the molecule

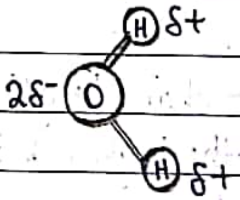
Fof molecules with the same elements and number, the shape will influence the strength of London forces. For example the molecules of C_5H_{12}:
Neo pentane $(CH_3)_4C$ is more compact than n-pentane which is $CH_3CH_2CH_2CH_2CH_3$.
The shape of $(CH_3)_4C$ does not allow for interaction compared to the straight chain moleculer compound.



$H_3C-C(CH_3)_2-CH_3$

= neopentane, makes a tetrahedral molecular structure because the central atom (C) is surrounded by four pairs of electrons.

- Intramolecular forces (within the molecule) may involve covalent or ionic bonding.
- When a substance such as water changes from solid to liquid to gas, the molecules remain intact. The changes in states are due to changes in the forces among the molecules rather than in those within the molecules.
- Dipole-dipole forces are forces that act between polar molecules. Molecules with dipole moments can attract each other electrostatically by lining up so that the positive and negative ends close up to each other. This is called dipole-dipole attractions.
- Dipole-dipole forces rapidly become weaker as the distance between the dipoles increases.



- Hydrogen bonds are a type of dipole-dipole attractions that are so unusually strong.
- Two factors account for the strengths of these interactions: (i) the great polarity of the bond and (ii) the close approach of the dipoles.

NOTE
- The reason why nonpolar tetrahedral hydrides of group 4A show a steady increase in boiling point with molar mass (that is, going down group) and the other groups' lighter members have unexpectedly boiling points that are higher is that there are large hydrogen bonding interactions that exist amongst the smallest molecules with the most polar X-H bonds.
- Methanol and ethanol have much higher boiling points than would be expected from their molar masses because of the polar O-H bonds which produce hydrogen bonding.

he importance of London dispersion forces increases greatly as the size of e atoms increases.

EMEMBER : Polarizability is the ease with which an electron "cloud" around an atom can be distorted to give a dipolar charge.

Large atoms with many electrons exhibit a higher polarizability than small atoms.

The same ideas also apply to non-polar molecules such as H_2, CH_4, CCl_4 and CO_2 since none of these molecules has a permanent dipole moment, their principal means of attracting each other is through London-dispersion forces.

REMEMBER : Dipole-dipole, dipole-induced dipole, and dispersion forces make up what chemists commonly call or refer to as van der Waals forces, after the Dutch physicist Johannes van der Waals.

Ions and dipoles are also attracted to one another by electrostatic forces called Ion-dipole forces, which are not van der Waals forces.

Depending on the phase of a substance, the nature of chemical bonds, and the types of elements present, more than one type of interaction may contribute to the total attraction between molecules.

Polarizability allows gases to condense, e.g He and N_2.

A kind of interaction as instantaneous dipole moments produces dispersion forces which are attractive forces that arise as a result of temporary dipoles induced in atoms or molecules.

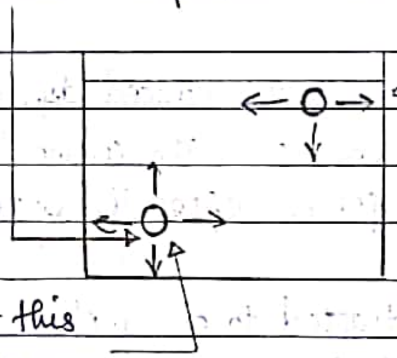
- The lower the number of electrons on atoms, the lower their polarizability, whereas the higher the number of electrons on atoms, their higher their polarizability.

SURFACE TENSION

The surface tension of a liquid is when the surface of any liquid behaves as if it was a stretched membrane.
Force tends to pull adjacent parts of a liquid's surface together, thereb decreasing surface area to the smallest possible size.

NOTE • The higher the attraction forces (intermolecular forces), the higher th surface tension. Surface tension causes liquid droplets to take a spherical shape, therefore we may have it that intermolecular forces caus surface tension which also causes a liquid droplet to become spherical.

A water molecule deep within the liquid is pulled equally from all sid



A water molecule at the surface lacks neighbouring water molecu towards the interface or surfa However, the net force then is n zero.

Net force for this molecule is zero.

This unequal attraction causes the water at the air-water interface act as a cohesive surface.

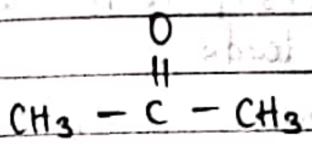
NOTE • Washing soap or powder reduces the intermolecular forces in water

• Surface tension of a liquid is the resistance of the liquid to an incr in its surface area.

If a liquid droplet is spherical, it has a low surface area because o surface tension. Therefore, liquids with relatively large intermolecular forces, such as those with polar molecules, tend to have high surface tensions. Note that for any volume given, a sphere has a smaller surfa than any other shape.

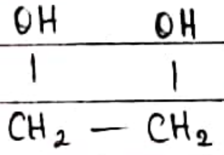
VISCOSITY

Flow is the change of form of a liquid or fluid.
At the same temperature different liquids experience different resistance to flow.
Viscosity is a measure of the liquid's resistance to flow, change in shape. Syrup is more viscous than water.
Viscosity is influenced by shape, intermolecular attractions and the size of the molecule.
The greater the intermolecular forces, the greater the viscosity, for molecules of the same size.
Compare acetone (nail polish remover) and ethylene glycol (car antifreeze), each have ten atoms.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Acetone



$$\overset{\overset{OH}{|}}{CH_2}-\overset{\overset{OH}{|}}{CH_2}$$

Glycol

Glycol is more viscous than acetone because it has both dipole-dipole interactions and hydrogen bonding whereas in acetone there are only dipole-dipole interactions.
Glycol — london forces plus hydrogen bonding are at play.
Acetone — experiences only dipole-dipole attractions and London forces.

Molecular size and ability of molecules to tangle with each other influences viscosity.

CH_4	Methane
$CH_3CH_2CH_3$	Ethane
$CH_3CH_2CH_2CH_3$	Propane
$CH_3CH_2CH_2CH_2CH_3$	Butane

Highly tangling molecules give rise to more viscous liquids. Example : heavy machine oil (mixture of non-polar hydrocarbons) + London force gives it viscosity that is 600 times that of water at 15 °C.

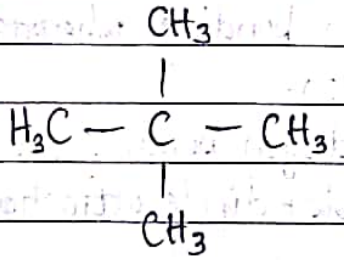
- More complex molecules are more likely to give rise to higher viscosity.
- Molecular complexity also leads to higher viscosity because very larg molecules can become entangled with each other.

For example : gasoline, a non viscous liquid, contains hydrocarbo molecules of the type $CH_3-(CH_2)_n-CH_3$, where n varies from about 3 to 8.

However, grease, which is very viscous, contains much larger hydrocarbon molecules in which n varies from 20 to 25.

- Viscosity is temperature dependant, as temperature is lowered becaus low temperatures lower down the kinetic energies of the molecules in a substa Conversely, an increase in the temperature leads to decrease in viscosit In the case of engine oil - light thin oil may be required in sub-ze temperatures, not the thick one(.

$CH_3CH_2CH_2CH_2CH_3$ ← n-pentane.



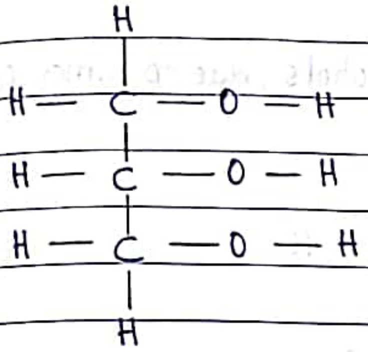
$$H_3C-\overset{\displaystyle CH_3 \atop |}{\underset{| \atop \displaystyle CH_3}{C}}-CH_3$$

← neo-pentane.

Neo-pentane and n-pentane have the same number of atoms, but are different from each other in shape.

- Viscosity has a strong dependance on intermolecular forces. Liquids wi high intermolecular forces tend to be highly viscous.

An example of such liquids is Glycerol whose structure has an unusu high viscosity due to its high capacity to form hydrogen bonds using OH groups.



• NOTE : Molecular complexity also leads to higher viscosity because very large molecules can easily become entangled with each other.

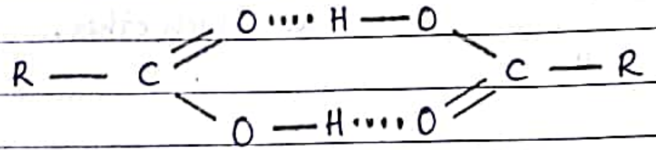
DIMERIZATION OF CARBOXYLIC ACIDS

Carboxylic acids e.g acetic acid when dissolved in an appropriate such as solvent benzene dimerize.

H-bonding enables the molecules to form bridges that result in "large" relative molecular mass.

232 BOILING POINTS

Higher boiling points than similar alcohols, due to dimer formation.

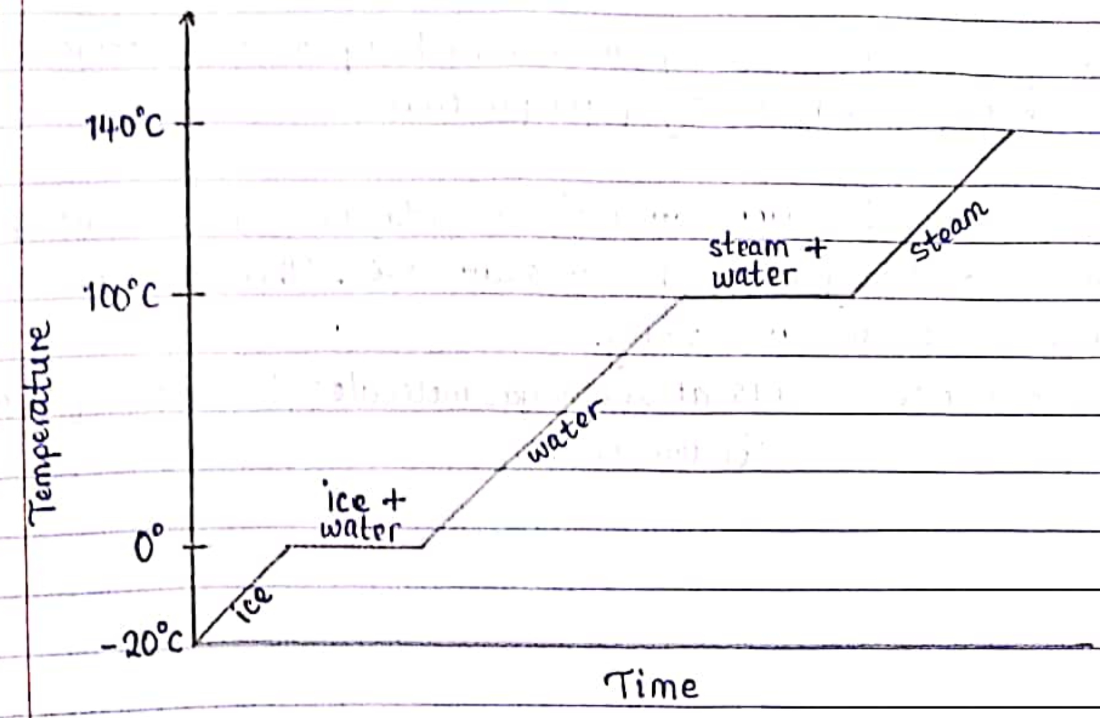


hydrogen-bonded acid dimer

CHANGE OF STATE

Consider applying heat to a solid — the solid changes to liquid, and on further heating it boils to form a vapour phase. Such as process represents a heating curve.

Consider the heating curve for water. As energy is absorbed, random vibrations increase and with increasing temperature they break free from lattice positions



At normal temperatures and pressures gas molecules are wide spread o separated with little interaction.

Low temperature and high pressure — molecules come closer and the force of attraction come in play.

Under critical conditions, a gas is able to turn into liquid

Liquid - vapour equilibrium — molecules in a liquid left in an open container escape into the space above, and this is called Evaporation o Vapourisation. The process is endothermic because energy is required t overcome the strongly interactive intermolecular forces in the liquid.

- The energy needed or required to vapourize 1 mole of liquid at 1 a is known as the Heat of Vapourisation or Enthalpy of Vapourisation denoted Hvap.

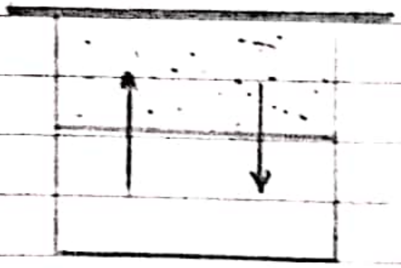
2. Maintain the temperature of the human body as temperature is controll through evaporation by way of perspiration.

Consider a liquid placed in a closed container. The amount of liquid decreases initially reaching a constant level. There is a net transfer of molecules into the gas initially.
The reverse process occurs at which gas molecules turn into liquid molecul
This process is called Condensation.

VAPOUR PRESSURE

At some point, the rate of evaporation equals the rate of condensation. There is no net change that occurs in the amount of liquid or vapour since the two opposite processes exactly balance each other. This stat is called Dynamic Equilibrium.
When molecules enter the vapour they exert a pressure known as the Equilibrium-Vapour pressure. It is, however, commonly referred to as vapour pressure.

$$P_{T_{(DAIR)}} = P_{AIR} - P_{H_2O}$$



NOTE: Vapour is a term usually used for the gas phase of a substance that exists as a solid or liquid at 25°C and 1 atm.
NOTE: ΔH_{vap} for water at 100°C is 40.7 kJ/mol.

- Vapourization is endothermic because energy is required to overcome the relatively strong intermolecular forces in the liquid.
  The energy required to vapourize 1 mole of a liquid at a pressure of 1 atm is called the Heat of Vapourization, or the Enthalpy of Vapourization, ΔH_{vap}.
- It is because of the strong hydrogen bonding among its molecules, that water has an unusually large heat of vapourisation (40.7 kJ/mol).
- The pressure of the vapour present at equilibrium is called the Equilibrium Vapour pressure, or the vapour pressure of the liquid.
  A single barometer can measure the vapour pressure of a liquid. This can be done as follows: The liquid is injected at the bottom of the tube of mercury and floats to the surface because the mercury is so dense. A portion of the liquid evaporates at the top of the column, providing a vapour whose pressure pushes down some mercury out of the tube. Then when the system reaches equilibrium, the vapour pressure can be determined from the change in the height of the mercury column since $P_{atm} = P_{vapour} + P_{Hg\ column}$.

$$P_{vapour} = P_{atmosphere} - P_{Hg\ column}$$

- Liquids with high vapour pressures are said to be volatile – they evaporate rapidly from an open dish.

TE : The vapour pressure is determined by the size of intermolecular forces in the liquids.

THE CLAUSIUS – CLAPEYRON EQUATION

$$\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

In which : P_1 and P_2 are the vapour pressures at T_1 and T_2 respectively.
T is given in Kelvin units
ln is the natural logarithm
R is the gas constant ($8 \cdot 314\ J\,K^{-1} mol^{-1}$)
ΔH_{vap} is the molar heat of vapourization.

For purposes of simply calculating, the above equation is used. However if the values of ln P and 1/T are available for each state, the graphical method is the more effective than the equation.

SOLUTIONS

Solutions are homogenous mixtures of two or more pure substances. In a solution, the solute is dispersed uniformly throughout the solvent.

OTE : The intermolecular forces between the solute and solvent particles must be strong enough to compete with those between solute particles and those between solvent particles.

How does a solution form ?
As a solution forms, the solvent pulls solute particles apart and surrounds, or solvates, them.

NOTE: If an ionic salt is soluble in water, it is because the ion-dipole interactions are strong enough to overcome the lattice energy of the salt crystal.

NOTE: $\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{solution}$

Three processes affect the energies of the process: (energetics)

(i) separation of solute particles.

(ii) separation of solvent particles.

(iii) new interactions between solute and solvent.

(iv) the enthalpy change of the overall process depends on ΔH for each of these steps.

Types of Solutions

Saturated : The solvent holds as much solute as is possible at that temperature. A dissolved solute is in dynamic equilibrium with solid solute particles.

Unsaturated : Less than the maximum amount of solute for that temp. is dissolved in the solvent.

Supersaturated : The solvent holds more solute than is normally possible at that temperature. These solutions are unstable; crystallization can usually be stimulated by adding a "seed crystal" or scratching the side of the flask.

238 Factors Affecting Solubility

1. Chemists use the axiom "like dissolves like".
   Polar substances tend to dissolve in polar solvents.
   Non-polar substances tend to dissolve in nonpolar solvents.
   The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

Gases in Solution — Henry's Law (Pressure Effect)

The solubility of liquids and solids does not change appreciabl with pressure.

NOTE: • The solubility of a gas in a liquid is directly proportional to its pressure. In other words, the amount of gas dissolved in a solutio is directly proportional to the pressure above the solution. This is called Henry's Law.

$$C = kP$$

where, P is the partial pressure of the gaseous solute above the solution.
k is the Henry's Law characteristics for a particular solut
C is the concentration of the dissolved gas.

Generally, the solubility of solid solutes in liquid solvents increase with increasing temperature. For some substances, solubility decrease with increasing temperature. This is why experiments need to be don in order to be certain.

- Pressure can and does increase the solubility of a gas.

NOTE • Henry's Law gives the relationship between the gas pressure and the concentration of dissolved gas. However, this law (Henry's) holds only when there is no chemical reaction between the solute and the solvent. Therefore, it is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent.

Remember: **Molality** is the ratio of the number of moles of a solute to the amount of solvent in kilograms. In other simple words, molality is the number of moles of solute per kilogram of solvent. Molality = m.

Remember; **Mole fraction** is the ratio of the number of moles of a given solute component to the total number of moles of solution. It is denoted by the lower case letter of the greek alphabet "chi" χ.

NOTE: When solvents are mixed, the liquids intermingle uniformly sometimes. Nevertheless, when liquids are mixed, the liquid present in larger amount is the Solvent.

A solution is a homogeneous mixture. Air, too, is a solution.

emember: The mass percent of a solution or mixture is the ratio of the mass of solute to the mass of the solution multiplied by 100%.

NOTE: For the mole fraction $(\chi) = \frac{n_A}{n_A + n_B}$, where A is the main component.

emember: Henry's Law is obeyed by oxygen gas in water, but it does not correctly represent the behaviour of gaseous hydrogen chloride because of its dissociation into ions when it is mixed or dissolved in water.

Example: A certain soft drink is bottled so that a bottle at 25°C contains CO_2 gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO_2 in the atmosphere is 4.0×10^{-4} atm, calculate the equilibrium concentrations of CO_2 in the soda both before and after the bottle is opened. The Henry's law constant for CO_2 in aqueous solution is 3.1×10^{-2} mol L^{-1}atm^{-1} at 25°C.

Solution: CO_2 gas is at 5.0 atm above or over the liquid.

The partial pressure ($P.P_{CO_2}$) for CO_2 is 4.0×10^{-4} atm.

HK (Henry's constant) = 3.1×10^{-2} mol/L·atm at 25°C.

Therefore; concentration of dissolved gas = HK × Partial pressure of the gaseous solute above the solution.

Henry's constant

* Before the bottle is opened there exists an equilibrium state between th gas above the liquid and the dissolved gas. Note that no gas has escaped whatsoever. Consequently, the equilibrium concentration of CO_2 will be:

$$C = HKP$$
$$C = 3.1 \times 10^{-2}\ mol \cdot L^{-1} \cdot \cancel{atm^{-1}} \times 5\ \cancel{atm}$$
$$C = 0.155\ mol \cdot L^{-1}$$
$$C = 0.16\ mol/L \approx \underline{1.6 \times 10^{-1}\ mol/L}.$$

* After the bottle is opened, the equilibrium concentration of CO_2 in the soda is expected to drop because some of the gas escapes into th atmosphere and therefore only an equilibrium state made by the atmospheric CO_2 and the dissolved CO_2 will exist.

$$C = HKP$$
$$C = 3.1 \times 10^{-2}\ mol \cdot L^{-1} \cdot atm \times 4.0 \times 10^{-4}\ atm$$
$$C = 0.0000124\ mol\, L^{-1}$$
$$C = \underline{1.24 \times 10^{-5}\ mol/L}.$$

Remember: Henry's law for CO_2 is $C_{CO_2} = K_{CO_2} P_{CO_2}$.
As expected the concentration of CO_2 after the bottle is opened is low than it was before the bottle was opened. This is why soda goes "flat" after being open for a while.

- Factors that affect solubility are as follows:
  (i) Structure effects
  (ii) Pressure effects (under which is Henry's Law).
  (iii) Temperature effects (for aqueous solutions).

Temperature Effects (for Aqueous Solutions).

24/

- The dissolving of a solid occurs more rapidly at higher temperatures, but the amount of solid that can be dissolved may increase or decrease with increasing temperature.
- The behaviour of gases dissolving in water appears less complex. The solubility of a gas in water typically decreases with increasing temperature.
- Warm water is less dense than cold water. Warm water also contains less than the normal concentration of oxygen and therefore tends to float on the colder water below, thus blocking normal oxygen absorption.
- The decrease in solubility of gases with increasing temperature is also responsible for the formation of boiler scale.

Vapour Pressures of Solutions.

- A nonvolatile solute has no tendency to escape from solution into the vapor phase.
- The presence of a nonvolatile solute lowers the vapour pressure of a solvent. This is because the non-volatility of the solution prevents vapour from accumulating or increasing thereby increasing the pressure as well if it were so.

NOTE
- The dissolved nonvolatile solute decreases the number of solvent molecules per unit volume and it should proportionately lower the escaping tendency of the solvent molecules. For example, in a solution consisting of half nonvolatile solute molecules and half solvent molecules, we might expect the observed vapour pressure to be half that of the pure solvent, since only half as many molecules can escape. In fact, this is what is observed.

Studies of the vapour pressures of solutions containing nonvolatile solutes were carried out by Francois M. Raoult (1830 - 1901). His results are described by the equation known as the Raoult's Law:

$P_{solution} = X_{solvent} P^0_{solvent}$; where $P_{solution}$ is the observed vapour pressure of the solution, $X_{solvent}$ is the mole fraction of the solvent, and $P^0_{solvent}$ is the vapour pressure of the pure solvent.

COLLIGATIVE PROPERTIES

- Changes in colligative properties depend only on the number of solute particles present, not on the identity of the soluble particles. Colligative properties are as follows : (i) Lowering Vapour Pressure, (ii) Boiling point elevation, (iii) Melting point depression and (iv) osmotic pressure. These properties are bound together by a common origin. Because of solute - solvent intermolecular attraction, higher concentrations of non-volatile solutes make it harder for the solvent to escape to the vapour phase. Therefore, the vapour pressure of a solution is lower tha that of the pure solvent.

NOTE : When using Raoult's Law, it is one of those times when you want make sure you have the mole fraction of the solvent.

Boiling point elevation.

Nonvolatile solute - solvent interactions also cause solutions to have higher boiling points and lower freezing points than the pure solvent. The change in boiling point is proportional to the molality of the solution : $\Delta T_b = K_b \cdot m$, where K_b = molal boiling point elevati constant, a property of the solvent.

NOTE • Since the normal boiling point of a liquid is the temperature at which it is 1.0 atm, at the normal boiling point of a pure liquid the vapou pressure will be less than 1 atm. Thus, a higher temperature is requi to attain a vapour pressure of 1 atm, and thus the boiling point of th solution is higher than that of the pure liquid. (Check a phase diagram).

Freezing Point Depression

The change in freezing point can be found similarly :

$$\Delta T_f = K_f \cdot m$$

Here, K_f is the molal freezing point depression constant

E • Because the triple - point temperature of the solution is lower than that of the pure liquid, the freezing point of the solution is lower than that of th pure liquid.

Colligative Properties of Electrolytes

Since colligative properties depends on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes.
However, a 1 M solution of NaCl does not show twice the change in freezing point that a 1 M solution of methanol does.

The van't Hoff Factor.

One mole of NaCl in water does not really give rise to two moles of ions. Some Na^+ and Cl^- reassociate for a short time, so the true concentration of particles is somewhat less than two times the concentration of NaCl. Remember that you have to also consider the Na^+ and Cl^- that reassociate. Re-association is more likely to occur at higher concentration than at lower concentration. Therefore, the number of particles present is concentration dependant.

Compound	0.100m	0.0100m	0.00100m	Limiting value
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

We can modify the previous two equations by multiplying by the van't Hoff factor, I:

$$\Delta T_f = K_f \cdot m \cdot I$$

mber: An ideal-gas obeys the ideal-gas law, and an <u>ideal solution</u> obeys Raoult's Law.

ember: The normal boiling point of a liquid is the temperature at which its vapour pressure equals 1 atmosphere or 1×10^5, (100 000), Pascals.

Some substances form semipermeable membranes, allowing some smaller particles t pass through, but blocking other larger particles.

In osmosis, there is net movement of solvent from the area of higher solvent concentration (lower solute concentration) to the area of lower solvent concentra (higher solute concentration).

Osmotic Pressure

The pressure required to stop osmosis, known as osmotic pressure, π, is

$$\pi = \left(n/V\right)RT = MRT$$, where M is the molarity

- Colligative properties are properties that depend on the quantity (concentration) but not on the kind or identity of the solute ~~properties~~ particles. Colligative means "depending on the collection". These properties are studied in solutions relative to pure solvents.

NOTE • A substance that has no measurable vapour pressure is Nonvolatile, whereas one that exhibits a vapour pressure is volatile.

- Lowering the vapour pressure is done by adding a nonvolatile solute to a solven

IOTE • "The partial pressure exerted by solvent vapour above a solution, P_A, equals the product of the mole fraction of the solvent in the solution, X_A, times the vapour pressure of the solvent which is pure, P_A°."

The above law is called Raoult's Law. $\boxed{P_A = X_A P_A^\circ.}$

This law expresses the fact that adding a nonvolatile solute lowers the vapour pressure of the volatile solvent.

E • Molarity depends on the volume of the solution, whereas molality depends on the mass of the solvent.

Organic Chemistry is the study of compounds of carbon.
Inorganic chemistry is the study of compounds of all other elements.

Sheer numbers is one reason why organic chemistry is a separate field of study in chemistry.

Organic compounds are the chemical basis of life itself as well as an important component of current high standard of living enjoyed by people in many countries.
Proteins, carbohydrates, enzymes, and hormones are all organic molecules. Organic compounds also include natural gas, petroleum, coal, gasoline, and many synthetic materials such as dyes, plastics and clothing fibres.

All Chemical Compounds

Organic compounds	Inorganic compounds
Organic chemistry	Inorganic chemistry
Study of compounds of Carbon excluding: CO, CO_2, CO_3^{2-}, HCO_3^-, C_2^{2-}, CN^-, O^{2-}, S^{2-}, CS, CS_2.	Study of compounds of all other chemical elements including CO, CO_2, CO_3^{2-}, HCO_3^-, C_2^{2-}, CN^-, O^{2-}, S^{2-}, CS, CS_2.

"Organ" is a greek word for "Life".

The carbon cycle begins and ends with atmospheric CO_2.

Animal and plants $\xrightarrow[\text{biodegradation}]{\text{expire}} CO_2 + H_2O + N_2 + CH_4$

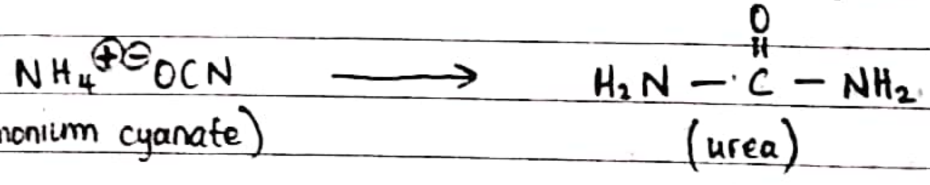
Compounds of carbon are the central substances of which all living things are made.

1. DNA – giant molecules that contain all the genetic information for a given species
2. Proteins – blood, muscle, skin
3. Enzymes – catalyze reactions that occur in biological systems (our bodies).

As a science, organic chemistry is less than 200 years old. Historical origi of the terms involve conceptual pairings:

(i) Organic – derived from living organisms
(ii) Inorganic – derived from inanimate materials.

In 1828, Friedrich Wohler, the father of organic chemistry, synthesi urea by heating ammonium cyanate, isolated from urine.



$$\underset{\text{(Ammonium cyanate)}}{NH_4^{\oplus}\,{}^{\ominus}OCN} \longrightarrow \underset{\text{(urea)}}{H_2N - \overset{\overset{O}{\|}}{C} - NH_2}$$

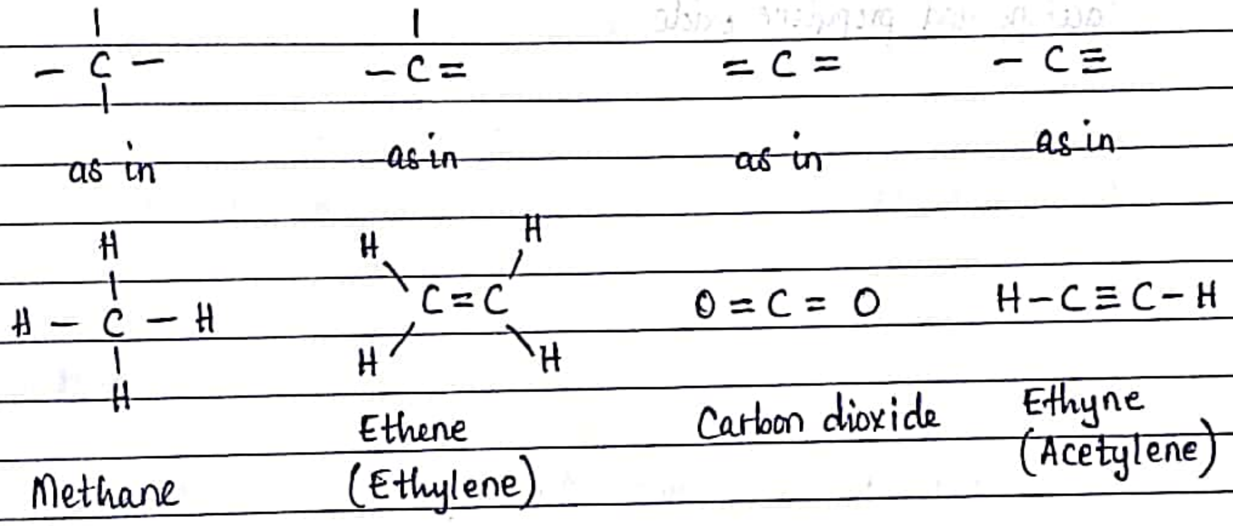
Carbon can form five times as many compounds as all the other elemen combined. This is because carbon has a unique ability to bond to each other in a wide variety of ways that involve long chains of C-atoms cyclic arrangements (rings) of C-atoms. Sometimes both chains and rings of C-atoms are present in the same molecule.

Carbon's unique atomic structure allows it to covalently bond with up to 4 (four) other atoms.

Carbon is the simplest element on periodic table that has also 4 (four) valence electrons (VEs).

If each valence electron bonds to one electron from another atom, carbon reaches 8 electron shell octet and is stable.

- Methane = Carbon-tetrahydride.
- The covalence of atoms of elements is the number of electrons they can share in forming covalent bonds.



Methane

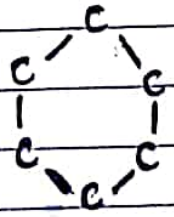
Ethene (Ethylene)

Carbon dioxide

Ethyne (Acetylene)

Saturated Hydrocarbons are compounds in which all carbon-to-carbon bonds are single bonds. They contain only sigma (σ) bonds. Examples are Acyclics and Cyclics.

C–C–C–C and



Unsaturated Hydrocarbons are compounds in which one or more carbon-to-carbon has multiple bonds. They contain sigma (σ) and pi (π) bonds.

- Hydrocarbons are compounds than contain only hydrogen (H) and carbon (C) and one or more additional elements.

- Constitutional or Structural isomers are different compounds that have same molecular formula but differ in the sequence in which their atoms are bonded, that is, in their connectivity. They usually have different physica properties (e.g boiling points, melting points and density) and different chemic properties (reactivity).
Examples of such constitutional isomers are dimethyl-ether and ethanol, acetone and propylene oxide

151 The sp orbitals of the C−H bonds of ethyne have 50% s character because they arise from the combination of one s orbital and one p orbital.

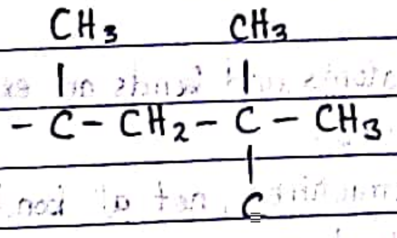
$s, p \longrightarrow sp$
$s, p, p \longrightarrow sp^2$
$s, p, p, p \longrightarrow sp^3$

* When you have more s orbitals, you have more acidity.

Being the most electronegative, the sp-hybridized C-atom of ethyne polarizes its C−H bonds to the greatest extent causing its hydrogens to be most positive. Therefore, ethyne donates a proton to a base more readily.

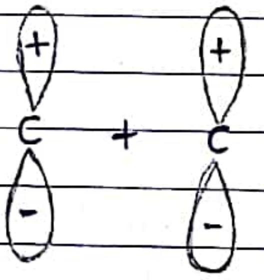
$$H-C\equiv C-H > H_2C=CH_2 > H_3C-CH_3$$

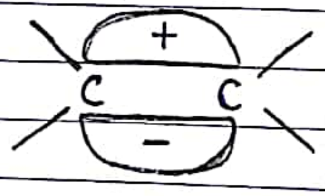
$$H-C\equiv C-H^+ + :B \quad H-C\equiv C^- + H{:}B^+$$


$$-\overset{CH_3}{\underset{}{C}}-CH_2-\overset{CH_3}{\underset{C}{C}}-CH_3$$

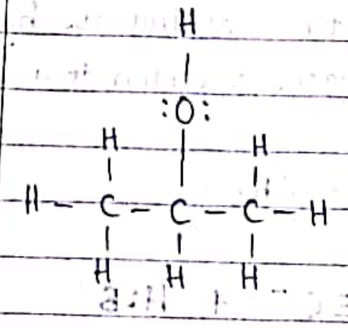
Comparison of σ (sigma) and π (pi) bonds.

	σ bond	π bond
Mode of formation	Head-on overlap of hybridized orbitals, or hybridized and un-hybridized orbitals of unhybridized orbitals oriented along a line (linear) connecting the nuclei.	sideways overlap of parallel, unhybridized p-orbitals oriented perpendicular to the line connecting the nuclei.
Electron density	Electron density centered along the line connecting the nuclei.	Most of electron density centered abo and below the line connecting the nuclei.
Shape of bond	Cylindrically symmetrical.	Non-cylindrically symmetrical.

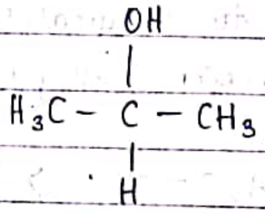




A primary (1°) carbon atom is an atom of carbon in an organic molecul that is bonded to only one other carbon atom.
A secondary (2°) carbon atom is a carbon atom in an organic molec that is bonded to two other carbon atoms.
A tertiary (3°) carbon atom is a carbon atom in an organic molecule t is bonded to three other carbon atoms.
A quaternary (4°) carbon atom is a carbon atom in an organic molecu that is bonded to four other carbon atoms.
The symbol R is used in organic chemistry to represent a generalized organic group. R can be methyl, ethyl, propyl or any of a multitude of others.



Lewis structure



Partially condensed structure.

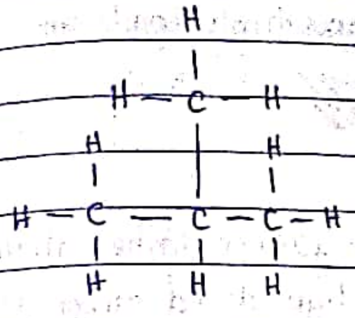
$(CH_3)_2CHOH$
Condensed structure

C_3H_8O
Molecular Formula.

- In Lewis structures, all atoms and bonds are explicitly drawn. This is practical for small molecules.
- In partially condensed structures, not all bonds are explicitly shown or drawn. This is only practical for small molecules.

- A structural formula in which a line represents a carbon-carbon bond and a carbon atom is understood to be present at every point where line meet and at the ends of the lines is called a Line-Angle structural formula.

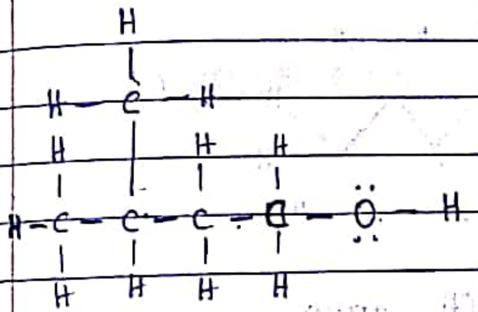
← line-angle structure



= $(CH_3)_3\,CH$ = Butane.

$CH_3(CH_2)_2\,CH_3$ or $CH_3CH_2CH_2CH_3$ = Butane.

2 CH_2 groups are bonded together.



= $(CH_3)_2\,CHCH_2OH$

Draw the heteroatoms without the lone pairs

(Expanded formula) (Condensed formula).

Bond-Line or Line Structure or Line - Angle Structure.

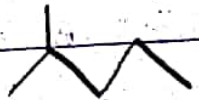
It is not practical to draw Lewis structures for all compounds, especially large ones.

Bond-line structures not only simplify the drawing process but also are easier to read.

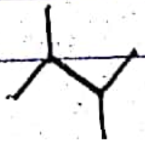
Bond-line structures are drawn in zig-zag format ( ) where each corner (intersection) or endpoint represents a carbon atom.

For example: each of the following compounds has six carbon atoms:

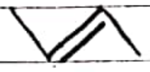
and



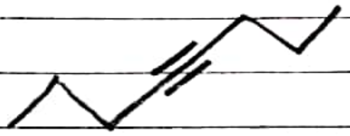
and



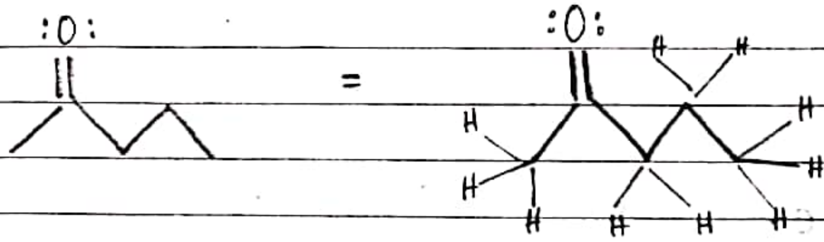
Double bonds are shown with two lines, and triple bonds are shown with three lines:

 and 

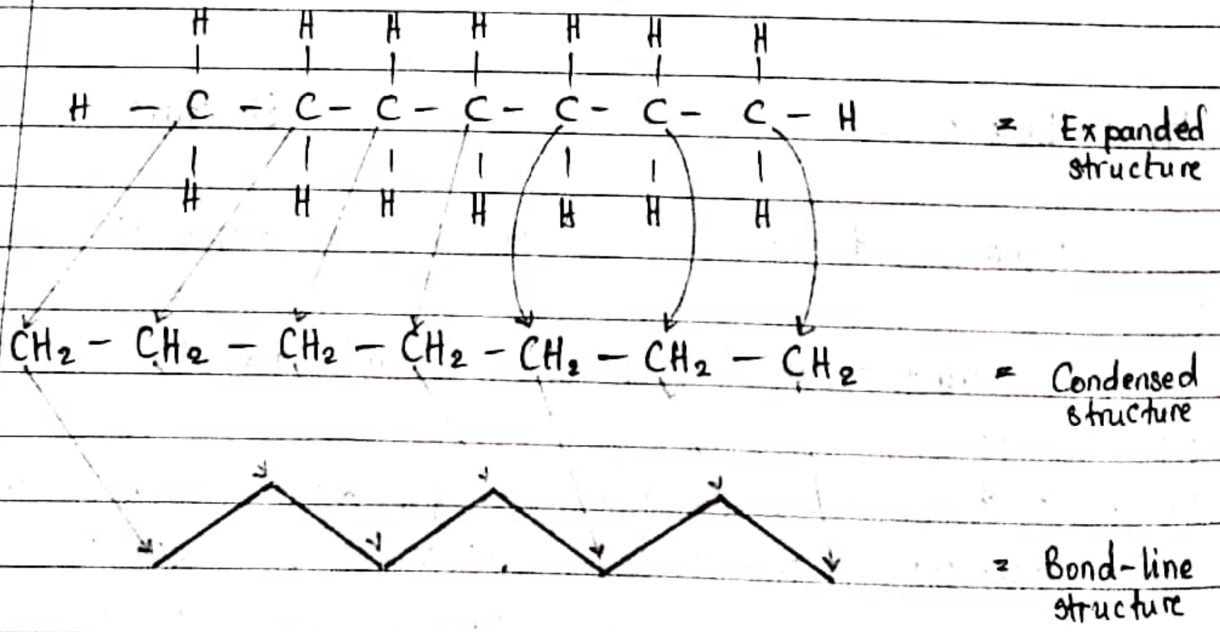
Note that triple bonds are drawn in linear fashion rather than in a zig-format because triple bonds involve sp-hybridized carbon atoms, which have linear geometry.



= C_8H_{14}



- A two-way intersection represents a CH_2 group.
- A three-way intersection represents a CH group.
- A four-way intersection is simply a carbon atom.



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NIC

- The zig-zag (sawtooth) pattern used in line bond formulas has a relationship to the three-dimensional shape of the molecules that are represented.

Short-hand Rules

1. Carbon atoms are not usually shown; they are at each intersection and end of each line.

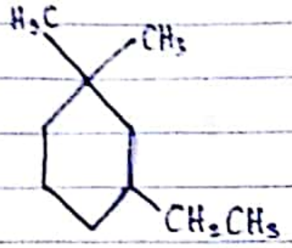
2. Hydrogen atoms are not shown.

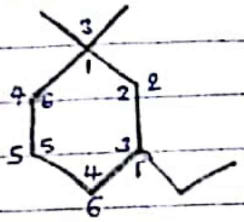
IUPAC = International Union of Pure and Applied Chemistry.

Systematic names are derived according to a prescribed set of rules, common names are not.
Many compounds, however, are better known by their common names than by their systematic names.

- The names methane, ethane, propane and butane have historical roots. From pentane onwards, alkanes are named using Greek words for the number of carbon atoms, plus the suffix "-ane" to identify the molecules as alkanes
- The alkane homologous series has the general formula : C_nH_{2n+2}.
The key to naming branched-chain alkanes is knowing the name of the branch or branches that are attached to the main carbon chain. These branches are formally called Substituents.
- A substituent is an atom or group of atoms attached to a chain of carbon atom

(c)

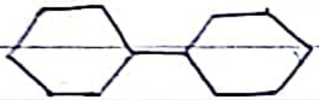




Name : 1 - Ethyl - 3, 3 - dimethyl - (outer ring counting) cyclohexane.
Name : 3 - Ethyl - 1, 1 - dimethylcyclohexane (inner ring counting).

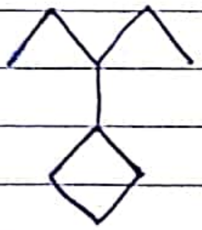
Therefore, the most suitable IUPAC name for the compound is given below:
3 - Ethyl - 1, 1 - dimethylcyclohexane.

(b)

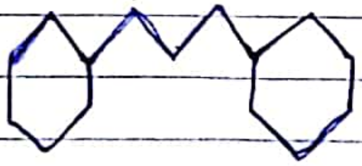


Name : cyclohexylcyclohexane.

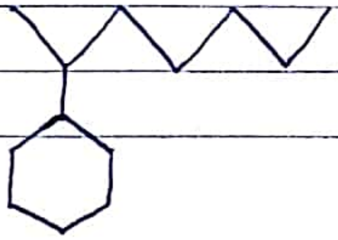
RULE 4 : When a single ring system is attached to a single chain with a greater number of carbon atoms, or when more than one ring system is attached to a single chain:



Name : 3 - Cyclobutylpentane

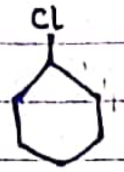


Name : 1, 3 - Dicyclohexylpropane

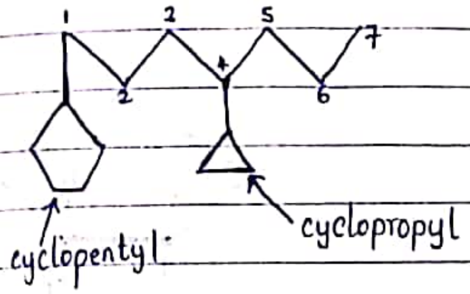


Name : 2 - Cyclohexylheptane

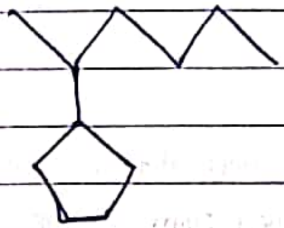
257 *. Remember that you don't add the number in the name when there is only one substituent. E.g



= Chlorocyclohexane.



= Cyclopentylcyclopropylheptane.



= 2-Cyclopentylhexane.

Geometrical (cis-trans) isomers

Geometrical isomers can be ~~used~~ caused if a structural reason stops the bond rotation which would let the isomers convert from one to the other.

Common in both alkenes, because of C=C, and ~~cyclohex~~ cycloalkanes, because of the ring.
Both of these features can cause substituents to have two different geometric relationships with one another.
These relationships are called: Cis = on the same side, or Trans = on the opposite side.
With their cyclic structures, cycloalkanes can be looked at from two sides, a "top" side and a "bottom" side.
Because of this, in substituted cycloalkanes, isomers become possible when the substituents have different geometric relationships to one another.

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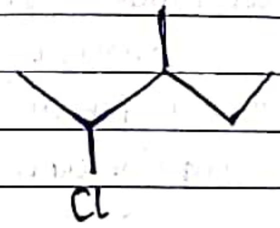
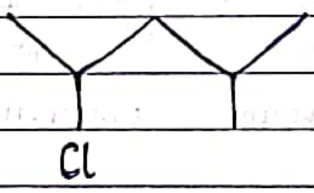
- Alkanes bearing hydrogen or any halogen substituent are named in the IUPAC substitutive system as Haloalkanes.

NOTE: (a) When the parent chain has both a halo and an alkyl group substituent attached to it, number the chain from the end nearer the first substituent, regardless of whether it is halo or alkyl. (b) If two substituents are at equal distance from the end of the chain, then number the chain from the end nearer the substituent that has alphabetical precedence.

CH_3CH_2Cl	$CH_3CH_2CH_2F$	$CH_3CHBrCH_3$
chloroethane	1-Fluoropropane	2-Bromopropane

(a)


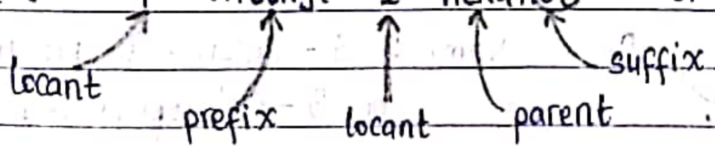
(b)


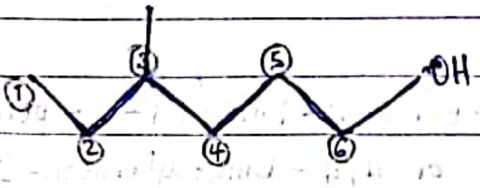
2-Chloro-3-methylpentane.   2-Chloro-4-methylpentane.

- In this common nomenclature system, called functional class nomenclature, haloalkanes are named as alkyl halides.

Nomenclature of Alcohols

In general, numbering of the chain always begins at the end nearer the group named as the suffix.

Name : 4-Methyl-1-hexanol or 4-Methylhexan-1-ol.




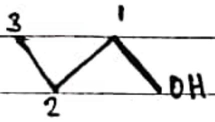
(This chain has six carbons in its length).

The locant for the suffix (whether it is for an alcohol or another functiona group) may be placed before the parent name as in the previous example, or according to a 1993 IUPAC revision of the rules, immediately before the suffix (as in 4-Methylhexan-1-ol.). Both methods are IUPAC approved

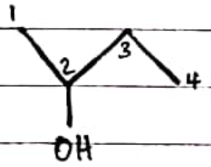
Procedure or Rules in giving alcohols IUPAC substitutive names

① Select the longest continuous carbon chain to which the hydroxyl is directly attached. Change the name of the alkane corresponding to this chain by dropping the final -e and adding the suffix -ol.

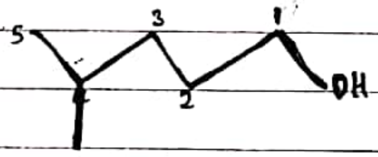
② Number the longest continuous carbon chain so as to give the carbon atom bearing the hydroxyl group the lower number. Indicate the position of the hydroxyl group by using this number as a locant; indicate the positions of other substituents (as prefixes) by using the numbers corresponding to their positions along the carbon chain as locant



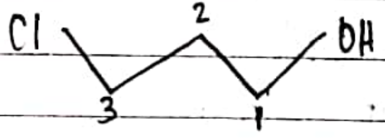
Name: 1-Propanol



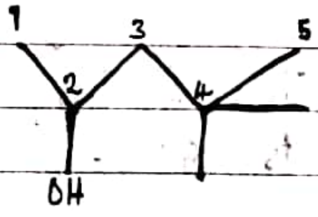
Name: 2-Butanol



Name: 4-Methyl-1-Pentanol
4-Methylpentan-1-ol
(not 2-methyl-5-pentanol).



Name: 3-Chloro-1-propanol
or 3-Chloropropan-1-ol.



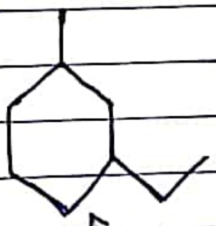
Name: 4,4-Dimethyl-2-pentanol.
or 4,4-Dimethylpentan-2-ol.

⇒ a Phenyl group.

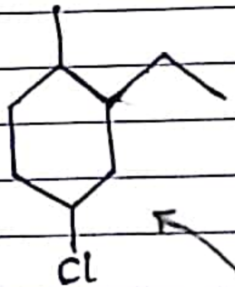
Naming Cycloalkanes : Monocyclic compounds.

Naming substituted cycloalkanes is straightforward. They are named as alkylcycloalkanes, halocycloalkanes, alkyl~~halo~~cycloalkanols, and so on. If only one substituent is present, it is not necessary to designate its position. When two substituents are present, we number the ring beginning with the substituent first in alphabet and number in the direction that gives the next substituent the lower number possible. When three or more substituents are present, we begin ~~at~~ the substituent that leads to the lowest set of locants.

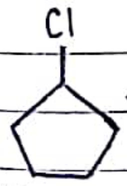
Isopropylcyclohexane.



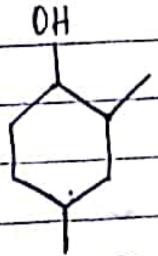
1-Ethyl-3-methylcyclohexane.



4-Chloro-2-ethyl-1-methylcyclohexane.

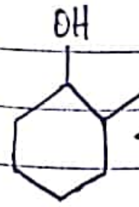


Chlorocyclopentane



2,4-Dimethylcyclohexan-1-ol.

or 2,4-Dimethyl[redacted]cyclohexanol.



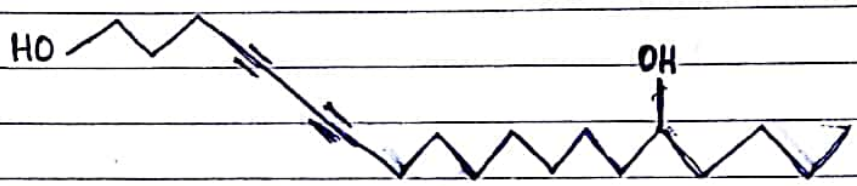
2-Methylcyclohexanol.

ALKYNES

Alkynes are unsaturated organic compounds with at least one carbon carbon triple bond.
Common name for this family is Acetylenes, after the simplest member:

$$H-C\equiv C-H$$

In nature, alkynes are found in some plants and fruits, but they are not common as alkenes.



cicutoxin (found in water hemlock).

C_2H_2 $H-C\equiv C-H$

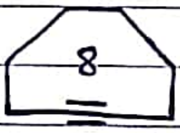
C_3H_4 $CH_3-C\equiv C-H$

C_4H_6 $CH_3-CH_2-C\equiv C-H$ or $CH_3-C\equiv C-CH_3$

C_5H_8

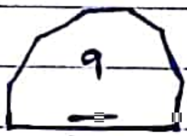
C_6H_{10}

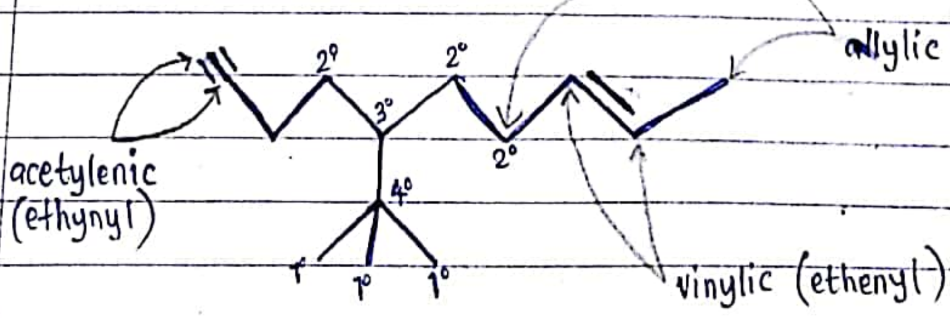
Cyclo octyne →



NOTE: 8 carbons is the least number of carbons required to form a cyclic compound of alkynes.

Cyclo nonyne →





Common names of alkynes, are described as

Many of an alkyne's chemical properties depend on whether there is an acetylene hydrogen or not

acetylenic hydrogen

$\boxed{H} - C \equiv C - CH_2 - CH_3$ $\qquad$ $CH_3 - C \equiv C - CH_3$

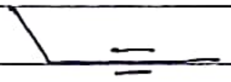
1 - Butyne, a terminal alkyne $\qquad$ 2 - Butyne, an internal alkyne

IUPAC Nomenclature of Alkynes (similar to that for alkenes).

Find the longest continuous chain of carbon atoms that includes the triple bond and change the -ane ending of the parent alkane to -yne.

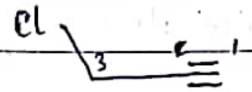
Chain is numbered from the end closest to the triple bond, and the position of the triple bond is designated by its lower-numbered carbon atom.

Substituents are given numbers to indicate their locations.

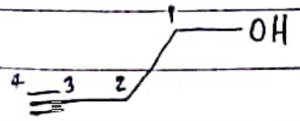


Name : 2- Pentyne or Pent-2-yne

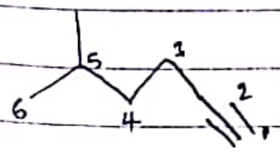
Name : 2- Butyne or But-2-yne



Name : 3-Chloropropyne



Name : 3- Butyn- 1-ol or But-3-yn-ol

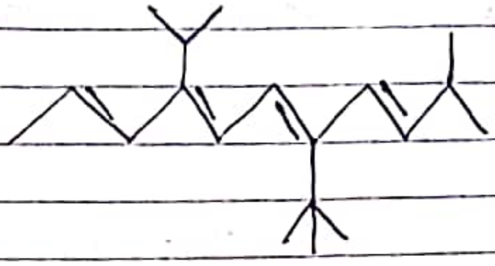


Name : 5-Methyl-1-hexyne

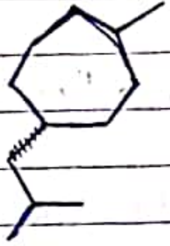
265

Problem Name the following compounds according to IUPAC.

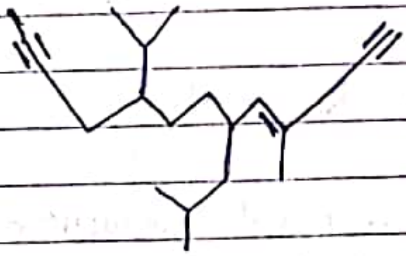
(a)



(b)



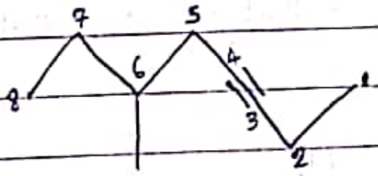
(c)



(a)

(b)

(c)



Name : 6 - Methyl - 3-octyne
6 - Methyloct - 3 - yne

RO^- = Alkoxy
$RO-H$ = Alkanol
CH_3O^- = Methoxy
CH_3O-H = Methanol

$-C\equiv C-$ → yne as parent name
yn as substituent

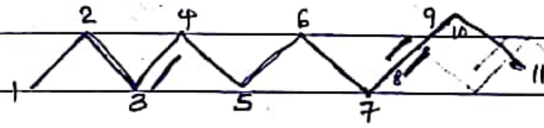
$>C=C<$ → ene as parent name
en as substituent

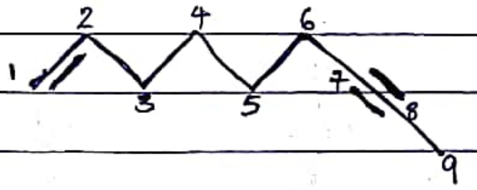
1. The triple bond is always the suffix because it is more oxidized.

2. Double bond is a substituent as en.

3. Preference for numbering is given to the double bond if the two are in equivalent positions from either side. Otherwise, the chain is numbered from the end closest to a multiple bond.

4

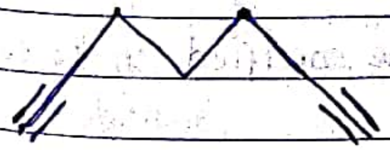




4. Hydrocarbons in which both double and triple bond's are present are called Alkenynes.

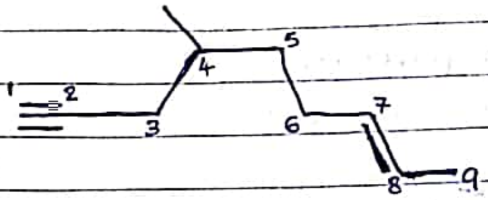
5. A double bond has priority over a triple bond in numbering the chain when numbering systems are equivalent. Other wise, the chain is numbered

6. from the end closest to a multiple bond.

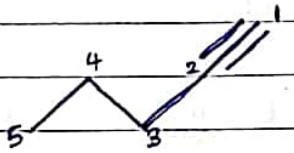


Name : 1,6 – Heptadiyne.
Hepta – 1,6 – diyne.

Name : 1 – Penten – 4 – yne
Pent~~e~~ 1-en – 4 – yne



Name: 4-Methyl-7-nonen-1-yne
4-Methylnon-7-en-1-yne.

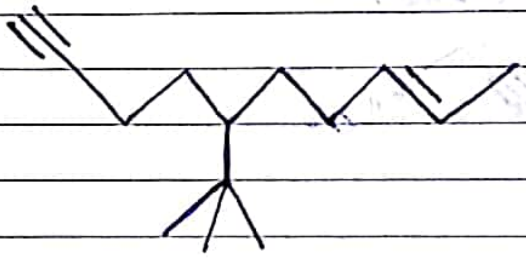


Name :

NOTE: Vinyl carbons are sp^2 hybridized, allylic carbons are sp^3 hybridized, and acetylenic carbons are sp hybridized.

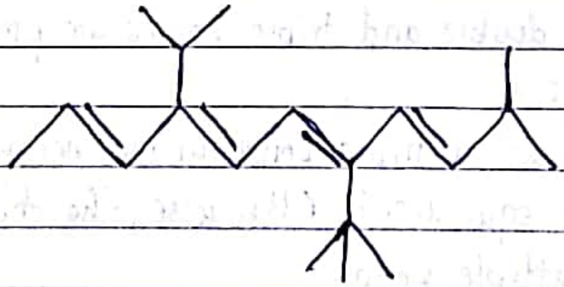
Name the following organic compounds:

(a)



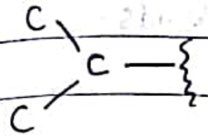
Name:

(b)

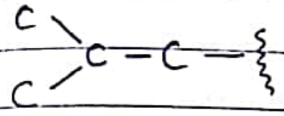


Name :

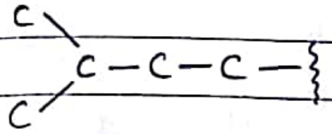
NOTE: The number of multiple bonds has to be specified in the suffix end.



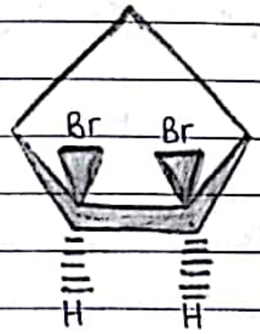
= isopropyl (an iso-)



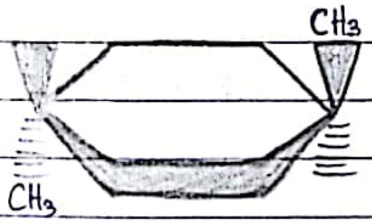
= isobutyl (an iso-)



= isopentyl (an iso-)

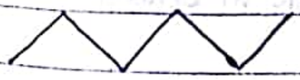


Name : cis – dibromocyclopentane .



Name : trans –

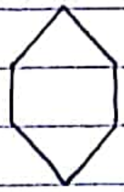
Organic compounds are classified even based on structure.



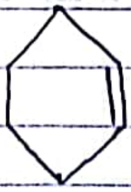
1

Aliphatic

- open chain

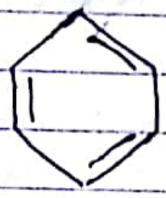


2 .



3

Cyclic



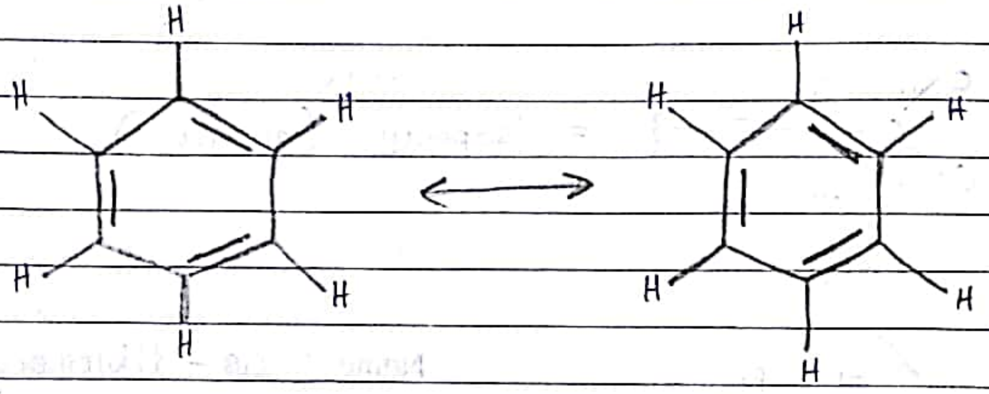
4

(conjugated double bonds)

Aromatic (Arene)

= conjugated double bonds.

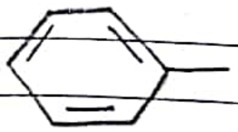
= isolated double bonds.



Kekule structures for Benzene
(in resonance forms)

The bonds between carbon atoms in benzene are in between the

2.71 Phenyl and Benzyl Groups



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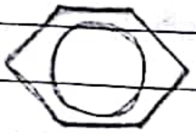
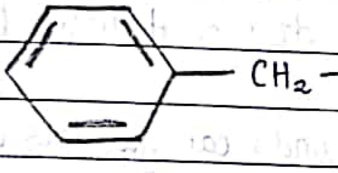


or C_6H_5 — or Ph —

or Ar — (if ring substituents are present) ; Ar = Aryl.



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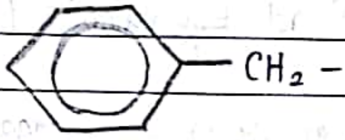

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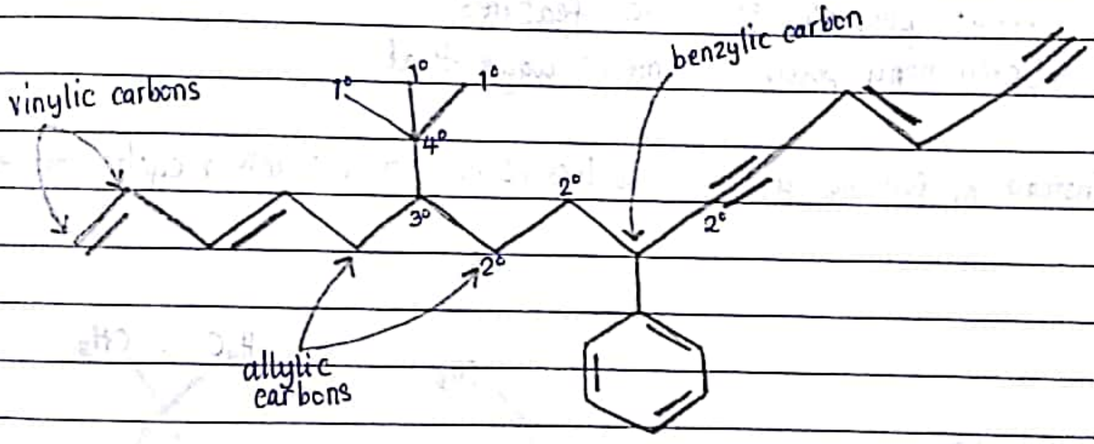
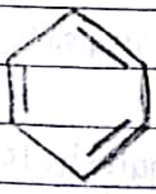
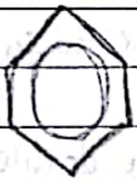
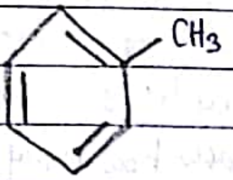


Nomenclature of Arenes

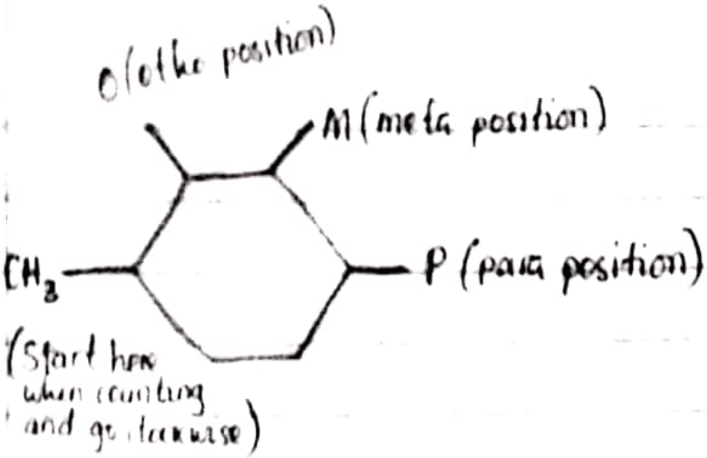






Toluene

There are two naming methods: ① Numbering carbons, and ② otho, met para (stomp) ⇒ Start = ST, Ortho = O, Meta = M and Para = P. giving us STOMP.



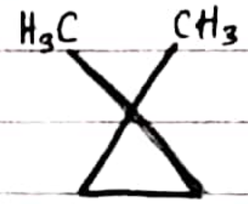
Double Bond Equivalents (DBE), Index of Hydrogen Deficiency (HD)

1. Molecular formula of organic compounds can give lots of information about possible structural features.
   Often many possible isomeric ways that

Instead of forming a C=C, the loss of H_2, can also give a cyclic structure.


bicyclo(2,1,0) pentane

methylbutane



1,1-dimethylcyclopropane.

Is there an easy way to explain these observations?
- One way to explain these facts is to use the formula equivalence between the unsaturated and cyclic structures.

Very useful to know how many of these double bond equivalents

The answer shows that the molecule must have one of the following
(i) 3 π-bonds (ii) 2π-bonds and 1 ring (iii) 1 π-bond and 2 rings
(iv) 3 rings.

Whenever you suggest a structure for any molecule, it is useful to check i
the DBE fits your structure.

175.
- Above the critical temperature, it is impossible to condense a gas into a liquid just by increasing the pressure.
- The molecules have to much energy to condense.

Que: What volume V of helium gas is needed if a ballon is to lift a load of 200kg (including the weight of the bellon)? Take the density of air to be $1.29\, kg/m^3$ and that ~~be~~ of helium as $0.179\, kg/m^3$.

276 Viscosity

Viscosity is the measure of the resistance to the flow of fluids. It is an intrinsic property of all fluids or liquids and gases.
Viscosity is affected by the size of the substances, intermolecul forces at play and the shape of the substance.
Viscosity is also dependant on temperature, meaning the higher the temperature the lower the viscosity and vice-versa.
Intermolecular forces at play in various substances (fluids) include London forces, hydrogen bonding and dipole-dipole interactions. For example, regarding hydrogen bonding, organic liqui or fluids have relatively higher viscosities than inorganic liquid i.e methanol, ethanol as compared to bromine e.t.c.

PHASE DIAGRAMS

- There are three lines on the phase diagram – points on the line correspond - temperature and pressure at which phase equilibria can exist between the two phases.
- The line AB is the vapour curve for solid (ice). Line gives temperature-pressure points at which ice and vapour coexist (sublimation line).
- BC is the solid-liquid equilibrium line (melting point line.)

The line BD is vapour curve for liquid water (boiling point line). Liquid-vapour are able to coexist. Note: at 100°C, the vapour pressur is 1 atm.

- The three lines intersect at B known as the triple point. Each substanc except for He (helium) has its characteristic triple point.

* Graphically represents pressure-temperature relationships.
* Will a substance be a solid, liquid or gas under given conditions of pressure and temperature.

** Useful information for freeze drying.

- The vapour pressure curve which starts at B terminates at D, Known as the critical point.
- The temperature and pressure are known as critical temperature, T_c, an critical pressure, P_c.

(1) Universal Gas Constant, R = $8.3145\ J\cdot mol^{-1}\cdot K^{-1}$
$0.083145\ L\cdot bar\cdot mol^{-1}\cdot K^{-1}$
$0.08206\ L\cdot atm\cdot mol^{-1}\cdot K^{-1}$
$62.364\ L\cdot torr\cdot mol^{-1}\cdot K^{-1}$
$62.364\ L\cdot mmHg\cdot mol^{-1}\cdot K^{-1}$

(2) Rydberg Constant, R_H = $1.097 \times 10^{7}\ m^{-1}$

(3) Mass of electron, m_e = $9.11 \times 10^{-31}\ kg$

(4) Planck's Constant, h = $6.626 \times 10^{-34}\ J\cdot S$

(5) Avogadro's Constant, N_A = $6.022 \times 10^{23}\ mol^{-1}$

(6) Faraday's Constant, F = $96485\ C\cdot mol^{-1}$

(7) Speed of light, C = $3.00 \times 10^{8}\ m\cdot s^{-1}$

(8) Acceleration due to gravity = $9.8\ m\cdot s^{-2}$

(9) Pressure conversions

$1\ atm = 1.01325 \times 10^{5}\ Pa = 1.01325 \times 10^{5}\ N\cdot m^{2}$
$= 760\ torr = 760\ mmHg = 1.01325\ bar$

(10) Other conversion factors

$V = J\cdot C^{-1}$ $1\ eV = 1.602 \times 10^{-19}\ J$

$1\ J = 1\ kg\cdot m^{2}\cdot s^{-2}$

STANDARD REDUCTION POTENTIALS

HALF-REACTION	$\mathcal{E}^\circ$ (V)
$F_{2(g)} + 2e^- \longrightarrow 2F^-_{(aq)}$	+ 2.87
$O_3(g) + 2e^- + 2H^+_{(aq)} \longrightarrow O_2(g) + H_2O$	+ 2.07
$Ag^{2+} + e^- \longrightarrow Ag^+$	+ 1.99
$CO^{3+}(aq) + e^- \longrightarrow CO^{2+}(aq)$	+ 1.82
$H_2O_2 + 2H^- + 2e^- \longrightarrow 2H_2O$	+ 1.78
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O$	+ 1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+ 1.61
$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$	+ 1.68
$2e^- + 2H^+ + IO_4^- \longrightarrow IO_3^- + H_2O$	+ 1.60
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+ 1.51
$Au^{3+} + 3e^- \longrightarrow Au$	+ 1.50
$PbO_2 + 4H^+ + 2e \longrightarrow Pb^{2+} + 2H_2O$	+ 1.46
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+ 1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+ 1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+ 1.21
$IO_3^- + 6H^+ + 5e^- \longrightarrow \frac{1}{2}I_2 + 3H_2O$	+ 1.20
$Br_2 + 2e^- \longrightarrow 2Br^-$	+ 1.09
$VO_2^+ + 2H^+ + e^- \longrightarrow VO^{2+} + H_2O$	+ 1.00
$AuCl_4^- + 3e^- \longrightarrow Au + 4Cl^-$	+ 0.99
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+ 0.96
$ClO_2 + e^- \longrightarrow ClO_2^-$	+ 0.954
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+ 0.91
$Ag^+ + e^- \longrightarrow Ag$	+ 0.80
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+ 0.80
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+ 0.77
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	+ 0.68
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+ 0.56
$I_2 + 2e^- \longrightarrow 2I^-$	+ 0.54

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	$Cu^+ + e^- \longrightarrow Cu$	$+0.52$
	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	$+0.40$
	$Cu^{2+} + 2e^- \longrightarrow Cu$	$+0.34$
	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	$+0.27$
	$AgCl + e^- \longrightarrow Ag + Cl^-$	$+0.22$
	$SO_4^{2-} + 4H^- + 2e^- \longrightarrow H_2SO_3 + H_2O$	$+0.20$
	$Cu^{2+} + e^- \longrightarrow Cu^+$	$+0.16$
	$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	$+0.13$
S.H.E	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
	$Fe^{3+} + 3e^- \longrightarrow Fe(s)$	-0.036
	$Pb^{2+} + 2e^- \longrightarrow Pb(s)$	-0.13
	$Sn^{2+} + 2e^- \longrightarrow Sn(s)$	-0.14
	$Ni^{2+} + 2e^- \longrightarrow Ni(s)$	-0.23
	$PbSO_4 + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.35
	$Cd^{2+} + 2e^- \longrightarrow Cd(s)$	-0.40
	$Fe^{2+} + 2e^- \longrightarrow Fe(s)$	-0.44
	$Cr^{3+} + 3e^- \longrightarrow Cr(s)$	-0.73
	$Cr^{3+} + e^- \longrightarrow Cr^{2+}(aq)$	-0.50
	$Zn^{2+} + 2e^- \longrightarrow Zn(s)$	-0.76
	$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	-0.83
	$Mn^{2+} + 2e^- \longrightarrow Mn(s)$	-1.18
	$Al^{3+} + 3e^- \longrightarrow Al(s)$	-1.66
	$H_2 + 2e^- \longrightarrow 2H^-$	-2.23
	$Mg^{2+} + 2e^- \longrightarrow Mg(s)$	-2.37
	$La^{3+} + 3e^- \longrightarrow La(s)$	-2.37
	$Na^+ + e^- \longrightarrow Na(s)$	-2.71
	$Ca^{2+} + 2e^- \longrightarrow Ca(s)$	-2.76
	$Ba^{2+} + 2e^- \longrightarrow Ba(s)$	-2.90
	$K^+ + e^- \longrightarrow K(s)$	-2.92
	$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	-2.89
	$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	-1.85
	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05

280 For more on the atomic structure, see Zumdahl, Zumdahl page 285 & 294

Waves have three properties : (i) Wavelength (λ : lambda) : the distance between two crests of a wave.

(ii) Frequency (in Hertz or cm/s(?))
(mu : μ) $\Rightarrow \lambda = \frac{1}{\mu}$.

(iii) Velocity of wave : distance travelled in time
(in m/s) $\Rightarrow \lambda = \frac{c}{\mu}$ at constant speed of light.

Problem: What is the μ of the radiation whose λ is 30×10^{-6} m ?

Answer:

- Electromagnetic Spectrum is the range of frequencies ~~of~~ or wavelengths of electromagnetic radiation
-

$\lambda^{(m)}$:	10^{-12}	10^{-10}	10^{-8}	10^{-7}	10^{-4}	10^{-2}	10^{4}
	X-ray	X-ray	Ultra violet	visible light	Infra-red	Micro waves	Radio waves

- As lambda (λ) increases, the frequency (μ) decreases.
- You are to understand what a continuous spectrum is.
- You are also to understand what a discontinuous spectrum is.

e^- only certain energies, or has quantised energy (energies)
e^- (electrons) have

NOTE * For linear regression, the standard linear equation is given by:

$$\begin{tikzcd} y \arrow[d, leftrightarrow] & = & b \arrow[d, leftrightarrow] & x \arrow[d, leftrightarrow] & + & a \arrow[d, leftrightarrow] \\ y & = & m & x & + & c \end{tikzcd}$$

$y = bx + a$ (standard linear equation: linear regression)

$y = mx + c$ (standard linear equation : common)

NOTE * Ideal-gases are not like real gases. Ideal gases are called so becau they can be at constant pressure, temperature, volume or density but it is almost not possible to maintain a real gas at constancy in any of the four dimensions namely pressure, temperature, volume or density.

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* Atomic size ⇒ size decreases (⟶)
size increases (↓)

CORRECT DEFINITIONS OF THE TERMS : ANODE AND CATHODE.

* The anode is the electrode at which oxidation takes place.

* The cathode is the electrode at which reduction takes place.

NOTE: An adduct is the product of an addition reaction between two compounds

* An electron carries a charge of 1.602×10^{-19} coulombs.

* An antilog is the inverse of log. Therefore, antilog is 10^x.

* A Phase is a homogenous part of the system in contact with other parts of the system but separated from them by a well defined boundary.

* Something that is analgesic reduces pain.

* Something that is anti-inflammatory reduces swelling.

* Capsaicin is the compound responsible for the 'spicy hot' tastes in some foods.

- tetraene

* undecatetraene for (a)

4 - isopropyl
7 - tert-butyl
10 - methyl

- The Avogadro constant is equal to 6.022×10^{23}. This means that the number of atoms in one mole of a substance. For example, in one mole of nitrogen gas, there are 6.022×10^{23} atoms present, the atoms being of nitrog element.

Here is how the conversion is done:

$$1 \text{ mole of atoms} = 6.022 \times 10^{23} \text{ atoms of the element present}$$
$$1 \text{ mol} = 6.022 \times 10^{23} \text{ atoms}$$

We shall now calculate and find out number of moles of one atom of an element.

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ atoms}$$
$$\frac{1 \text{ mol}}{6.022 \times 10^{23}} = \text{the moles of one atom of an element}$$
$$1.6605 \times 10^{-24} = \text{the moles of one atom of an element}$$

Therefore, the number 1.6605×10^{-24} will serve as the conversion factor whenever we shall want to find out the number of moles of a given amoun of atoms and vice-versa.

8. (e) BH_3 where there is BH_4

10. (b) $NO_2^- + Al \rightarrow NH_4 + AlO_2^-$

DO NOT FORGET! * Do not multiply the molar mass of a compound by its stoichiometrical coefficient.

& Average velocity = mean velocity.

et of
rbitals
ubshells)

s. = sharp
p = principle
d = distinct
f = fundamental

17 Example: What is the Empirical Formular of a sugar (that contains Carbon Hydrogen and Oxygen only) that gives 2.2g of CO_2 and 0.9g of H_2O upon combustion? The amount of sugar was 1.5g.

Solution:

$$M_x = \frac{A_x \cdot S_x \cdot M_y}{M_y}$$

, where x is the element and y is the compound in which the element is.

$$\text{Mass of Carbon} = \frac{\text{Atomic Weight} \times \text{Number of atoms present in } CO_2 \times \text{Mass of } CO_2}{\text{Molar mass of } CO_2}$$

$$M_c = \frac{12.01\,g/mol \times 1 \times 2.2g}{44\,g/mol}$$

$$M_c = 0.6005\,g$$

$$M_H = \frac{1.01\,g/mol \times 2 \times 0.9g}{18\,g/mol}$$

$$M_H = 0.1g$$

M_o = mass of compound − (mass of C + mass of H)

$M_o = 1.5g - (0.6 + 0.1)$

$M_o = 1.5g - 0.7g$

$M_o = 0.8g$

Mass of Oxygen = 0.8g

C	H	O
$\frac{0.6}{12.01}$	$\frac{0.1}{1.01}$	$\frac{0.8}{16}$
$\frac{0.049958368}{0.049958368}$	$\frac{0.0990099}{0.049958368}$	$\frac{0.05}{0.049958368}$
$\frac{1}{1}$	$\frac{1.981848166}{2}$	$\frac{1.000833334}{1}$

The empirical formular is CH_2O.

LIMITING AND EXCESS REAGENTS

Limiting reagents get exhausted during a chemical reaction. It is in limited supply. Excess reagent is left over after the reaction.

To determine the limiting reagent:

1. Calculate the number of moles for each reactant
2. Divide the moles of each reactant by each stoichiometric coefficient (number in the balanced equation).
3. The smallest ratio represents the limiting reagent.